

41. Physical Chemistry in *Helvetica Chimica Acta*, from 1918 to 1992

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Introduction. – Physical Chemistry is the only one of the classical disciplines of chemistry with a known birthdate, ... and with three fathers. These were *Jacobus Henricus van't Hoff* (1852–1911), *Svante August Arrhenius* (1859–1927), and *Wilhelm Ostwald* (1853–1932) [1]. In retrospect, however, the first chemist to practice what we would now call Physical Chemistry was *Mikhail Vasilevich Lomonosov* (1711–1765)¹⁾, founder of the University of Moscow, now carrying his name [2] [3]. However, 'Physical Chemistry' was established as a field of its own only in 1887, when *Wilhelm Ostwald* founded the *Zeitschrift für Physikalische Chemie*, and when he accepted in the same year the very first chair in Physical Chemistry, created at the University of Leipzig.

Sixteen years later, in 1903, *Philippe-Auguste Guye*²⁾ (1862–1922) [4], then 'professeur ordinaire de chimie théorique et technique'³⁾ at the University of Geneva, created the French pendant to *Ostwald's* journal, namely the *Journal de Chimie Physique*, published until 1922 in Geneva, and since then in Paris. Irrespective of its strange name, *Guye's* chair was *de facto* the first chair of Physical Chemistry in Switzerland. Full professorships in Physical Chemistry were created at the Universities of Basle and Zurich only in 1920, although lectures in this field had been given regularly before⁴⁾.

¹⁾ *Lomonosov* was the first to look at chemistry from the standpoint of physics and mathematics. He thought that matter was composed of small, imperceptible particles which are the cause of all properties, and that their oscillatory and gyratory motions are increased, when matter is heated. He did not believe in phlogiston. His theory of the gaseous state assumed that the particles (atoms) moved rapidly, constantly colliding with each other, and his ideas about the compressibility of gases were close to those of *Van der Waals*. He had a rather clear conception of the absolute zero, and he thought – anticipating *Berzelius* – that differences in properties could be due to differences in the arrangement of the atoms.

²⁾ A portrait of *Ph. A. Guye* has been presented in [5].

³⁾ In a historical review, on the occasion of the 100th anniversary of the Departement of Chemistry of the University of Geneva [6], *Ch. K. Jørgensen* writes: 'On se demande si l'on a demandé le conseil d'un logicien avant de faire cette coexistence'. It is noteworthy that in 1922, *Guye's* successor *E. Briner* was still asked to occupy this strangely named chair.

⁴⁾ At the University of Basle, *Georg W. A. Kahlbaum* (1853–1905) [7], best known for his contributions to the history of chemistry, began to lecture on physical chemistry in 1892. These lectures were taken over in 1912 by *August Leonhard Bernoulli* (1879–1939) [8], who became full professor in 1917, was nominated in 1920 to the newly created chair in Physical Chemistry, and named the first director of the *Physikalisch-chemische Anstalt* established in 1926. In Zurich, at the University, *Paul Pfeiffer* (1875–1951) [9] was charged in 1908 with the course on 'Physikalische und Theoretische Chemie', which was taken over in 1914 by Privatdozent *Israel Lifschitz* (1888–?). In 1920, *Victor Henri* (1872–1940) [10] was nominated as the first professor of Physical Chemistry, after *William D. Treadwell*, then professor of Inorganic Chemistry at the Federal Institute of Technology, Zurich, had declined the offer [11].

To set our review in its proper perspective, some general remarks about *Physical Chemistry in Switzerland* and its reflection in *Helvetica Chimica Acta (HCA)* are needed. Certainly, readers of *HCA* can not help noticing that compared to inorganic, and particularly to organic chemistry, physical chemistry occupies a rather small place, even if we use this term as a catch-all for *e.g.* thermochemistry, thermodynamics, reaction kinetics, electrochemistry, spectroscopy, or theoretical chemistry. However, there are some good reasons for this ‘discrimination’.

Switzerland being a country without natural resources – apart from hydroelectric power and tourists – its chemical industry is almost entirely oriented towards fine chemicals, *e.g.* pharmaceutical products, dyestuffs, or agrochemicals, fields in which the Swiss Chemical Companies belong to the worldwide leaders. As a consequence, organic chemistry plays the dominant role not only in industry but also at the universities and institutes of technology which provide the necessary academic manpower. It is, therefore, not surprising that *HCA* became over the years a journal mainly addressed to an auditorium of organic chemists, which is less interested in the – sometimes arcane – topics dear to their colleagues from physical chemistry. Thus, *HCA* developed into a less attractive medium for such contributions, which are preferentially published in specialized journals, such as *Guye’s Journal de Chimie Physique*, and many others. This trend became more and more pronounced over the years, so that practically all of the present out-put of our Institutes of Physical Chemistry bypasses *HCA*.

A second important point concerns the turn that physical chemistry took in Switzerland. Because of the analytical needs of our organic-chemistry-oriented industry and university research groups, a large section of our physical chemists concerned themselves preferentially with spectroscopic methods and/or the investigation of properties of covalent molecules. Soon, the organic chemists themselves began to use these techniques, and to integrate such methods into their own research, sometimes to the extent of practicing what is now known as physical-organic chemistry. This makes it sometimes difficult to draw a sharp line between the disciplines organic/inorganic chemistry on the one side, and physical chemistry on the other. It is, therefore, not surprising that some of the publications relevant for the present review have already been included in previous contributions to this series.

In contrast to the preceding reviews, each of which dealt with the development of a limited field ‘*as mirrored in HCA*’, the development of ‘*Physical Chemistry*’ is certainly not ‘*mirrored*’ in *HCA*. What we can read in *HCA* are publications dealing with unrelated topics from quite different parts of physical chemistry, yielding at best a patchwork-type overview. Therefore, the reader is asked to bear with us, if our choice of topics and/or examples is – up to a point – somewhat arbitrary and subjective. In addition, we shall – for the sake of clearness – not rely on a historical sequence, but pool related publications into separate sections, independent of their date of publication.

1. Spectroscopy. – 1.1. Electronically Excited States: UV/VIS Spectra. In 1860, *Gustav Robert Kirchhoff* and *Robert Bunsen* published the historical paper ‘*Chemische Analyse durch Spektralbeobachtungen*’ [12] which marks the beginning of the application of spectroscopic methods to chemical problems. Although these early applications of atomic emission spectra were of a purely analytical nature, they were eminently successful, as evidenced by *Bunsen*’s discovery – in the same year 1860 – of the new element Caesium, and of Rubidium in 1861 [13]. The use of absorption spectroscopy – what we would now call UV/VIS spectroscopy – was introduced on a purely qualitative level in 1879 by *Walter Noel Hartley*, then professor at the Royal College of Science in Dublin. (For an account of the early history of absorption spectroscopy applied to organic chemistry, see [14]). The first systematic investigations of such spectra, in particular their interpretation in terms of the structure and bonding of the absorbing molecules is mainly due to **Victor Henri** (1872–1940)⁵⁾ [10], who became full professor of physical chemistry at the University of Zurich in 1920 [11]. His field of research is best characterized by the title of his ‘*Antrittsrede*’, namely: ‘*Pluralität der Zustände der Atome und Molekel und deren Bedeutung für die physikalische Chemie*’. From his many fundamental contributions to electronic spectroscopy and photochemistry, we only quote the discovery of predissociation in 1923 and his work on chain reactions (with *René Wurmser*) in 1927. Certainly his pioneering research is at the root of a long and eminently successful spectroscopic tradition at the University of Zürich, and thus in Switzerland. However, not a single one of his many papers was published in *HCA*.

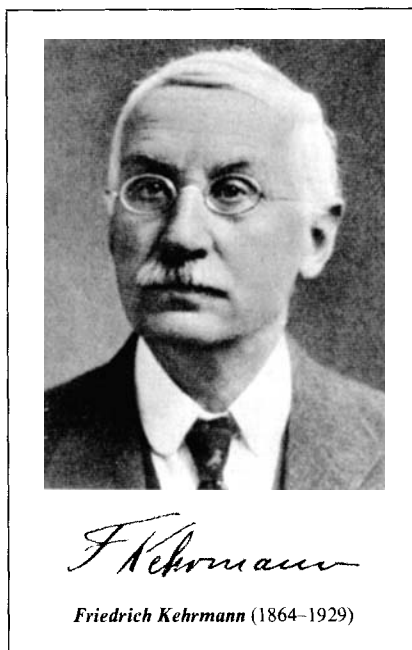
It is, therefore, amusing to note that notwithstanding *Victor Henri*’s reticence to publish in *HCA*, the very first paper [15] in the first issue of *HCA* stems nevertheless from the University of Zurich and deals with electronic spectra. It is due to **Alfred Werner**⁶⁾, and contains the optical rotatory dispersion spectra of the isomeric forms of *cis*-[Co(NO₂)₂(en)(pn)]X, (en = ethylenediamine; pn = propane-1,2-diamine; X = counterion) shown on page 23 of [16]. It is remarkable that this powerful method, *i.e.* the use of CD spectra for the characterization and discrimination of enantiomers – routinely used in *Werner*’s research group – almost completely disappeared from the literature for close to 40 years, until it was reintroduced on a large scale by *Carl Djerassi* and developed into a fine art by *Günther Snatzke* [17], both of which have published extensively in *HCA*, in

⁵⁾ *Victor Henri*, born 1872 in Marseille of Russian parents, had an unusual scientific career. In 1891, he first studied mathematics at the Sorbonne in Paris, then philosophy in Göttingen, where he obtained a ‘Dr. phil.’ with a thesis ‘*Localisation des sensations du gout*’. He returned to the Sorbonne, to do work on physico-chemical problems in biology, which led in 1902 to his second degree, a ‘Dr. ès sciences’. He remained at the Sorbonne, investigating the electronic spectra of biomolecules until 1914, when he was appointed French ambassador in Russia, a post he occupied until 1920, the year he was offered the professorship at the University of Zurich. In 1930, *Victor Henri* left Zurich to move to the University of Liège, where he occupied the chair in Physical Chemistry. In 1939, at the beginning of the second world-war, he was asked to return to France, and to assume together with *Paul Langevin* the direction of the ‘Laboratoire de Physique’ of the ‘Centre National de Recherche Scientifique’ in Paris. In June 1940, after the collapse of the French front, he and his colleagues had to leave Paris for La Rochelle, where he died the same year of a pulmonary congestion. He was undoubtedly one of the most important pioneers of spectroscopy and photochemistry. A typical feature was his tendency to seek completely original and personal solutions, sometimes at the cost of a critical evaluation. Thus, he proposed benzene to be non-planar, ammonia to be flat and asymmetric, and that methane has a distorted structure.

⁶⁾ A portrait of *Alfred Werner* is shown in [16], p. 24.

collaboration with various research groups from Swiss universities, cf. e.g. [18]. In this connection, it should be mentioned that the early theory of CD spectra is due to *Werner Kuhn* (see *Chapt. 2*).

Volume I of *HCA* contains the first communication [19] of a series of contributions (e.g. [20]) by **Friedrich Kehrman** (1864–1929) [21], professor at the University of Lausanne, which are devoted to the systematic investigation of the connection between the (electronic) structure and the UV/VIS absorption spectra of molecules, in particular of dyestuffs.



A short biography of *Kehrman* and an appreciation of his important contributions to Color Chemistry has already been presented by *Zollinger* on pp. 1731 to 1734 of [22]. We might add that *Kehrman*'s interest in the relationship between color and constitution dates back to 1890, when he was an assistant of *A. Classen* at the Technische Hochschule Aachen. To document – in addition to Fig. 4 of [22] – the quality of absorption spectra obtainable around 1920, we show in *Fig. 1* some of *Kehrman*'s spectra of oxazine dyestuffs, a sample taken from [23], one of the long list⁷⁾ of *Kehrman*'s papers.

The band envelopes of the long-wave part of the spectra were estimated visually with a *Zeiss* spectroscope, using solutions of concentrations $n/1500$, $n/3000$, $n/6000$, down to $n/48000$, a path-length of $d = 4.5$ mm, and smoothing out complicated features of the

⁷⁾ This list is not easy to follow because of *Kehrman*'s private and inaccessible way of numbering his contributions: 'Die No. XIII entspricht der neuen Numerierung der Artikel 'Konstitution und Farbe' in Band IV meiner gesammelten Abhandlungen', Footnote in [24].

Spectres d'absorption dans le visible de quelques matières colorantes oxaziniques

par F. Kehrman et Pierre Borgeaud¹⁾.

(27. VIII. 26.)

Planche I

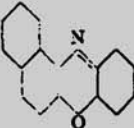
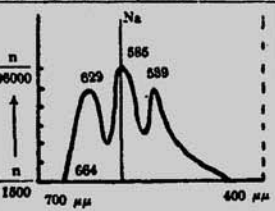
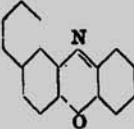
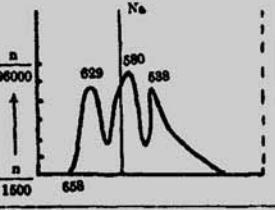
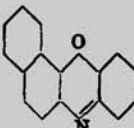
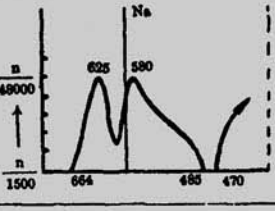
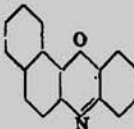
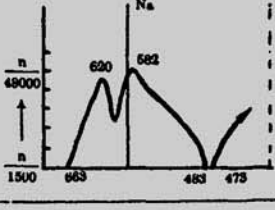
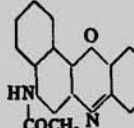
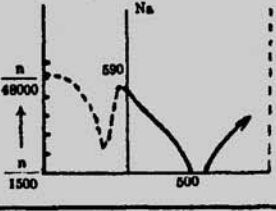
Formules	Courbes d'absorption		Remarques
	Spectre visible	Maxima	
 <p>N(CH₂H₅)₂ ClO₄ I</p>		539 585 629	Solution alcoolique avec traces de HCl dilués violet
 <p>N(CH₂H₅)₂ Cl II</p>		538 580 629	Solution alcoolique avec traces de HCl dilués violet moins bleuâtre
 <p>N(CH₂H₅)₂ ClO₄ III</p>		580 625	Solution alcoolique avec traces de HCl dilués couleur d'œuf blanc
 <p>N(CH₂H₅)₂ NO₂ IV</p>		582 620	Solution alcoolique avec traces de HCl dilués couleur d'œuf blanc
 <p>N(CH₂H₅)₂ Cl V</p>		590	Solution alcoolique avec traces de HCl dilués couleur d'œuf blanc

Fig. 2

Einige Beobachtungen über Beziehungen des Fluoreszenzlichtes und der Lösungsfarben der Amino-carbazone in verschiedenen farblosen Lösungsmitteln zu anderen optischen Eigenschaften dieser Lösungsmittel.

VIII. Mitteilung über farbige Derivate des Tetraphenyl-methans

von F. Kehrman, H. Goldstein und F. Brunner¹⁾.

(20. I. 26.)

Tabelle I.

Lösungs- mittel	2-Amino-diphenyl-carbazon	Maxima	Bemerkungen
Äthylalkohol		595	Dünne Schicht: blau Dicke Schicht: rot
Methyl- alkohol		591	wie Äthylalkohol, aber eine Spur rotstichiger
Pyridin		564	Dünne Schicht: violett Dicke Schicht: violettrot Starke rote Fluorescenz
Aceton		548	Dünne Schicht: violettrot Dicke Schicht: fuchsinrot Starke rote Fluorescenz
Äther		512	Dünne Schicht: violettrosa Dicke Schicht: rotorange Schwache Fluorescenz
Schwefel- kohlenstoff		508	wie Äther, aber keine Fluorescenz

band. The UV part was recorded with a *Paschen* spectrograph. The abscissae correspond to the instrument scales, and the ordinates are the concentrations in steps by factors of 1/2.

Another example concerns an early investigation of the solvent dependence of absorption (and emission) spectra of organic molecules. To shed more light on this problem, *Kehrmann* investigated the solvent dependence of the position and intensity of the long-wave band of a dyestuff, as shown in *Fig. 2* for 2-aminodiphenyl-carbazone [25]. It was found that the shift of the band maximum parallels the dielectric constant of the solvent, and that the band-shape remains the same.

Concerning *Kehrmann's* contributions to the interpretation of the color of dyestuffs in terms of molecular structure, the reader is referred to *Zollinger's* review [22].

As a further example of the state of the art of absorption spectroscopy in 1922, we present in *Fig. 3* the long-wave VIS absorption spectrum of potassium permanganate, recorded by *Hagenbach* and *Percy* of the University of Basle [26]. It also shows the authors' proposal, how this wide feature should be deconvoluted into partial bands, under the limiting assumption that no more than three partial bands overlap at any wavelength.

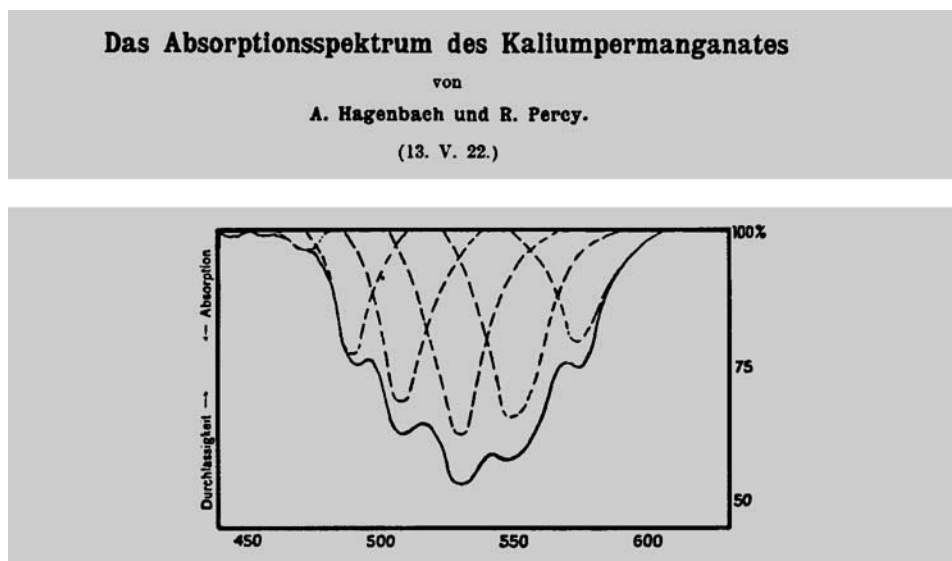
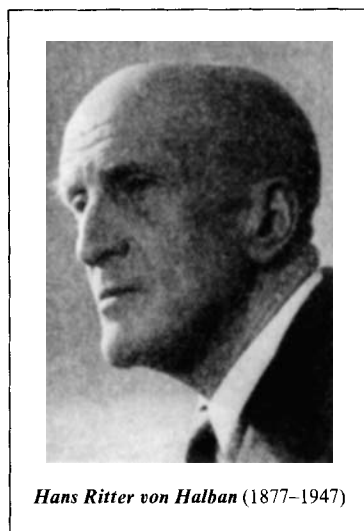


Fig. 3

After *Victor Henri's* retirement in 1930⁵⁾, the chair in Physical Chemistry at the University of Zurich was taken over by *Hans Ritter von Halban* (1877–1947)⁸⁾ [11] [27] who carried on the spectroscopic tradition of the institute.

⁸⁾ *Von Halban* was born in 1877 in Vienna. After two semesters at the Technische Hochschule Wien, he moved to the University of Zurich, where he obtained, in 1902, a Ph. D. in Inorganic Chemistry, having worked for four years under the direction of *Werner*. He then spent some time with *W. Ostwald* and *M. Le Blanc* at the University of Leipzig, where he got his formation as a physical chemist. From 1909 until 1929 – interrupted by four years of service in the Austrian army during the war – he worked at the University of Würzburg, first as a Privatdozent, and later as a.o. Professor for Physical Chemistry. In 1930 he returned to the University of Zurich, to occupy the chair of Physical Chemistry. He died, shortly before his 70th birthday, in 1947.



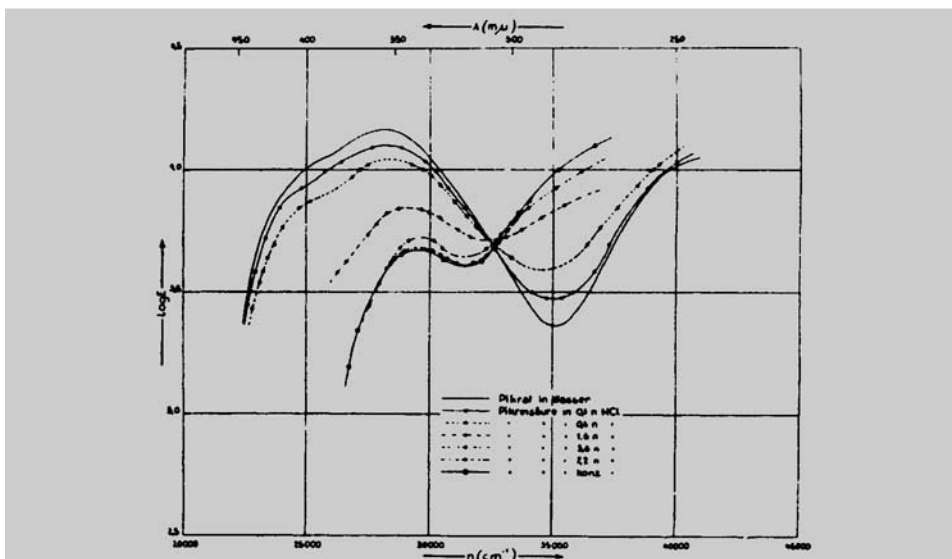
Von Halban's research concerned mainly two topics: the improvement of spectroscopic techniques, in particular, precision measurements for the investigation of weak electrolytes, ion pairs or ion associations in solution, and – as we shall see later (*cf. Chapt. 2*) – photochemistry.

Fig. 4

3. Über Ionenassoziation und Absorptionsspektrum II¹⁾

von H. v. Halban und M. Litmanowitsch.

(18. XII. 40.)



As an example taken from his work on ion association [28] [29], we show in *Fig. 4* the pH dependence of the UV spectrum of picric acid (= 2,4,6-trinitrophenol), a molecule studied in great detail by *von Halban*.

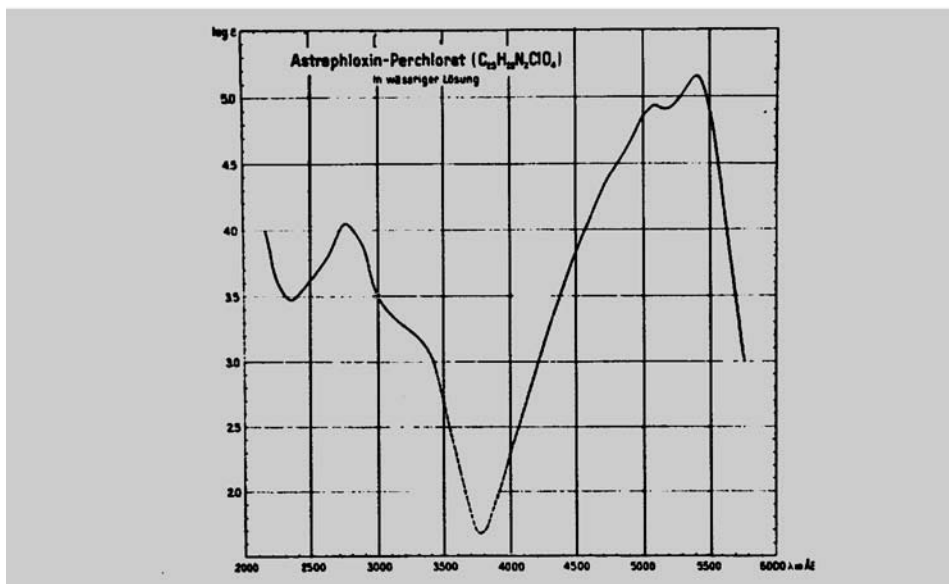
A detailed analysis of the sources of error in UV/VIS spectroscopy in particular with respect to the measured absorption intensities, has been given in [30]. As a result, it was proposed that the experimental set-up should consist of a particular hydrogen lamp, developed by *Almasy*⁹⁾ [31], a centro-symmetric *Pool* sector which avoids chopping the light beam, and only a single *Baly* cuvette, *i.e.* using the same cuvette alternatively for the solution and the solvent. The quality of the absorption spectra of organic compounds that could be obtained by this improved technique in 1944 is documented by the spectrum of astraphloxine perchlorate **1** (*cf. Fig. 5*), a compound which *von Halban* and *Karl Wieland* introduced into UV/VIS spectroscopy as a calibration standard [32].

119. Über eine Eichsubstanz für spektrographische Absorptionsmessungen¹⁾

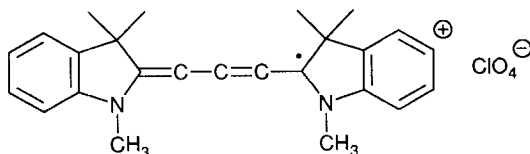
von H. v. Halban und K. Wieland.

(20. V. 44.)

Fig. 5



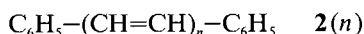
⁹⁾ *Felix Almasy* was a student of *Victor Henri*. He became a Privatdozent for physico-chemical biology at the faculty of veterinary medicine of the University of Zurich in 1935, but worked with *von Halban* in the Institute of Physical Chemistry [11].



1

By the time *von Halban* assumed the direction of the Institute of Physical Chemistry, *i.e.* around 1930, UV/VIS absorption spectroscopy was, in principle, available to organic chemists as an instrument for the elucidation of molecular structures – although this was certainly not true for every laboratory¹⁰⁾! As an illustration we mention two early and important examples, both of which have already been discussed (in part) in previous contributions to this series.

In 1927, *Richard Kuhn* and *Alfred Winterstein* synthesized the series of α,ω -diphenylpolyenes **2**(*n*) with *n* = 1 to 8 [33], to investigate their properties as a function of the number of double bonds, *n*.

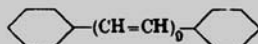


(The relevance of this work for the investigation of carotinoids has been discussed by *C. H. Eugster* [34].) Although the dependence of the color of these molecules on the number of double bonds is an obvious candidate for spectroscopic investigation, no

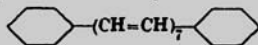
Fig. 6

Über konjugierte Doppelbindungen X¹⁾.
Zur Kenntnis der Äthylengruppe als Chromophor
 von **Richard Kuhn** und **Alfred Winterstein**.
 (14. VIII. 29.)

Wenn wir Norbixin und Iso-norbixin mit der Farbenskala der Diphenyl-poly-ene vergleichen, so kommen diese Verbindungen unmittelbar hinter das Diphenyl-hexadeca-octa-en zu stehen²⁾. Die Farbe des neunfach ungesättigten Bixins entspricht derjenigen, die wir für den Kohlenwasserstoff



erwarten. Die Farbe des siebenfach ungesättigten α -Crocetins ist von derjenigen des Diphenyl-tetradeca-hepta-ens



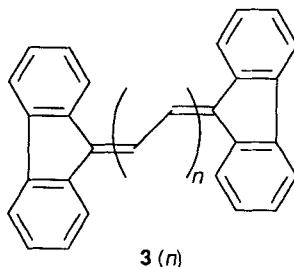
kaum zu unterscheiden.

²⁾ Wir vergleichen die Farben der fein kristallisierten Verbindungen gegen einen schwarzen Untergrund, um von dem lebhaften Oberflächenglanz grösserer Krystalle nicht gestört zu werden. Man kann auch die Farben der Präparate nach dem Verreiben auf weissen Tonplatten vergleichen.

¹⁰⁾ As *V. Prelog* told us, what impressed him most, when he visited for the first time *L. Ruzicka*'s laboratory at the ETH in Zurich in 1937, was the *Hilger UV Spectrograph*.

spectra were recorded, not even for the work 'Zur Kenntnis der Äthylengruppe als Chromophor', shown in Fig. 6. In this, the number of double bonds in bixin and α -crocetin was assessed by matching their color with those of the above polyenes, all compounds in the solid state [35].

The lack of spectroscopic data in [35] is surprising, because *Kuhn* and *Winterstein* had presented λ_{\max} values for the long-wave transition of 'biphenylene-polyenes' **3**(*n*), *n* = 0, 1, 2 (*i.e.* with 1, 2, and 3 double bonds) in an earlier paper [36].

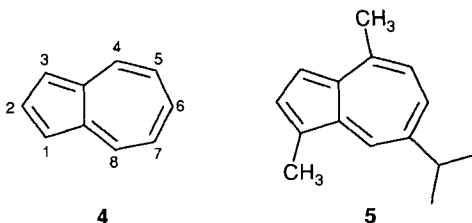


Only in 1935 did *K. W. Hausser* and *R. Kuhn* record the UV/VIS spectra of the ϵ,ω -diphenyl-polyenes **2**(*n*) [37]. It was shown that with increasing number *n* the position λ_{\max} of the first transition shifts systematically towards longer wavelengths, according to the empirical formula

$$\lambda_{\max} = k_1 \sqrt{n} + k_2 \quad (1)$$

and that the intensity, *i.e.* $\log(\epsilon)$, increases.

Another illustration of the importance of UV/VIS spectroscopy as a structure-analytical tool in the mid 1930s is provided by the classical work of **Placidus Andreas Plattner** (1904–1975)¹⁾ [38] on azulenes. (This has been reviewed in some detail by *Heimgartner* and *Hansen* on pp. 394 to 400 in [41].) After the parent hydrocarbon azulene $C_{10}H_8$ (**4**) had



¹⁾ *Placidus Andreas Plattner* was born in Chur in 1904. He studied chemistry at the Universities of Fribourg, Geneva, and Bern from 1924 to 1929, and worked for his thesis under the direction of Prof. *Emile Cherbuliez* in Geneva. After having obtained his Ph. D., he joined the *Givaudan* Company in Geneva. It is there that he did his memorable work on azulenes, in collaboration with *Alexander Stefan Pfsau*. In 1937, *Leopold Ruzicka* offered him a position at the Laboratorium für Organische Chemie of the Federal Institute of Technology in Zurich. In 1940, *Plattner* became a Privatdozent, and in 1945 Professor, a position he assumed until 1952, when he moved to the company *F. Hoffmann-La Roche* in Basel, to become its director of research. He retired in 1970 and died in Basel in 1975. Apart from his important contributions to organic chemistry (*cf.* [39–41]), it is noteworthy that *Plattner* was one of the first to make extensive use in his research of quite diverse physical methods, thereby becoming effectively the first physical-organic chemist in Switzerland. Portraits of *Plattner* can be found in the reviews by *Tamm* [39], p. 2143, and by *Kalvoda* [40], p. 2384.

Fig. 7

**64. Etudes sur les matières végétales volatiles VI¹⁾.
Sur les spectres d'absorption de l'azulène, du gaïazulène et du
vétivazulène**

par B. Susz, Alexandre St. Pfau et Pl. A. Plattner.

(1. IV. 37.)

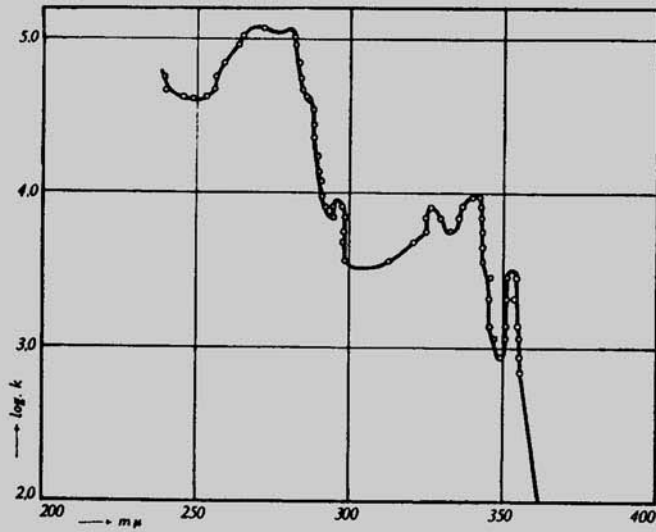


Fig. 1. Azulène.

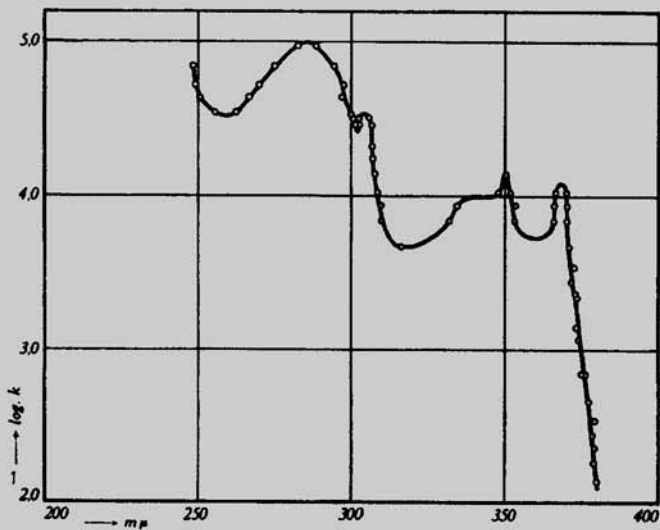


Fig. 2. S-Gaïazulène.

been synthesized by *Pfau* and *Plattner* [42], the identity of its chromophore with that of native azulenes, e.g. of guajazulene (= 7-isopropyl-1,4-dimethylazulene; **5**), was demonstrated by *Susz*, *Pfau*, and *Plattner* [43] through a comparison of their UV spectra, as shown in *Fig. 7*.

In 1941, *Plattner* discussed the long-wave-absorption band of azulene (**4**) and of alkyl(methyl)-substituted azulenes, to which these molecules owe their blue color [44]. This band, the 1L_b band in *Platt*'s nomenclature [45], exhibits a detailed vibrational fine structure, which allows an exact determination of the band positions. Unfortunately, this fine structure remained unresolved in the spectra obtained with the UV spectrographs then available – because of their poor dispersion in the red part of the spectrum – but the wave-numbers ν_{\max} of the positions of the individual fine-structure maxima could be measured visually with a *Löwe-Schumm* spectroscope [44]. Only later, the 1L_b bands of

Fig. 8

119. Zur Kenntnis der Sesquiterpene.

(76. Mitteilung¹).

Die Absorptionskurven des Azulens und der fünf Monomethyl-azulene im sichtbaren Bereich

von Pl. A. Plattner und E. Heilbronner.

(27. III. 47.)

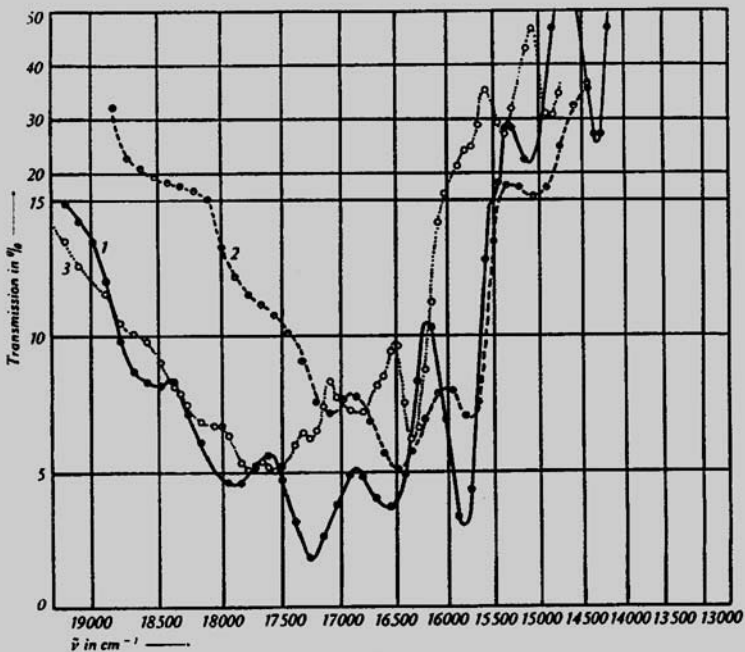


Fig. 1.

Transmissionskurven von Azulens (1), 1-Methyl-azulens (2) und 2-Methyl-azulens (3).

azulenes have been recorded using a photometrical procedure [46], yielding transmission curves, such as shown in *Fig. 8*¹²⁾.

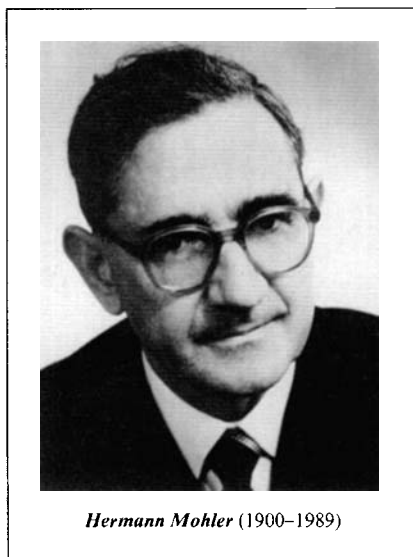
Plattner observed [44], that alkyl substitution at C(1) (= C(3)), and/or C(5) (= C(7)) of the azulene nucleus shifts the ¹L_b band bathochromically, *i.e.* towards longer wavelengths – as expected according to previous experience with unsaturated and aromatic hydrocarbons – but that alkyl substitution at C(2), C(4) (= C(8)), or C(6) yields, surprisingly, hypsochromic shifts, *i.e.* towards shorter wavelength. Because these shifts occur in the absence of steric hindrance, *i.e.* without a steric inhibition of the coplanarity of the π system, they are called ‘natural’ hypsochromic shifts.

In addition, *Plattner* could show that the shifts follow an additivity rule, meaning that the ¹L_b band position ν_{\max} of a polyalkyl-substituted azulene can be predicted fairly accurately by adding shift increments $\Delta\nu_{\mu}$ for each alkyl substituent in position μ (*Plattner*’sche Verschiebungsregel’):

$$\nu_{\max} = \nu_0 + \sum_{\mu} \Delta\nu_{\mu} \quad (2)$$

(with mean values $\nu_0 = 17270 \text{ cm}^{-1}$, $\Delta\nu_1 = -810 \text{ cm}^{-1}$, $\Delta\nu_2 = +430 \text{ cm}^{-1}$, $\Delta\nu_4 = +320 \text{ cm}^{-1}$, $\Delta\nu_5 = -300 \text{ cm}^{-1}$, $\Delta\nu_6 = +400 \text{ cm}^{-1}$ [47]).

An explanation of both these observations in terms of the particular electronic structure of the ‘non-alternant’ hydrocarbon azulene **4** was given much later [48]. It is found [49] that the large bathochromic and, in particular, the ‘natural’ hypsochromic shifts are mainly due to the inductive effect of the alkyl groups.



Hermann Mohler (1900–1989)

¹²⁾ *Plattner*’s graphical representation of the positions ν_{\max} of the vibrational fine-structure components of the ¹L_b band (mean spacing 730 cm^{-1}) of a series of azulenes, taken from [44], has been reproduced in [41], p. 398.

In 1937, **Hermann Mohler** (1900–1989)¹³⁾ professor at the Physikalisch-chemische Anstalt of the University of Basle and director of the Städtisches Chemisches Laboratorium of Zurich begins to publish systematic studies of the UV/VIS spectra of organic molecules, and especially of compounds used in chemical warfare [50]¹⁴⁾. *Fig. 9* shows on top the UV spectra of some enones, taken from his first paper on ‘*R₁-R₁ systems*’ [52], which, in *Mohler*’s nomenclature, are systems containing two conjugated chromophores R₁, such as R₁ = C=C, C=O, C≡N, NO₂, or a halogen atom. On the lower part of *Fig. 9*, is shown a sample of the UV spectra of polynuclear aromatic hydrocarbons, which *Mohler* recorded on the request of *Bergmann* [53].

Fig. 9

**39. Lichtabsorption der R₁-R₁-Systeme I.
Spektrn von Cholestenon, Cholestenon-oxim, Mesityloxyd,
Pulegon und Carvon**

von H. Mohler.

(15. II. 37.)

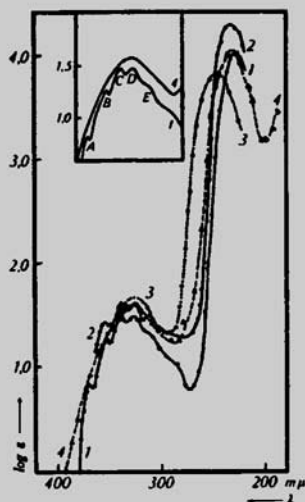


Fig. 1.

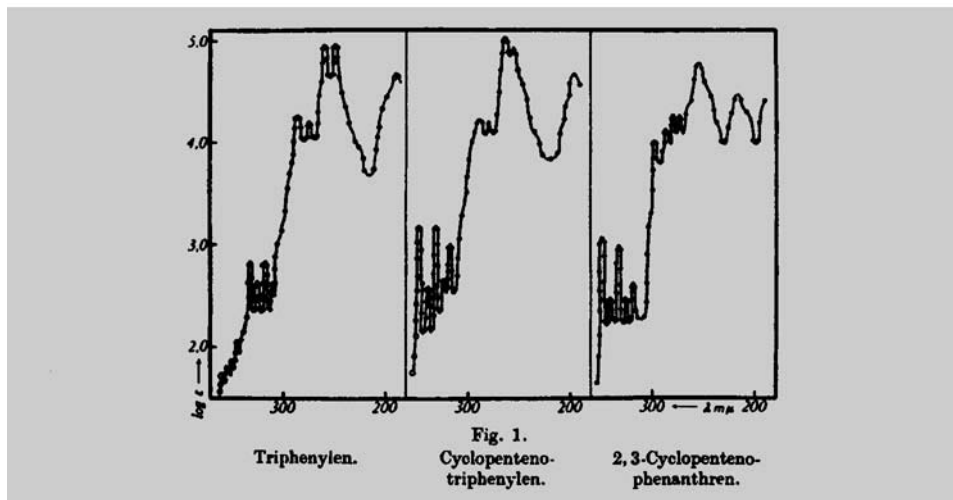
- | | |
|----------------|------------|
| 1. Carvon | } in Hexan |
| 2. Cholestenon | |
| 3. Pulegon | |
| 4. Mesityloxyd | |

¹³⁾ *Hermann Mohler*, born in Basle in 1900, studied Chemistry at the Universities of Basle and Berne. He obtained his Ph. D. in physical chemistry in 1925, and was elected in 1932 as director of the Chemical Laboratories of the city of Zurich. In 1937 he became ‘Privatdozent’ and in 1947 a.o. Professor of Physical Chemistry at the University of Basle. During the years 1951 to 1954, he directed an UNESCO mission with the aim of establishing a chemical faculty at the University of Bagdad. After his return to Switzerland, he became director of the research department of the *Knorr* Foodstuff Company. He retired from this post in 1965, and died in Basle in 1989.

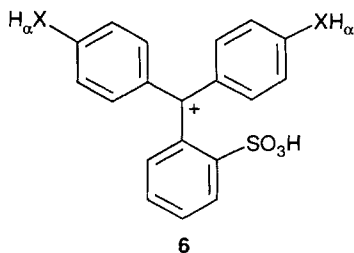
¹⁴⁾ Later publications in this series are concerned with the dipole moments and other physico-chemical properties of these compounds [51].

Fig. 9
(cont.)

29. Ultravioletabsorption einiger polycyclischer Kohlenwasserstoffe
 von H. Mohler und J. Sorge.
 (30. XII. 38.)

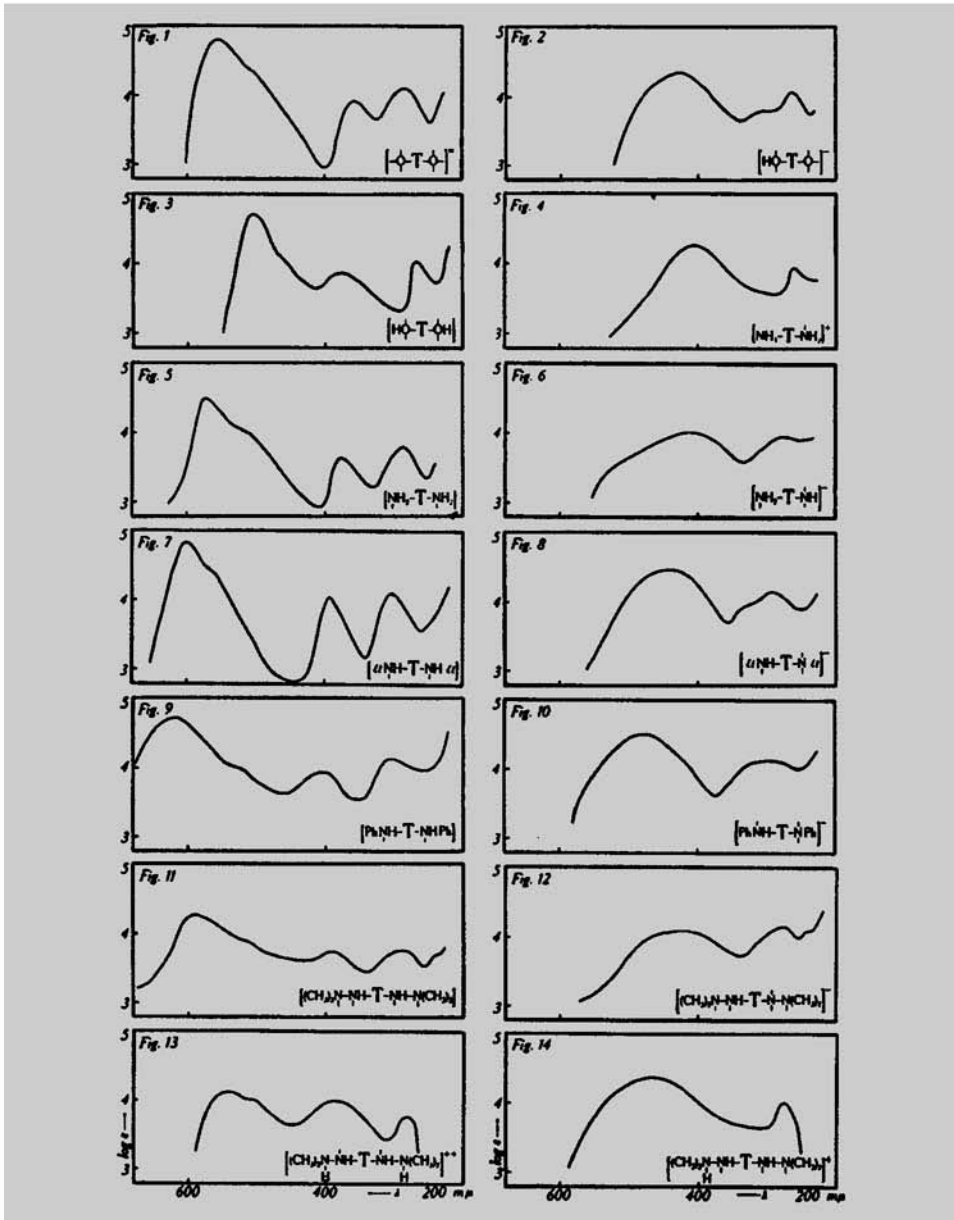


In collaboration with *Schwarzenbach*, *Mohler* investigated the absorption spectra of sulfone-phthaleins $H_xX-\overline{T}-XH_x$ (**6**), where \overline{T} stands for the sulfurated triphenylcarbonium ion, and XH_x for an auxochromic group, e.g. $XH_x = NH_2$. In this paper – Part IV of *Schwarzenbach*'s series on resonance systems which will be discussed in *Chapt. 3* – it is shown that the absorption spectra reflect the symmetry of the system, the symmetric systems $H_xX-\overline{T}-XH_x$ and $H_{x-1}X-\overline{T}-XH_{x-1}$ exhibiting the same type of band contour, quite different from that of the unsymmetric systems $H_x-1X-\overline{T}-XH_x$, as can be seen in *Fig. 10*, taken from [54].



These studies formed the background for his book '*Das Absorptionsspektrum der chemischen Bindung*' [55], to our knowledge the first book on this topic in German, aimed at the practicing chemist. It was widely used as an introduction to the field, and as a reference manual. Its popularity can be judged by the fact that its first edition was out of print in eight months.

85. Molekulare Resonanzsysteme IV¹.
Die Absorptionsspektren einiger Sulfon-phtaleine
 von H. Mohler, H. Forster und G. Schwarzenbach.
 (22. V. 37)



A further important spectroscopic contribution, which *Mohler* published in *HCA*, concerns the investigation of the far-UV absorption spectra of organic molecules in the range below 200 nm [56]. By using the experimental set-up built around a *Cario-Schmidt* spectrograph, as shown in *Fig. 11* [56], he extended substantially the spectral range, so far available, with conventional instruments, which had allowed only the recording of not very inspiring ‘end absorptions’ of ‘small’ chromophores, e.g. of carbonic acids [57]. It should also be mentioned that *Mohler* built in 1941 a self-recording UV spectrometer, the first instrument of its kind in Switzerland [58].

Fig. 11

36. Absorptionsspektrophotometrie von Lösungen im kurzwelligigen Ultraviolett
 von **H. Mohler.**
 (15. II. 37.)

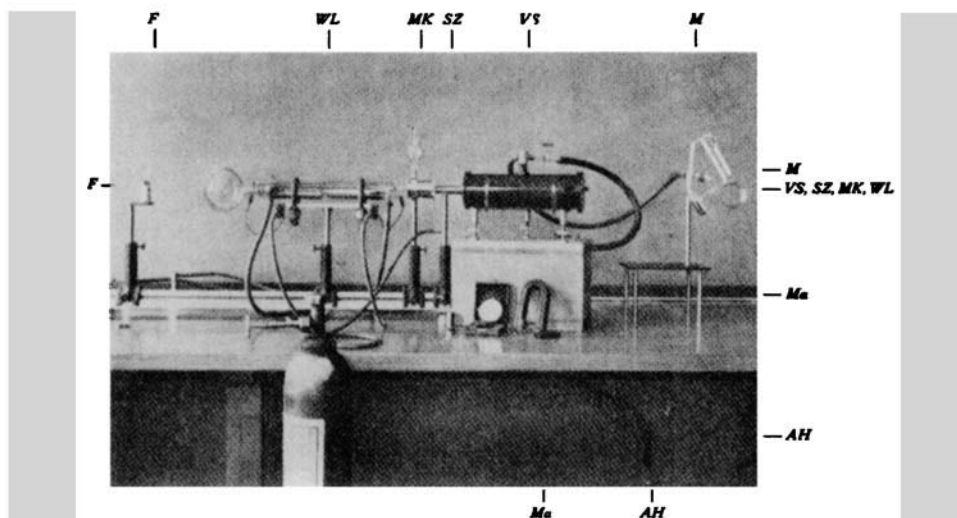
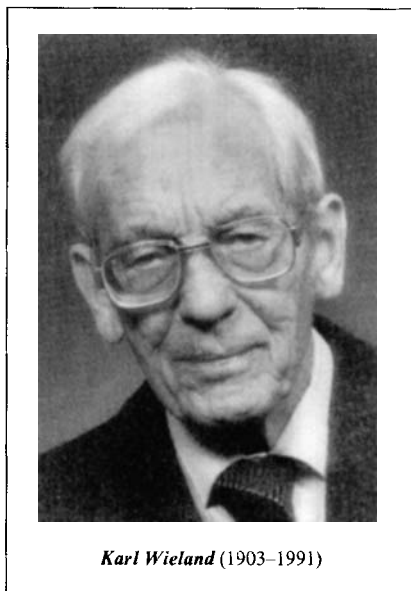


Fig. 1.

<i>M—M</i>	Manometer
<i>VS—VS</i>	Vakuumspektrograph
<i>SZ—SZ</i>	Stickstoffzuführung
<i>MK—MK</i>	Mikroküvette
<i>WL—WL</i>	Wasserstofflampe
<i>AH—AH</i>	Anschluss an die Hochvakuumpumpe
<i>Ma—Ma</i>	Magnet
<i>F—F</i>	Funken für Vergleichsspektrum

We mention briefly that *Briner* and *Perottet* studied, in 1940, the pH dependence of the absorption and fluorescence spectra of luminol [59].



At the University of Zurich, in the Institute of Physical Chemistry directed by *von Halban*, **Karl Wieland**¹⁵⁾ (1903–1991) [60] began to investigate the high-temperature band spectra (in the range of 800 to 1200 °C) of small molecules and radicals in the gas phase, in particular of Hg³⁵Cl and Hg³⁷Cl [61] shown in *Fig. 12*, of CdI₂ and CdI [62], and of HgI₂ and HgI [63].

The same technique and experimental set-up was later used by *Wieland* and one of the authors to record in 1946 the gas-phase spectrum of azulene (**4**) at temperatures of ~ 400°, shown in *Fig. 13* [64]. In the course of this investigation, the rearrangement of azulene into its isomer naphthalene was discovered, as already mentioned and briefly discussed in [41].

173. Spektroskopische Bestimmung der Anreicherung eines Chlorisotopen mit minimalen Mengen von Quecksilber(II)-chlorid (Sublimat)

von **K. Wieland**.

(6. IX. 43.)

Fig. 12

¹⁵⁾ *Karl Wieland* was born in Basle in 1903, where he studied physics, chemistry, and mathematics at the University. He completed his Ph. D. as an experimental physicist in 1929. After having worked as a postdoctoral fellow with – among others – *James Franck* in Göttingen, he took a position as assistant of *H. von Halban* at the Institute of Physical Chemistry at the University of Zurich. There, he became a ‘Privatdozent’ in 1941, and ‘Titularprofessor’ in 1953. After a stay at the University of California at Berkeley, he left Zurich in 1962, to return to Basle where he worked in the Institute of Physics of the University. He died in Basle in 1991.

Fig. 12
(cont.)

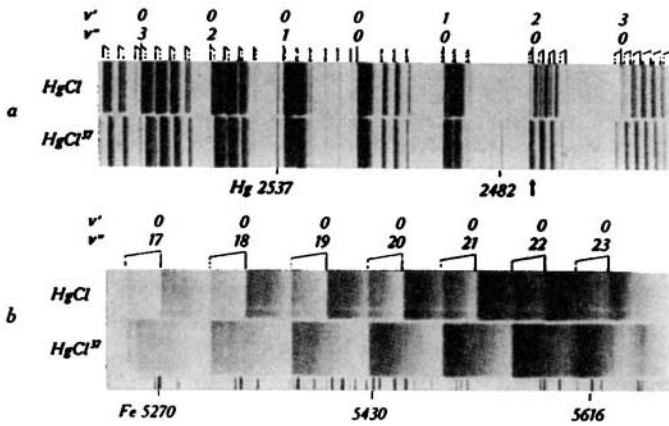


Fig. 2.

Spektrum von $HgCl$

Die vollen Striche markieren die Kanten von $HgCl^{36}$
die punktierten Striche markieren die Kanten von $HgCl^{37}$

- a) Bandensystem D in Emission, elektrisch erregt.
oberer Teil: natürliches $HgCl$ ($Cl^{36} : Cl^{37} = 3,11 : 1$)
unterer Teil: angereichertes $HgCl^{37}$ ($Cl^{36} : Cl^{37} = 1 : 11,5$)
- b) Bandensystem B (langwelliger Teil) in Fluoreszenz, bei Zusatz von $300\ mm\ N_2$.
oberer Teil: natürliches $HgCl$
unterer Teil: angereichertes $HgCl^{37}$ (wie bei a).

Fig. 13

122. Spektrographische und thermochemische Untersuchungen
an dampfförmigem Azulen

von E. Heilbronner und K. Wieland.

(28. III. 47.)

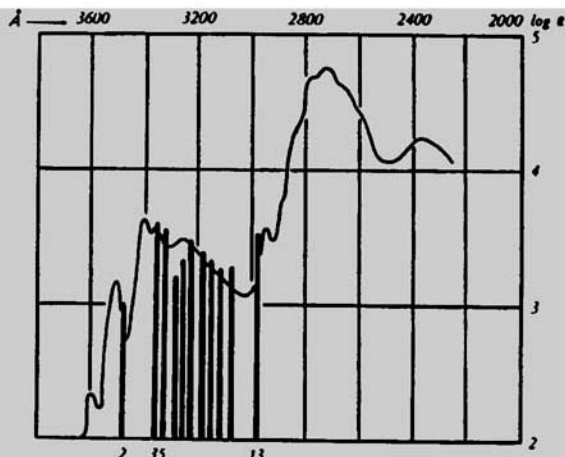


Fig. 2.

Absorptionswerte von Azulen in Lösung (Kurve) und in Dampfphase (Striche).

Von Halban's successor (1947) as professor of Physical Chemistry at the University of Zurich was *Klaus Clusius* (see Sect. 4.2). Under his directorship, research at the institute turned towards thermodynamics and kinetics, in particular to the investigation of the physical and chemical properties of isotopically labeled molecules. After his death in 1963, **Heinrich Labhart** (1919–1977)¹⁶⁾ [65] resumed the spectroscopic tradition of the institute, having been elected as its director in 1964.



Heinrich Labhart (1919–1977)

A large part of *Labhart's* oeuvre deals with quantum-chemical problems, and will be dealt with in detail in *Chapt. 3*. Here, we concentrate on two important contributions to experimental spectroscopy of organic molecules, namely the influence of electric fields on the absorption of light by such molecules, and the observation of triplet spectra of molecules in solution.

A first contribution [66] deals with the theory concerning the relative change $\Delta J/J$ of the absorbed light intensity J , under the influence of a strong electric field F . The

¹⁶⁾ *Heinrich Labhart* was born in 1919 in Künsnacht, Kanton Zurich. He studied physics at the Federal Institute of Technology (ETH) in Zurich and worked, under the direction of *Paul Scherrer* and *Georg Busch* for his Ph. D., which he obtained in 1947. After a two-year stay (1947–1948) at the laboratory of the University Hospital of Basle, he returned to the ETH where he worked in the Department for Industrial Research until 1951. He became a 'Privatdozent' in 1952, after having joined, the previous year, the Physics Section of *Ciba AG*, Basle. He remained in this position for 13 years, with a short interruption in 1956, when he stayed with *R. S. Mulliken* and *John R. Platt* at the University of Chicago. In 1958, the University of Basle awarded him the title of a.o. Professor, and in 1964 he was elected as o. Professor, and director of the Institute of Physical Chemistry of the University of Zurich. He died in 1977.

Fig. 14

55. Beeinflussung der Lichtabsorption organischer Farbstoffe durch äussere elektrische Felder

I. Theoretische Betrachtung

von **Heinrich Labhart**

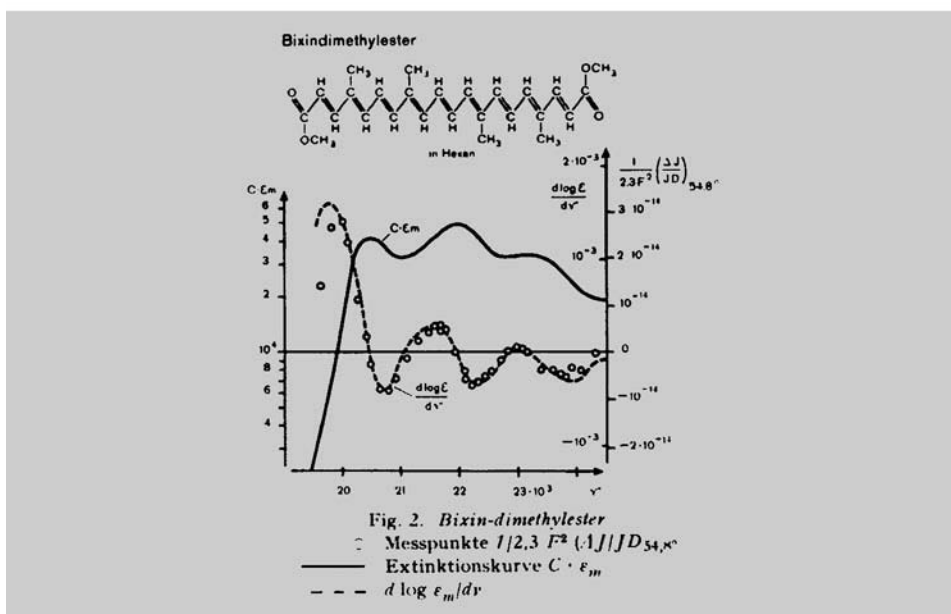
(13. I. 61)

56. Beeinflussung der Lichtabsorption organischer Farbstoffe durch äussere elektrische Felder

II. Experimentelle Untersuchungen an Polyenen

von **Heinrich Labhart**

(13. I. 61)



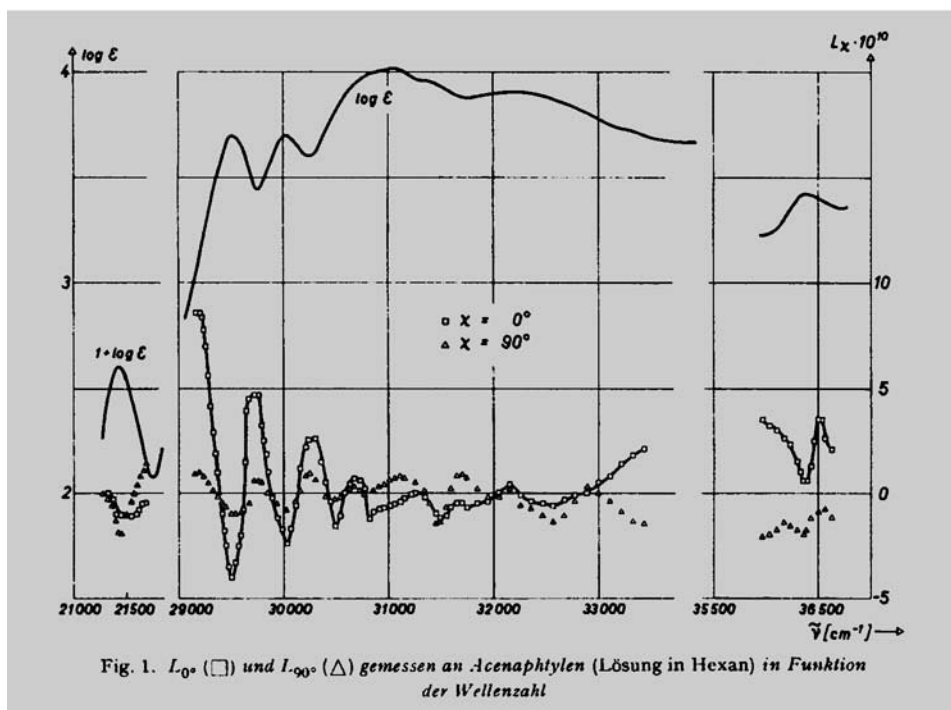
theoretical results could be verified by measuring $\Delta J/J$ for e.g. bixin dimethyl ester, as shown in Fig. 14 [67].

Another spectroscopic effect, due to the application of a strong electric field to a solution of dipole molecules, is the induction of a dichroism, as consequence of their partial orientation. This method, originally pioneered by *Werner Kuhn* and his coworkers [68] in 1940, and taken up by *Labhart* in a more sophisticated manner [69], allows the determination of the orientation of electronic transition moments with respect to the

molecular frame, and the change of dipole moment on excitation. This permits the deconvolution of strongly overlapping bands, as *Labhart* showed, for example, in the case of annellated tropones [70]. As a more recent illustration, we reproduce in *Fig. 15* the results for acenaphthylene, obtained by *Seibold*, *Zahradnik*, and *Labhart* in 1970 [71].

**91. Untersuchung des UV. Spektrums
von Acenaphthylen durch Beobachtung des durch ein elektrisches
Feld induzierten Dichroismus**
von **K. Seibold¹⁾**, **R. Zahradnik²⁾** und **H. Labhart¹⁾**
Akademie der Wissenschaften, Prag, und
Physikalisch-chemisches Institut der Universität Zürich
(9. IV. 70)

Fig. 15



In 1964, *Labhart* described an experimental method for the measurement of the singlet-triplet transition probabilities, and of the triplet spectra of organic molecules [72]. In *Fig. 16* is reproduced the triplet spectrum of 1,2-benzanthracene obtained by this method.

The last paper by *Labhart*, published posthumously with *Huggenberger* [73], dealt with the luminescence of luminol in various solvents.

Fig. 16

252. Eine experimentelle Methode zur Ermittlung der Singulett-Triplett-Konversionswahrscheinlichkeit und der Triplett-Spektren von gelösten organischen Molekeln
Messungen an 1,2-Benzanthracen

von **Heinrich Labhart**

(15. X. 64)

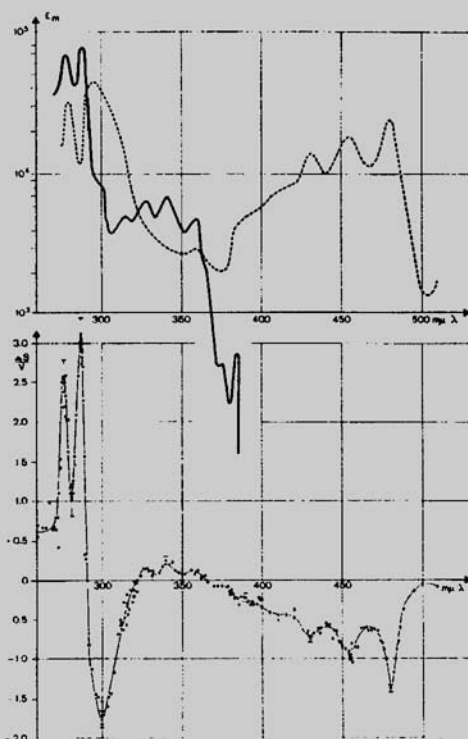


Fig. 5. Messungen an 1,2-Benzanthracen

unten: Messwerte $\Delta S/V$ in Funktion von λ

oben: ausgezogene Kurve: Singulett-Singulett-Spektrum, gestrichelte Kurve: gemäss Gl. 14 mit $1/m = 1,8 \cdot 10^4 \text{ l Mol}^{-1} \text{ cm}^{-1}$ ermitteltes Triplett-Triplett-Spektrum

To conclude this section, we quote the following isolated publications as typical representatives of work dealing with electronic transitions (see also *Sect. 1.3*).

a) *Optical Rotation*. As mentioned at the beginning of this section, the first theory of optical rotation stems from *Werner Kuhn* [74] (see also *Chapt. 3*). Together with *Rometsch*, he published in *HCA* two papers reporting their investigations of optically active diphenyl derivatives [75] in different solvents. As an example, we show in *Fig. 17* the

Fig. 17

125. Untersuchungen über optisch aktive Diphenylverbindungen I
(Problemstellung und experimentelle Ergebnisse)

von **W. Kuhn** und **R. Rometsch**.

(21. VI. 44.)

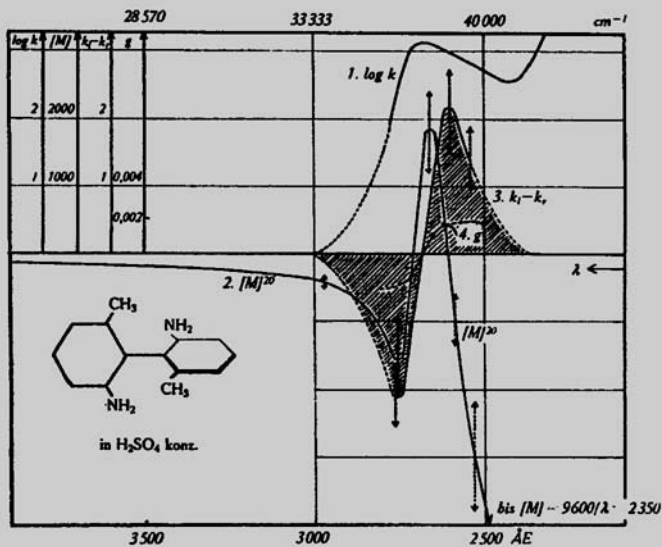


Fig. 14.

Absorption ($\log k$), Rotationsdispersion $[M]$, Zirkulardichroismus ($k_1 - k_2$) und Anisotropiefaktor $g = (k_1 - k_2)/k$ von 2,2'-Dichlor-6,6'-dimethylbenzidin in konz. Schwefelsäure (⬆ Fehlergrenzen).

results obtained for '2,2'-dichloro-6,6'-dimethylbenzidine' (correct name: 2,2'-diamino-6,6'-dimethyl-1,1'-biphenyl) in sulfuric acid. These experiments were undertaken to demonstrate that the optical rotation at a given wavelength is the sum of the contributions due to the individual absorption bands.

An interesting application of CD measurements is due to *Georges Wagnière* and his coworkers at the University of Zurich, who investigated the electronic properties of optically active oligopeptides, in particular cyclohexapeptides [76], a sample of which is presented in Fig. 18. In the formulae shown, G stands for glycine, and L for L-alanine.

The magnetic circular dichroism of various molecules has been recorded by *Harold Baumann*, from the ETH-Zurich, in collaboration with research groups in Japan. These measurements were undertaken in order to assign the absorption spectra of e.g. 2-methyl-1,3-diazaazulene [77] (see Fig. 19) or of trophothione [78].

b) *Transition Moments*. In addition, the work of *Labhart* discussed above, we mention briefly two other methods for the determination of the transition moments of molecules, which have appeared in *HCA*. One example is due to *Robert Stupp* and *Hans Kuhn* [79]

Fig. 18

95. Electronic Properties and Optical Activity of Oligopeptides. III. Some Cyclohexapeptides with Glycine, L- and D-Alanine

by Max Isell and Georges Wagnière¹⁾

Physikalisch-Chemisches Institut der Universität Zürich, Winterthurerstr. 190, CH-8057 Zürich

and by J. Georges Brahms and Sabine Brahms

Institut de Recherche en Biologie Moléculaire de la Faculté des Sciences, Université de Paris,
2, place Jussieu, Paris 5eDedicated to Professor *André Dreiding* for his 60th anniversary

(7.11.79)

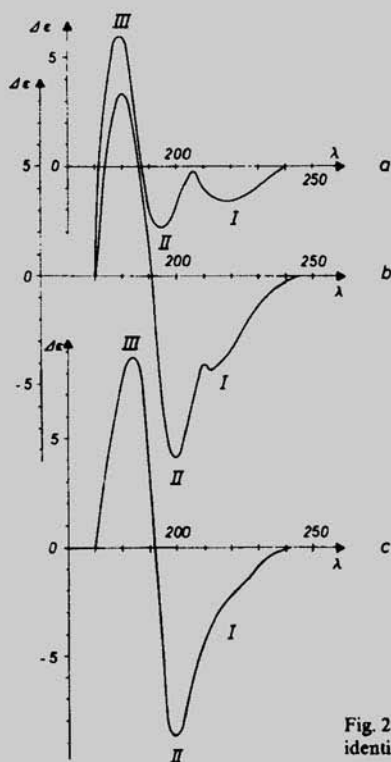


Fig. 2. CD. spectra of peptides a, b, c (for identification see Fig. 1) in D₂O.

229. Magnetic Circular Dichroism and Absorption Spectra of 2-Methyl-1,3-diazaazulene

by Hiroyuki Yamaguchi¹⁾, Masafumi Ata and Koichi Toyoda

Department of Chemistry, Faculty of Science, Kumamoto University, 2-39-1 Kurokami,
Kumamoto 860, Japan

Hiroaki Mametsuka and Hitoshi Takeshita

Research Institute of Industrial Science, Kyushu University, Fukuoka 812, Japan

and Harold Baumann

Laboratorium für Organische Chemie der Eidgenössischen Technischen Hochschule,
Universitätstrasse 16, CH-8092 Zürich

(18. VIII. 81)

Fig. 19

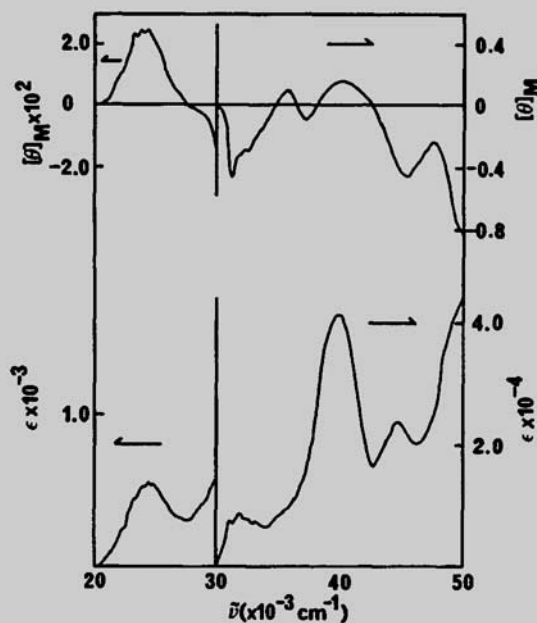


Figure 2. Magnetic circular dichroism (top) and absorption (bottom) spectra of 2-methyl-1,3-diazaazulene (2) in cyclohexane

who determined the orientation of the transition moments of chlorophyll by measuring the polarisation of its fluorescence, as shown in Fig. 20.

The other example refers to the determination of the linear dichroism of a molecule dissolved in a stretched polymer. In Fig. 21 is shown the result for 'bicyclobutylene-benzene' [80], obtained by Erik W. Thulstrup, one of the pioneers of this method, Rolf Gleiter, and their coworkers.

Fig. 20

304. Chlorophyll a. Untersuchung der Polarisation des Fluoreszenzlichts zur Ermittlung der Richtungen der Übergangsmomente von Absorptionsbanden

von Robert Stupp und Hans Kuhn.

(11. X. 52.)

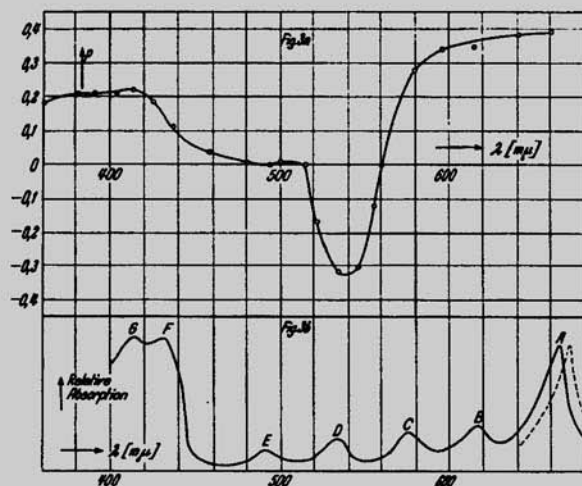


Fig. 3.

Chlorophyll a in Rizinusöl ($\eta = 9,48$ poise).

- a) Ordinate: Polarisationsgrad p des Fluoreszenzlichts. Abszisse: Wellenlänge λ des einfallenden Lichts.
- b) Absorptionsspektrum (ausgezogener Linienzug); Fluoreszenzspektrum (gestrichelter Linienzug). Schematisch, Nebenbanden überhöht dargestellt.
- Man beachte, dass p zwischen $520 \text{ m}\mu$ und $580 \text{ m}\mu$ (im Bereich der Bande D) negatives Vorzeichen besitzt.

Fig. 21

63. Electronic States of Phenylene and Naphthylene Bicyclobutanes. Linear Dichroism in Stretched Polyethylene

by Jens Spanget-Larsen, Klaus Gubernator and Rolf Gleiter

Institut für Organische Chemie der Universität, D-6900 Heidelberg 1

Erik W. Thulstrup

Department of Chemistry, Royal Danish School of Educational Studies, DK-2400 Copenhagen NV

and Bernard Bianco, Gérard Gandillon and Ulrich Burger

Département de chimie organique de l'Université, CH-1211 Genève 4

(23. XII. 82)

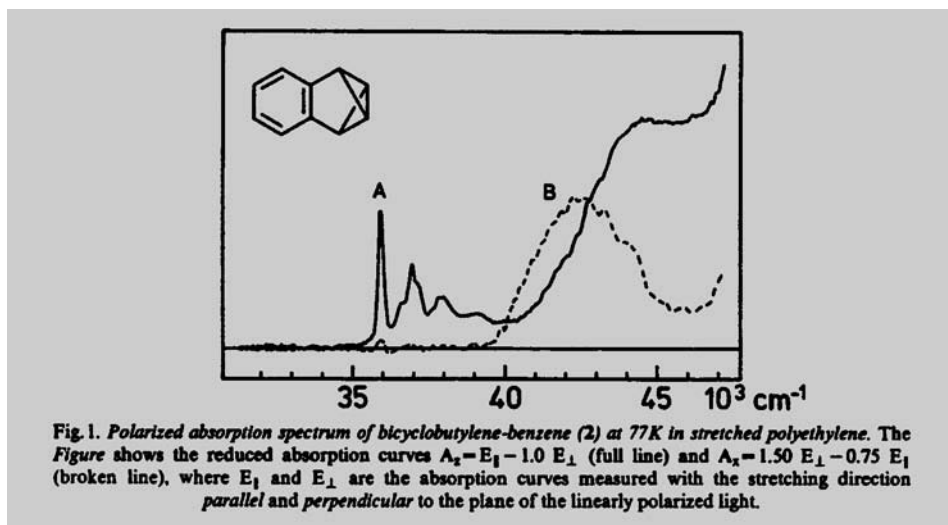


Fig. 21 (cont.)

c) *Solvent Effects.* In 1972, *Heinz Christen*, in collaboration with *Peter A. Straub* [81] and *Else Kloster-Jensen* [82], investigated the influence of non-polar solvents on the electronic spectra of apolar solutes. The theoretical results, based on a model which takes only energy delocalization between solvent and solute into account, could be verified by recording the absorption spectra of polyacetylenes in hydrocarbon/carbon-disulfide mixtures [82]. A typical example is shown in *Fig. 22*, which refers to di(*tert*-butyl)-pentaacetylene.

175. Über den Einfluss nichtpolarer Lösungsmittel auf Lage und Intensität von Absorptionsbanden in den Elektronenspektren apolarer Molekeln: II. Polyacetylene

von **Heinz Christen** und **Else Kloster-Jensen**¹⁾
 Physikalisch-Chemisches Institut der Universität Basel,
 Klingelbergstrasse 80, 4056 Basel

(7. III. 73)

Fig. 22

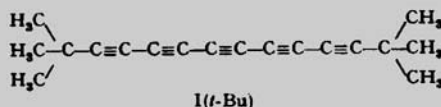
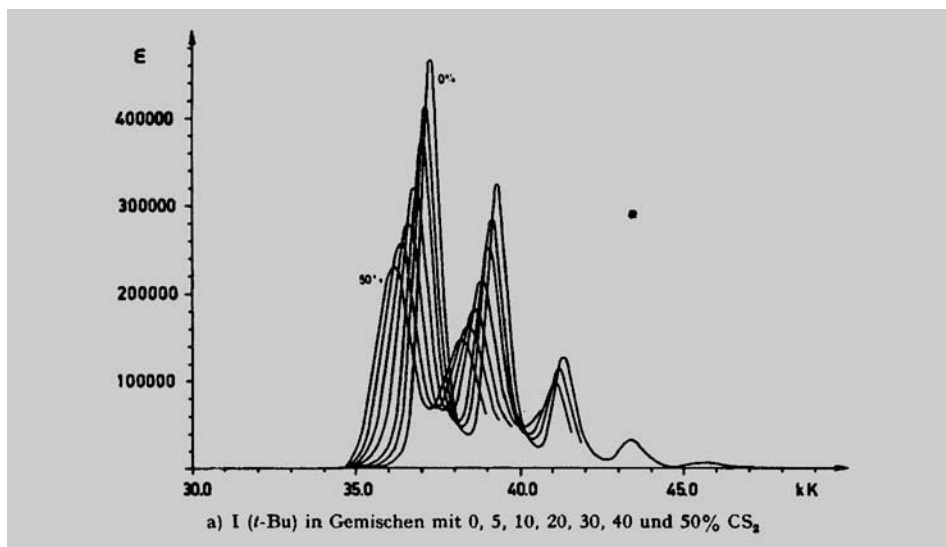


Fig. 22
(cont.)

An interesting application ‘in reverse’ of the solvent effect is described in the publication by *Erika Schmidt*, *Hans Loeliger*, and *René Zürcher* [83], the title of which is presented in Fig. 23. By matching the ‘solvent effect’ of a polymer matrix on the electronic spectrum of an incorporated ‘solute’ molecule with the corresponding effects of different, liquid solvents, it was possible to draw conclusions about the micro-environment, in which the molecule is imbedded in the polymer.

Fig. 23

39. What is the ‘Solvent’ Effect on the Electronic Spectra of a Solute in a Polymer Matrix?

by *Erika Schmidt*, *Hans Loeliger* and *René Zürcher*¹⁾

Physik, Funktion Forschung, CIBA-GEIGY AG, CH-4002 Basel

Dedicated to the memory of Professor *Heinrich Labhart*

(14.XI.77)

1.2. IR and Raman Spectroscopy. In this section, we limit ourselves to either early publications describing the application of vibrational spectroscopy for the elucidation of molecular structure, or to papers dealing with either experimental or theoretical problems arising in this field. From about 1960 on, the use of vibrational spectroscopy – especially the recording of IR spectra – had become a standard routine for solving structural problems. Although this aspect is of considerable importance, we shall not be concerned with it in the following review.

The first appearance of IR spectra in *HCA*, more precisely of near-infrared (NIR) spectra, occurs in 1937. They are found in the summary of a talk given by *J. Errera* at the Geneva meeting of the Swiss Chemical Society¹⁷⁾ [84]. It deals with the dependence of the fundamental (3600–3100 cm⁻¹) and the first overtone (at 1.51 μm) in the absorption spectra of OH groups, on intra- and intermolecular H-bonding. An example is shown in Fig. 24.

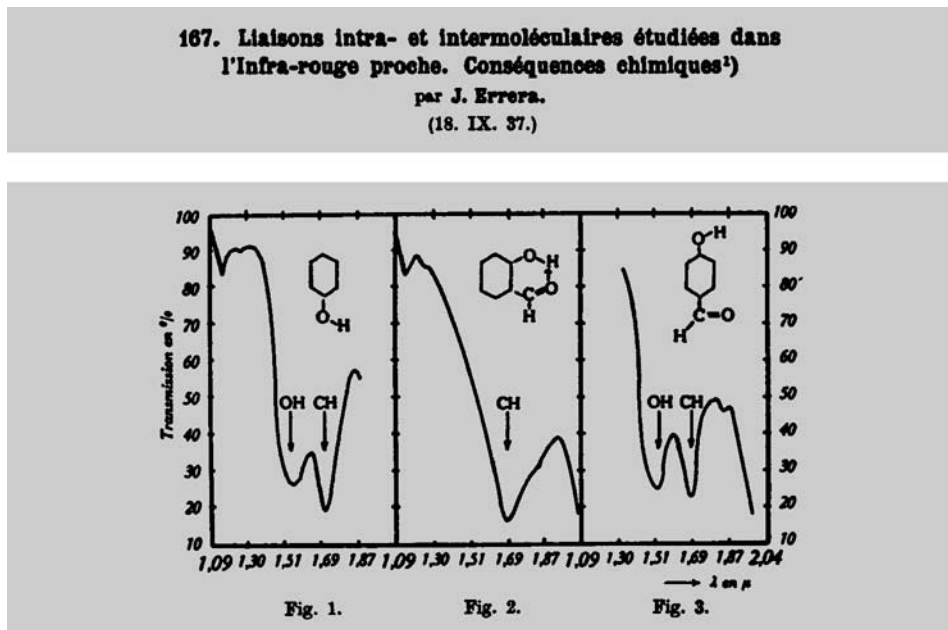


Fig. 24

However, the first paper in *HCA* dealing with the application of vibrational spectroscopy to a chemical problem was published as early as in 1932 by *Rudolf Signer*¹⁸⁾ and *J. Weiler* [85]. It concerned the *Raman* spectrum (RE) of polystyrene, reproduced in Fig. 25. It was shown that polystyrene of an average molar mass of 40 000 g · mol⁻¹ yields RE spectra with narrow lines, similar to those of low-molecular-weight compounds, such as ethylbenzene. This was an important confirmation of the chain structure suggested by *Hermann Staudinger* for such polymers [86].

A year later, the same authors reported a *Raman* study of the esters of orthosilicic acid and of its low polymeric forms [87], with special emphasis on the dependence of the characteristic mode of the SiO₄ group on the degree of polymerisation.

¹⁷⁾ Although the work was performed at the Laboratoire de chimie physique polytechnique de l'Université de Bruxelles, and that *Errera* was not Swiss, the paper was accepted for publication in *HCA* – under the then valid regulation –, because it had been presented at a meeting of the Swiss Chemical Society.

¹⁸⁾ A short curriculum and a portrait of *Signer* are presented in *Sect. 4.1*.

Fig. 25

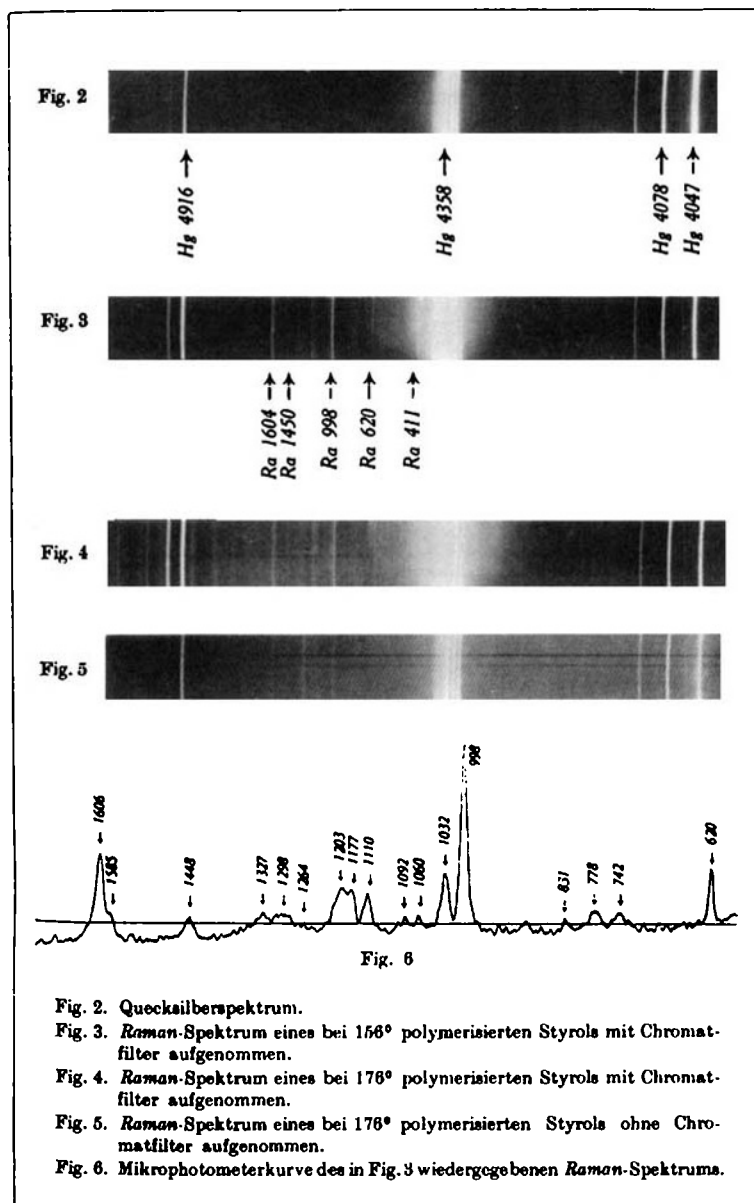
Raman-Spektrum und Konstitution hochmolekularer Stoffe

62. Mitteilung über hochpolymere Verbindungen²⁾

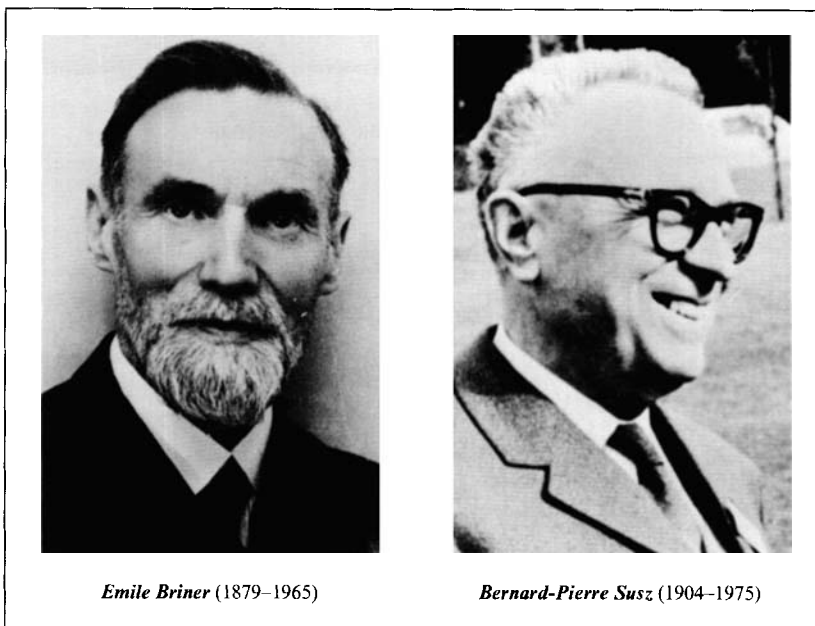
von R. Signer und J. Weller.

(26. III. 32.)

Tafel I.



From 1935 onwards, RE spectroscopy was used rather regularly as a structure diagnostic method. Among the research groups, most active in this field, were those of **Emile Briner** (1879–1965)¹⁹⁾ [88] and of **Bernard-Pierre Susz** (1904–1975)²⁰⁾ [89], both at the Institut de Chimie Physique de l'Université de Genève. Typical examples of work stemming from their laboratory are, for example [90] [91], or [92], in which they suggested the use of color film for the registration of *Raman* spectra. (Further contributions by *Briner* and *Susz* are discussed below.)

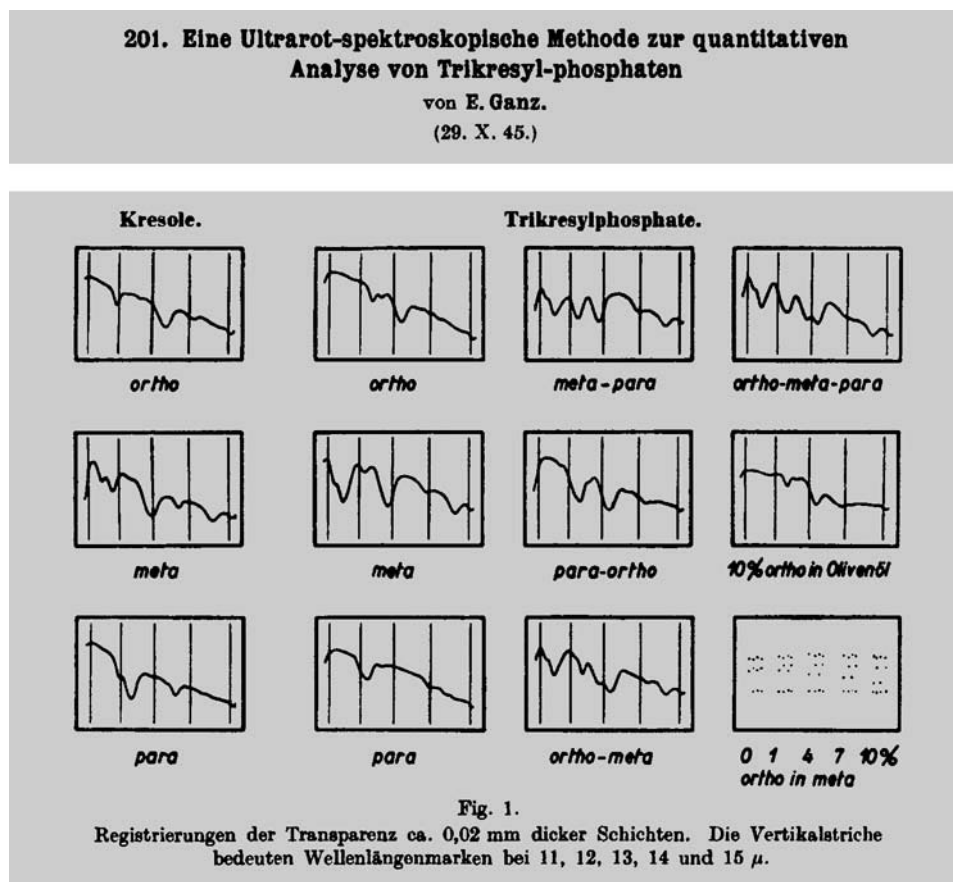


¹⁹⁾ *Emile Briner* was born in Geneva in 1879. He studied chemistry at the Université de Genève, worked for his doctorate under the direction of *Philippe Auguste Guye*, and obtained his Ph. D. in 1902. After having spent a year in Paris with *Henri Moissan*, he returned to Geneva. In 1903, he became a 'privat docent', and gave a course on chemical thermodynamics. In 1918, he was promoted to the rank of professor, and in 1922, he succeeded *Guye* as director of the Institut de Chimie Physique. *Briner* had widespread interests, of which we mention only his very detailed study of ozone, ozonides, and of the reactions of ozone, his investigations of chemical equilibria, his contributions to spectroscopy in all its forms, and last but not least his technological work, documented by many patents. He died in Geneva in 1965.

²⁰⁾ *Bernard-Pierre Susz* was born in Geneva in 1904. He studied chemistry at the Université de Genève, where he also obtained his Ph. D. in 1929, after having worked under the direction of *Emile Briner*. He then spent a year in Berlin with *Max Bodenstein* at the *Kaiser-Wilhelm-Institut* (now *Max-Planck-Institut*). After his return to Geneva, he became in 1930 a 'privat docent' of Physical Chemistry and a close collaborator of *Briner*. For ca. 20 years, *Susz* taught chemistry at the Collège de Genève (now Collège Calvin). One of the authors, *E. H.*, an 'ancien collègien', remembers fondly his exciting chemistry course which, in 1938/39, was much more modern than many of those given nowadays. In 1953, *Susz* was promoted to the rank of Professor, and in 1954, he became the successor of *Emile Briner* as director of the Institut de Chimie Physique de l'Université. He retired in 1970, and died in Geneva in 1975. The majority of his work is concerned with different spectroscopic methods (IR, RE, UV/VIS), and with the investigation of the structure of complexes between molecules containing a CO group, and *Lewis* acids.

In 1945, *Ernst Ganz* published the first set of mid-IR spectra [93], recorded with a home-built, self-recording instrument – to our knowledge the first in Switzerland. In this publication, from which *Fig. 26* has been reproduced, the quantitative analysis of isomeric tricresyl phosphates is described.

Fig. 26



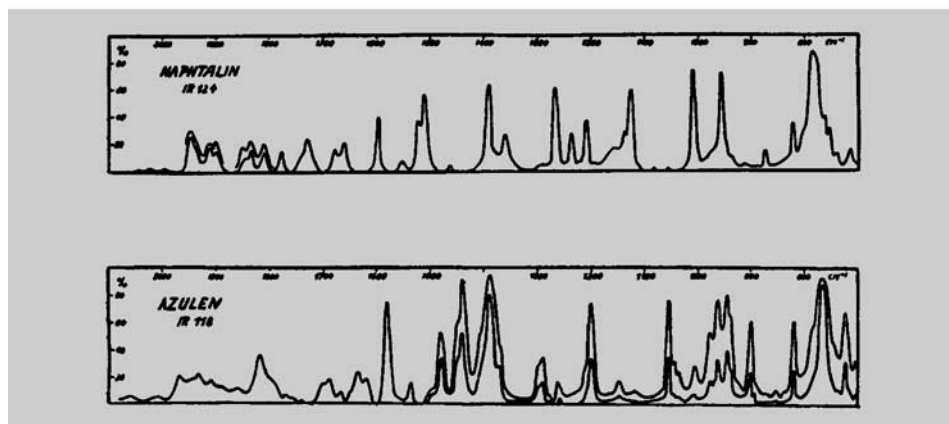
The rapid technological development in anglo-saxon countries during the war made commercial IR spectrometers available after 1945. The first such instrument was operated at the Laboratorium für Organische Chemie of the ETH, due to the initiative of *Leopold Ruzicka*²¹⁾.

²¹⁾ Such instruments were still exceedingly expensive, and it took all of *Ruzicka*'s persuasiveness to convince the 'Schulratspräsident' to make the necessary funds available. After having finally agreed to provide the necessary money, the 'Schulratspräsident' said: 'Knowing you, Professor *Ruzicka*, I guess that you have already ordered the instrument'. To which *Ruzicka* replied: 'No, No! The instrument has already been installed, and it is working perfectly'.

The beginning of the era of the use of such instruments is documented in *HCA* for the first time by a paper of *Hans H. Günthard* and *Ruzicka* [94], which concerns structural studies in the irone and ionone series. This was followed by numerous applications of IR spectroscopy in the important field of natural compounds, such as mono- and polyterpenes, or steroids. The power of *Raman* spectroscopy was significantly improved by including polarization measurements, as documented by the work of *Susz*, *Briner*, and their coworkers [95]. As a further example, we quote the investigation of azulenes [96], due to *Günthard* and *Plattner*, from which *Fig. 27* has been taken.

39. Zur Kenntnis der Sesquiterpene und Azulene.
84. Mitteilung¹).
Infrarotspektren der Azulene
von **Hs. H. Günthard** und **Pl. A. Plattner**.
(21. XII. 48.)

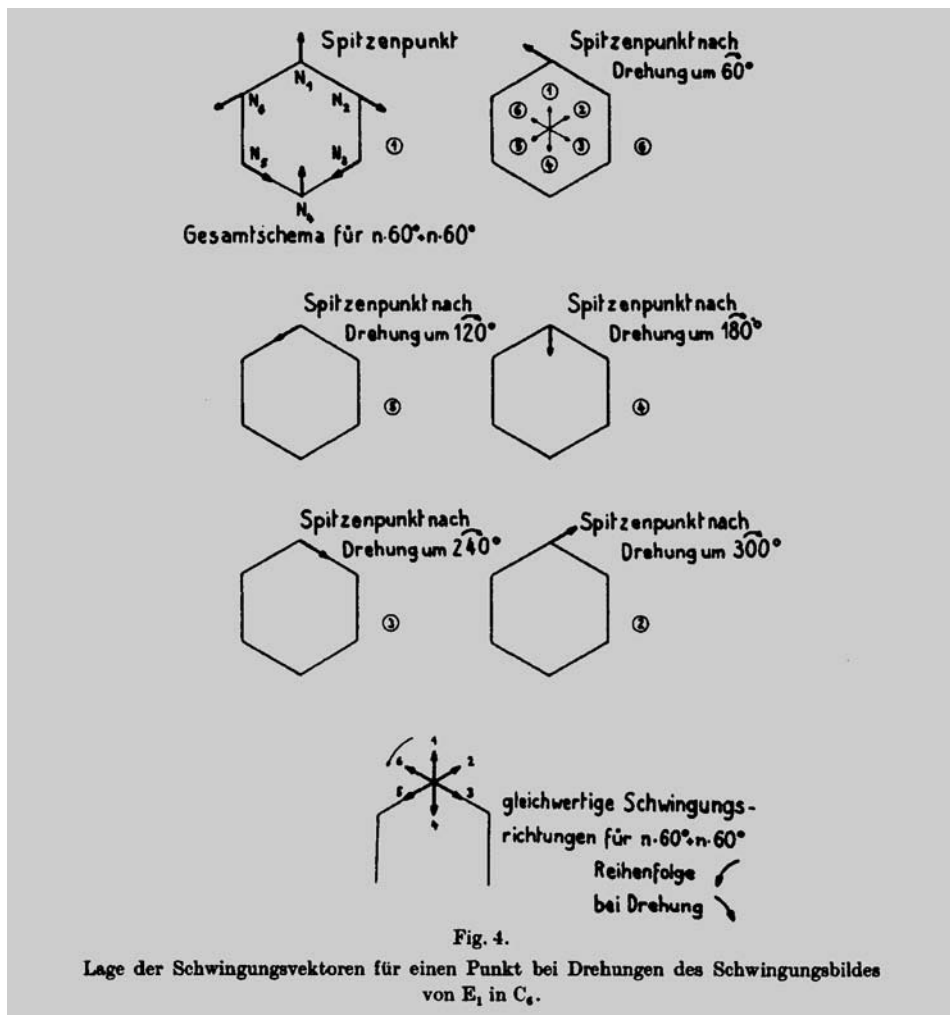
Fig. 27



In 1948, *Paul Niggli* published an elementary geometrical method for the enumeration of normal modes and the derivation of selection rules for symmetrical molecules and for crystals [97] (see *Fig. 28*).

**101. Die geometrischen Grundlagen der Auswahlregeln
der Eigenschwingungen und Term-aufspaltungen in Molekel- und
Krystallverbindungen**
von **Paul Niggli**.
(28. XII. 48.)

Fig. 28

Fig. 28
(cont.)

In the same vein, Günthard, and his coworkers presented a fairly complete system of internal (vibrational) coordinates for the analysis of vibrational spectra of small molecules in terms of valence force fields [98], and the computation of statistical thermodynamic functions of *e.g.* ethylene oxide [99]. A detailed theoretical study of the typical vibrational spectra of chain molecules $X(\text{CH}_2)_nX$ in the (*all-trans*)-conformation was published by Hans Primas and Günthard in 1953 [100], from which the characteristic pattern of the twisting frequencies is reproduced in Fig. 29. These studies served as a basis for the analysis of experimental IR spectra of long-chain molecules in the solid state, *e.g.*

**205. Die Infrarotspektren von Kettenmolekeln
der Formel $R'CO(CH_2CH_2)_nCOR''$.**

I. Rocking- und Twisting-Grundtöne

von H. Primas und Hs. H. Günthard.

(24. VII. 53.)

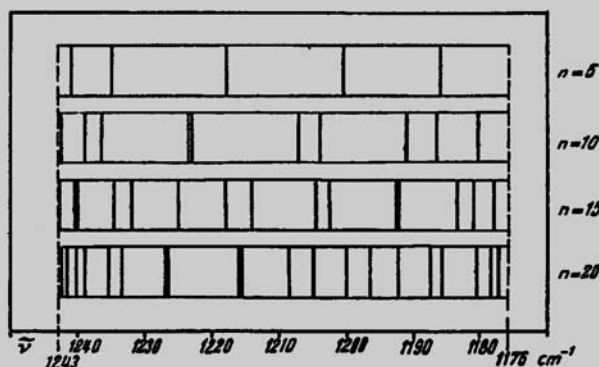


Fig. 3.

Twisting-Frequenzen von $X-(CH_2-CH_2)_n-X$

of α,ω -dicarboxylic acids, and for the determination of their length from IR data [101], as shown in Fig. 30.

Strongly distorted line shapes are often observed in IR spectra of organic molecules dispersed in paraffin oil. This initiated a theoretical analysis of the line shapes of vibrational transitions of spherical particles, based on *Hulst's* asymptotic approximation (*Christiansen effect*), which covered a wide range of phenomena observed when working with organic suspensions [102], cf. Fig. 31.

From the very numerous, systematic studies of specific classes of organic compounds, we quote as typical examples the extensive work by *Briner* on ozonides [103] (see Fig. 32), and by *Th. Bürer* and *Günthard* on cyclanes and cyclanones [104].

An early attempt to measure optical rotation in the near IR region of the spectrum, has been reported by *H. J. Hediger* and *Günthard* in 1945 [105]. Furthermore, *K. Frei* and *Günthard* described the use of modern methods of signal-detection theory, to find the optimum conditions for RE line detection, when photographic plates are used for their registration [106]. From the same laboratory stem investigations by IR spectroscopy of intramolecular H-bonds, e.g. in spironanediols [107] (see Fig. 33), or 1,2-dioles [108], to support and extend previous work by *L. P. Kuhn* [109].

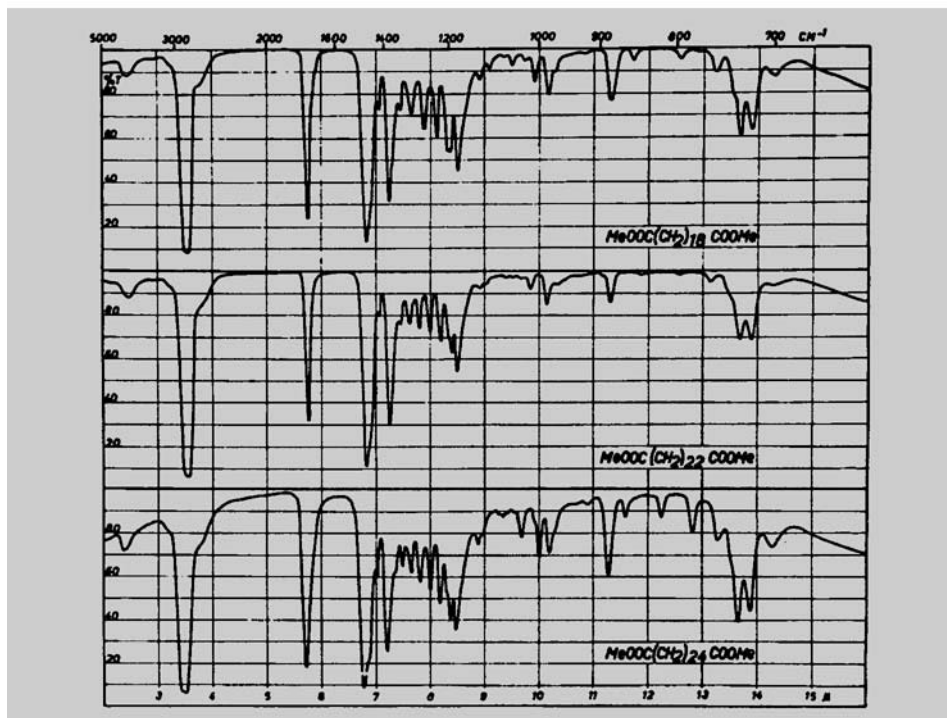
A detailed study of the CH stretching bands of alkanes and their halogen derivatives, based on solution and solid-state spectra, has been provided by *M. Avanesoff*, *Ho Dac Thang*, and *T. Gämman* [110], which yielded a relatively simple interpretation of the complex data, an example of which is shown in Fig. 34.

Fig. 30

143. Über einige höhere normale α, ω -Dicarbonsäuren

von Hs. H. Günthard, S. D. Heinemann und V. Prelog.

(13. VI. 53.)



M. Rossi and *E. Haselbach* used FIR spectroscopy to study donor-acceptor interactions in weak complexes between tetracyanoethylene and hydrocarbons [111]. Such interactions could be shown to give rise to typical FIR bands.

An important contribution to the field was the development of vibrational Raman optical activity (VROA) spectroscopy by *Werner Hug* [112]. As a typical example of the

Fig. 31

44. Theorie der Form von Absorptionsbanden suspendierter Substanzen und deren Anwendung auf die Nujolmethode in der Infrarotspektroskopie

von H. Primas und Hs. H. Günthard.

(7. XII. 53.)

Fig. 31
(cont.)

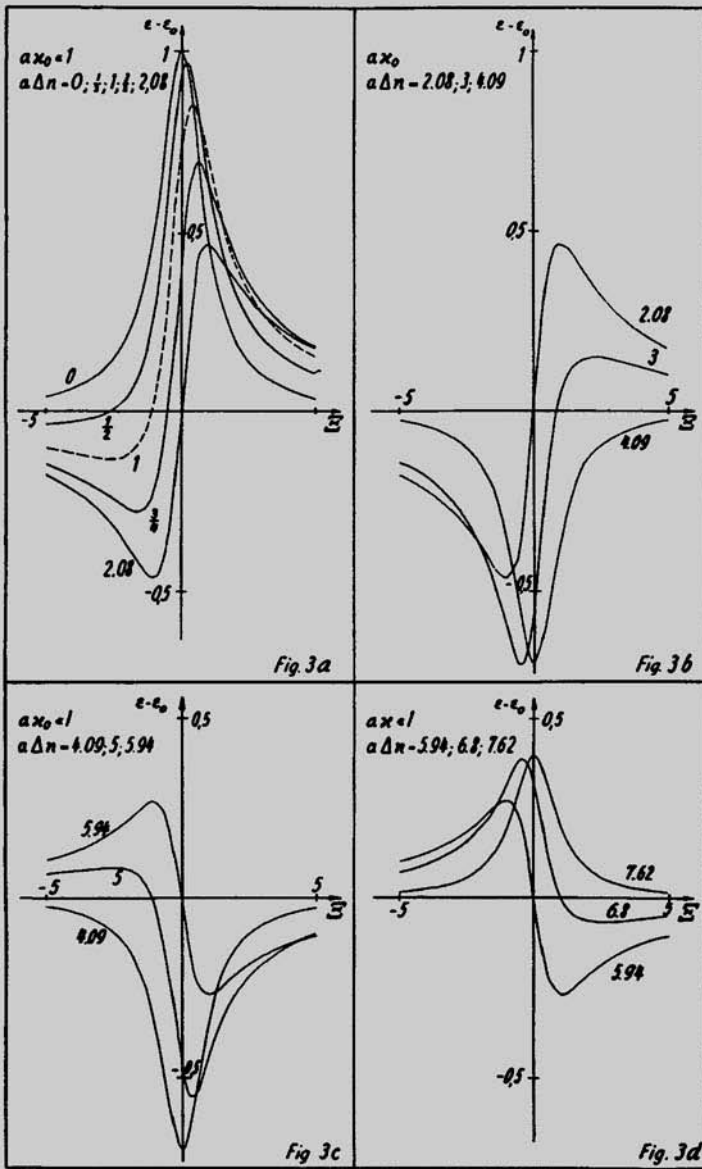


Fig. 3.

Extinktionskurven absorbierender K ugelchen f ur kleine αK_0 und verschiedene Δn .

Fig. 32

**74. Recherches sur le spectre d'absorption infrarouge des ozonides.
VIII. Détermination des spectres des ozonides de quelques esters
comportant une double liaison éthylénique: acrylate d'éthyle,
méthacrylate de méthyle, chloracrylate de méthyle, fumarate de
méthyle et cinnamate d'éthyle**

par E. Dallwigk et E. Briner.

(25 I 54)

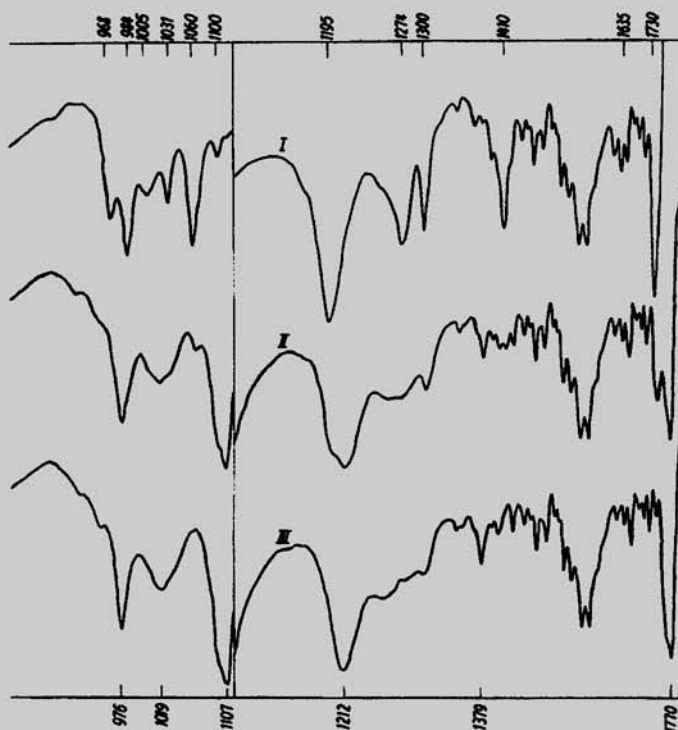


Fig. 1.

Ozonation de l'acrylate d'éthyle.

I. Solution d'acrylate d'éthyle. II. Solution ozonée au degré 50%.

III. Solution ozonée au degré 80%.

Fig. 33

**190. Spektroskopische Untersuchung der Wasserstoffbrücken
in Spiro[4,4]nonandiolen**

von Th. Bürer, E. Maeder und Hs. H. Günthard.

(8. VI. 57.)

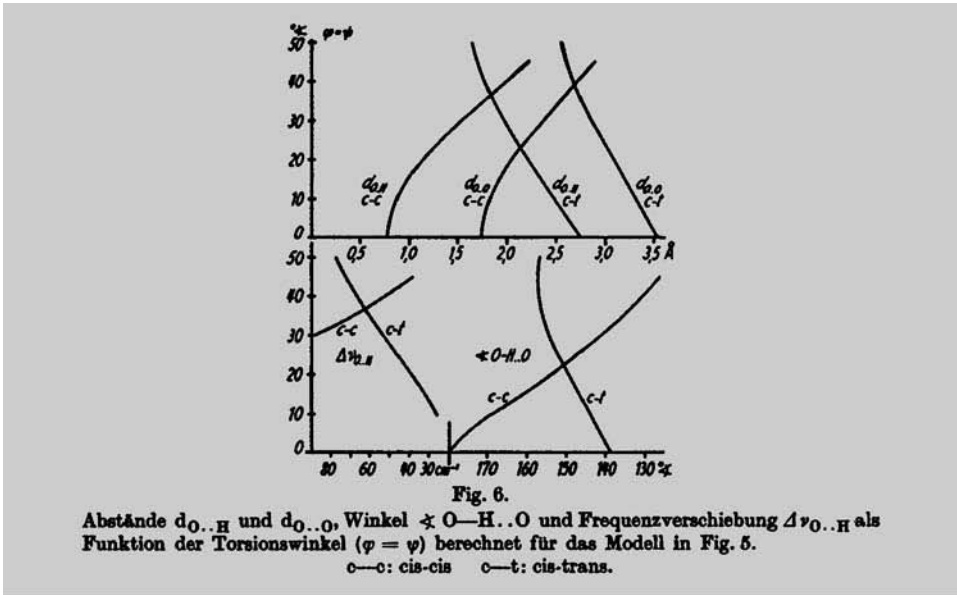
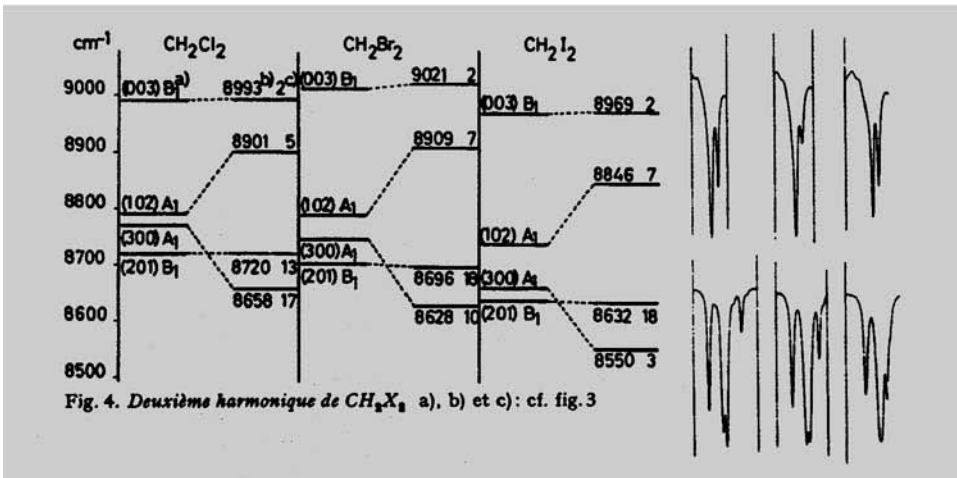


Fig. 33 (cont.)

101. Vibrations de valence C-H/C-D fondamentales et harmoniques de dérivés halogénés du méthane et du deutériométhane
 par M. Avanesoff, Ho Dac Thang et T. Gäumann
 Institut de Chimie Physique, Ecole Polytechnique Fédérale, Lausanne
 (8 III 71)

Fig. 34



application of this highly interesting method, we show in *Fig. 35* such a spectrum, recorded in the course of an investigation by *H.-J. Hansen*, *H.-R. Sliwka*, and *W. Hug* of the absolute configuration of 1-methylindane (7) [113].

Fig. 35

115. The Absolute Configuration of 1-Methylindane

by Hans-Jürgen Hansen*), Hans-Richard Sliwka*)¹⁾ and Werner Hug**)

*)Institute of Organic Chemistry and

***)Institute of Physical Chemistry, University of Fribourg, CH-1705 Fribourg, Pérolles

(21.III.79)

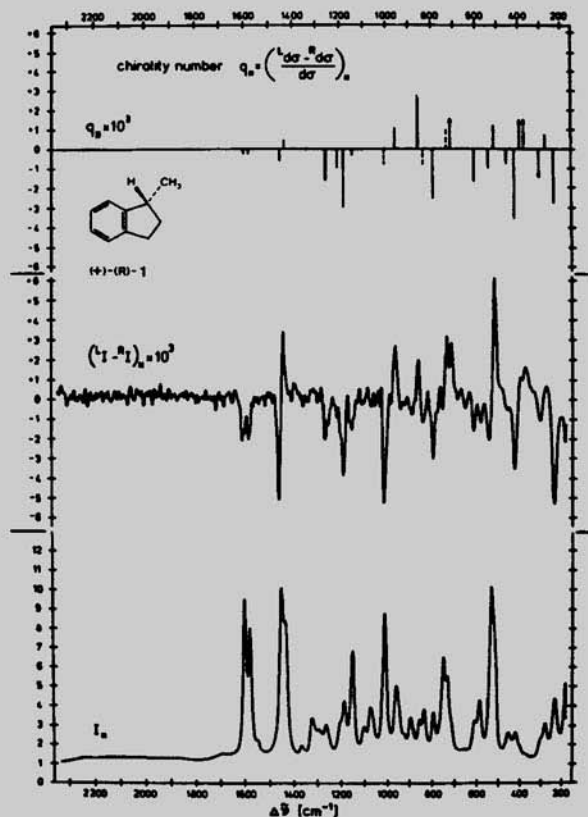
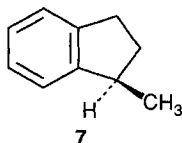


Fig. 1. The depolarized (measured in parallel polarization \parallel) Raman and circular difference Raman spectrum of (+)-R-1-methylindane ($\rho = 1.00$). The data are not corrected for instrument response. Slitwidth is 9 cm^{-1} . $Ld\sigma$ and $Rd\sigma$ denote differential scattering cross sections for left and right circularly polarized light, respectively; see [27]. q -Numbers of strongly polarized bands are indicated by dashed lines; see text.



Applications of IR-matrix and microwave (gas phase) spectroscopy for the detection of short-lived reaction products, obtained in the course of a gas-phase ozonolysis, were reported by *J. Dommen, M. Forster, H. Ruprecht, A. Bauder, and Hs. H. Günthard* [114]; see Fig. 36. These investigations demonstrated the enormous discrimination power of

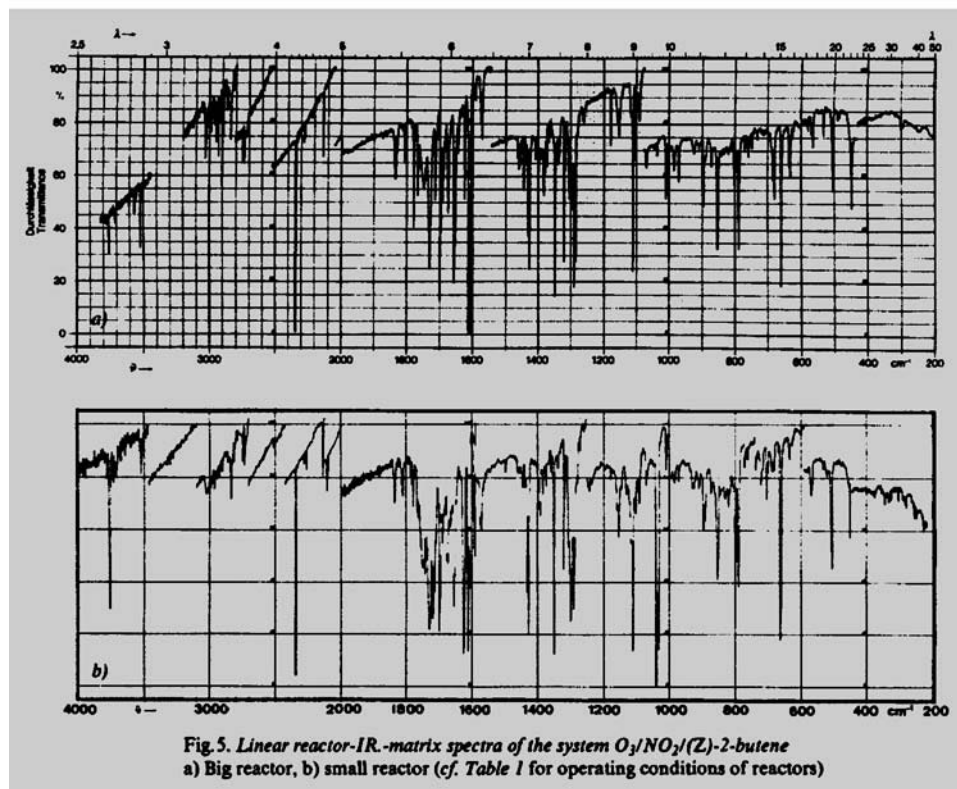
Fig. 36

50. Linear-Reactor-IR.-Matrix and Microwave Spectroscopy of the System $O_3/NO_2/(Z)$ -2-Butene

by *Joseph Dommen, Martin Forster, Heidi Ruprecht, Alfred Bauder and Hans-Heinrich Günthard*¹⁾

Laboratorium für Physikalische Chemie, Eidgenössische Technische Hochschule, CH-8092 Zürich

(3.XII.81)



both techniques for the product analysis of complex gas-phase reactions, quite apart from providing a detailed insight into the mechanism of an olefin ozonolysis.

As demonstrated by *R.-P. Müller, S. Murata, M. Nonella, and J. R. Huber*, matrix IR spectroscopy allows to show (see *Fig. 37*) that HNO is an intermediate in the light-induced rearrangement reactions of organic nitrosooxy compounds and of nitrosamines [115].

Fig. 37

107. HNO, an Intermediate in (Light-induced) Rearrangement Reactions of Nitrosooxy Compounds and Nitrosamines

by René-Pierre Müller, Shigeo Murata¹⁾, Marco Nonella, and J. Robert Huber*

Physikalisch-Chemisches Institut der Universität Zürich, Winterthurerstrasse 190, CH-8057 Zürich

(13.III.84)

Summary

IR-spectroscopic investigations of light-induced rearrangement reactions of nitrosooxymethane (CH_3ONO), nitrosooxyethane ($\text{CH}_3\text{CH}_2\text{ONO}$) and *N,N*-dimethylnitrosamine ($(\text{CH}_3)_2\text{NNO}$) in low-temperature rare-gas matrices have established that these molecules are transformed in two photolysis steps to the previously unknown *C*-nitroso compounds nitrosomethanol ($\text{CH}_2(\text{OH})(\text{NO})$), 1-nitrosoethanol ($\text{CH}_3\text{CH}(\text{OH})(\text{NO})$), and methyl(nitrosomethyl)amine ($\text{CH}_2(\text{NO})(\text{NH})\text{CH}_3$). Evidence for a similar rearrangement reaction has been advanced for *N*-nitrosopyrrolidine ($\text{C}_4\text{H}_8\text{NNO}$) which is converted to *C*-nitrosopyrrolidine ($\text{C}_4\text{H}_7\text{CH}(\text{NO})(\text{NH})$). The matrix-isolation technique in combination with wavelength-selective irradiation allowed to trap and characterize an intermediate of the rearrangement which revealed to be a nitroxyl (HNO) complex ($\text{CH}_2\text{O}\dots\text{HNO}$, $\text{CH}_3\text{CHO}\dots\text{HNO}$, $\text{CH}_3\text{N}=\text{CH}_2\dots\text{HNO}$, and $\text{C}_4\text{H}_7\text{CH}=\text{N}\dots\text{HNO}$). Since these findings have a close resemblance with rearrangement reactions of more complex nitrosooxy compounds, nitrosamines, or nitrosohydrazines used in organic synthesis, it is suggested that also in these reactions nitroxyl is present as an intermediate species.

The study of surface reactions on germanium by *G. Calzaferri* and *M. Gori* [116] is a nice example for the use of *Fourier*-transform IR spectroscopy for the elucidation of the mechanism and of the kinetics of a reaction. A very recent development of vibrational spectroscopy is documented in *HCA* through a publication by *W. D. Lupo, M. Quack, and B. Vogelsanger* [117] on IR laser spectroscopy, in which the potential of this new discipline of photochemistry is elegantly demonstrated. A similar study has been published by *T. Gäumann, J. M. Riveros, and Z. Zhu* [118], in which IR multiphoton ionization of molecular ions has been observed (see *Fig. 38*).

119. The Infrared Multiphoton-Dissociation Spectra of Bromopropene Isomeric Cations

by Tino Gäumann*, José M. Riveros¹⁾, and Zhiqing Zhu

Institute of Physical Chemistry, Federal School of Technology, CH-1015 Lausanne

(7.V.90)

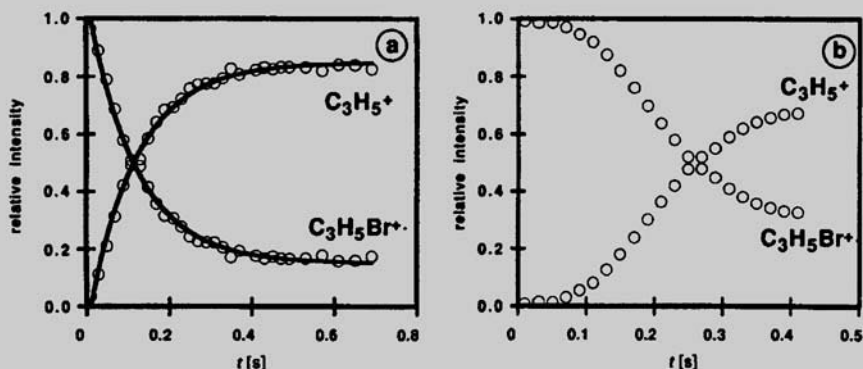
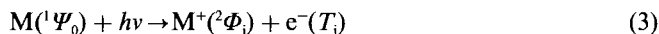


Fig. 1. a) Normalized photofragmentation plot of the molecular and fragment ions of 3-bromopropene at 10.248 μm . The experimental points for the primary ion are shown for convenience as the sum of the two isotopic species of $\text{C}_3\text{H}_5^{79}\text{Br}^+$ ($m/z = 120$) and $\text{C}_3\text{H}_5^{81}\text{Br}^+$ ($m/z = 122$). The full curve represents the calculated fitting for a photodissociation constant of 8.50 s^{-1} and a plateau value $a_2 = 0.15$ for the molecular ions and $b_1 = 0.85$ for $m/z = 41$. b) Typical normalized photofragmentation plot of the molecular ions of 1-bromopropene at 10.59 μm showing an induction time.

1.3. Photoelectron Spectroscopy and Related Topics. Although UV-photoelectron spectroscopy (UPS) was invented independently by *Vilesov*, *Kurbatov*, and *Terenin* [119], and by *Turner* and *Al-Joboury* [120], there is no doubt that its development into a useful tool is due to *Turner* [121], to *Price* [122], and their coworkers. In contrast to *Siegbahn's* ESCA [123] (ESCA = Electron Spectroscopy for Chemical Analysis), which uses X-ray excitation (XPS), UPS has lost by now much of its attraction, having been replaced in the meantime by more precise and efficient methods yielding the same (or similar) results.

The primary process investigated by UPS is the ionization of a molecule M , usually in its singlet electronic ground state ${}^1\Psi_0$, through absorption of a photon $h\nu$, yielding the radical cation M^+ in a doublet state ${}^2\Phi_j$ and an electron e^- which carries off the excess kinetic energy T_j :



By measuring the kinetic energies T_j , one obtains the ionization energies

$$I_j = E({}^2\Phi_j) - E({}^1\Psi_0) = h\nu - T_j \quad (4)$$

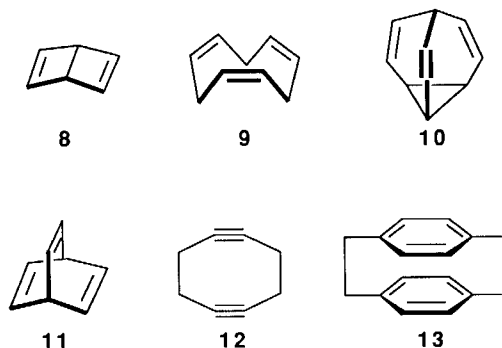
i.e. the energy differences between the radical cation states ${}^2\Phi_j$ and the molecular ground state ${}^1\Psi_0$. However, in the majority of publications reporting PE spectra, a given ionization energy I_j is assumed to be equal to the negative orbital energy $-\varepsilon_j$ of the vacated molecular orbital ϕ_j of the neutral molecule M . It is this approximation

$$I_j = -\varepsilon_j \quad (5)$$

known as *Koopmans'* theorem [124], which made PE spectroscopy popular among chemists, because it suggested that this technique provides information about molecular orbitals ϕ_j , widely used – in the wake of the *Woodward-Hoffmann* rules [125] – for the interpretation of physical and chemical properties of molecules. Although excessive application of *Koopmans'* theorem may be a hazard, we shall use it for presenting the following examples drawn from *HCA*.

A) *Orbital Interactions*. The first set of PE spectra published in *HCA* [126] yielded an estimate of the size of the interaction between non-conjugated double bonds in bicyclic hydrocarbons, *e.g.* in norbornadiene (= bicyclo[2.2.1]hepta-2,3-diene) reproduced in *Fig. 39*.

This and closely related investigations on other bicyclic dienes, such as *Dewar* benzene (**8**) [127], allowed a (semi)quantitative assessment of the relative and absolute sizes of 'through-space' and 'through-bond' interactions of π orbitals, as postulated by *Roald Hoffmann* [128].



Other typical examples of these kind of interactions between three symmetry-equivalent π orbitals are provided by the 'homo-aromatic' molecule (*Z,Z,Z*)-cyclonona-1,4,7-triene (**9**) [129], and by bullvalene (**10**) [130], and barrelene (**11**) [131]. A special case occurs, when two π systems are held in close proximity, such as those of the two triple bonds in cycloocta-1,5-diyne (**12**) [132], or the two benzene π systems in cyclophanes **13** [133]. An example dealing with the orbital interactions in Ni-diallyl, stemming from *Rolf Gleiter's* group [134], is shown in *Fig. 40*.

B) *Polyacetylenes*. Of the many applications of UPS, the extensive study of the radical cations of acetylene, polyacetylenes, and their halogen-substituted derivatives proved particularly informative, because of the high symmetry of these molecules. In *Fig. 41* is shown the first set of monohaloacetylene PE spectra published in 1970 [135].

Such spectra yield information about the energies $E({}^2\Phi_j)$ of the radical-cation states ${}^2\Phi_j$ (*cf.* formula (4)), or – in *Koopmans'* approximation (5). – of the individual orbital

174. Photoelektronenspektroskopische Bestimmung der Wechselwirkung zwischen nicht-konjugierten Doppelbindungen [1]

Vorläufige Mitteilung¹⁾

von P. Bischof, J. A. Hashmall, E. Hellbronner und V. Horning

Physikalisch-chemisches Institut der Universität Basel

(12. VII. 69)

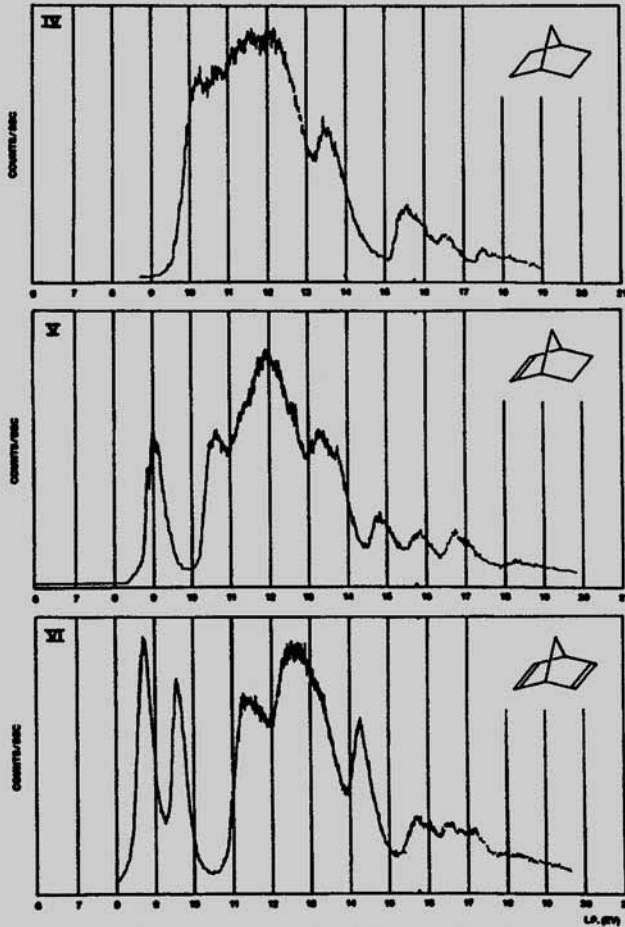


Fig. 2. PE-Spektren des Norbornans (IV), Norbornens (V) und Norbornadiens (VI)

Fig. 40

106. The Photoelectron Spectra of Ni, Pd, Pt-Diallyl¹⁾

by Michael C. Böhm²⁾, Rolf Gleiter³⁾ and Christopher D. Batich⁴⁾

Institut für Organische Chemie der Technischen Hochschule, D-6100 Darmstadt (W.-Germany)

Organisch-Chemisches Institut der Universität Heidelberg, D-6900 Heidelberg (W.-Germany)

and Physikalisch-Chemisches Institut der Universität Basel, CH-4056 Basel (Switzerland)

(22. II. 80)

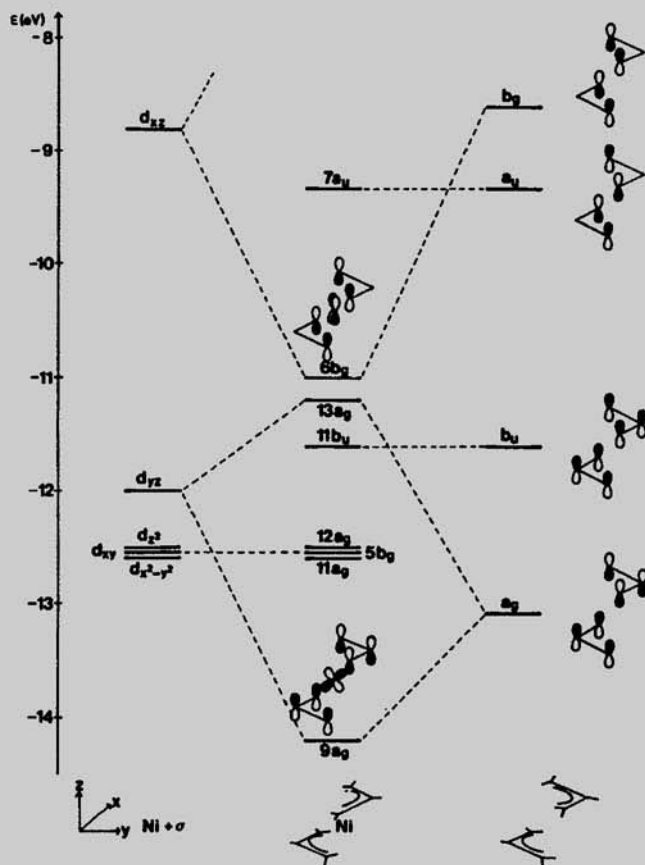


Fig. 1. Interaction diagram between the 3d-orbitals of Ni and the π -orbitals of the allylic moieties of 1a. The 3d orbitals of Ni are split due to the interaction with the σ -orbitals of the ligands.

Fig. 41

124. Die Photoelektron-Spektren der Monohalogenacetylene¹⁾

von H. J. Haink, E. Heilbronner, V. Hornung und Else Kloster-Jensen

Physikalisch-chemisches Institut der Universität Basel

(9. V. 70)

Fig. 41
(cont.)

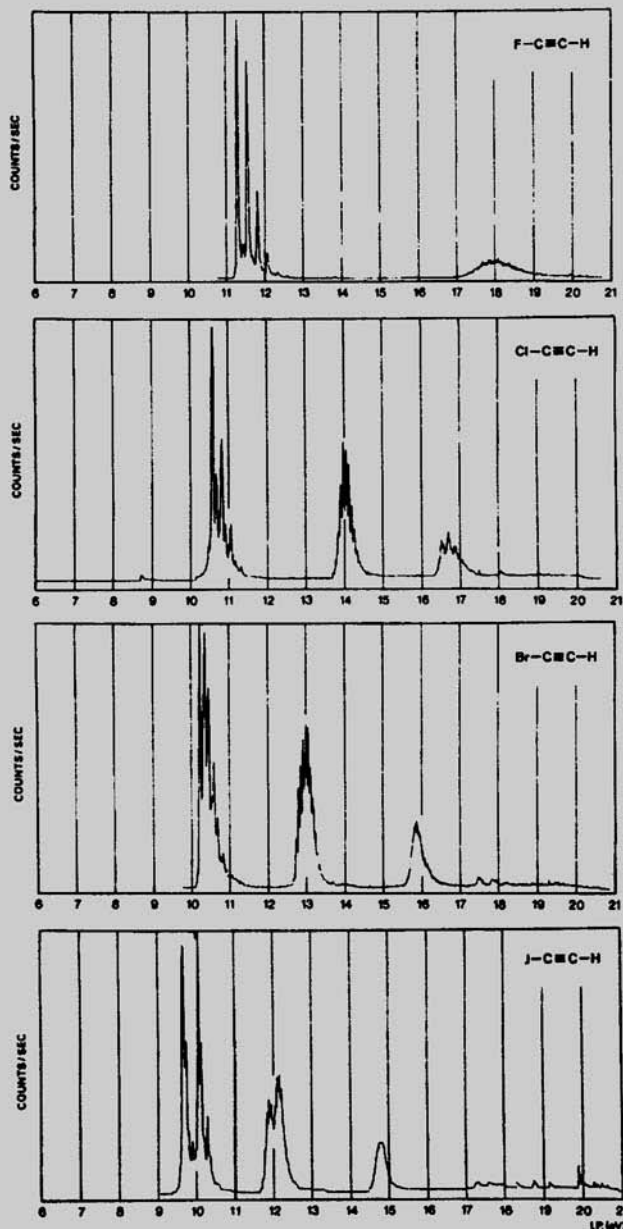


Fig. 1. Photoelektron-Spektren des Fluor-, Chlor-, Brom- und Jodacetylens.
Abzisse: Ionisationspotentiale in eV; Ordinate: Zählrate in willkürlichen Einheiten

energies ϵ_j . In addition, an analysis of the vibrational fine structure of the *Franck-Condon* envelopes provides insight into the changes of interatomic distances on ionization [136].

In this particular field – and in quite a few others – traditional UPS has been made obsolete by the much more sophisticated and refined techniques developed – among others – by *John Paul Maier* and his coworkers at the University of Basle [137]. As an example, we show in *Fig. 42* the $\tilde{A}^2E \rightarrow \tilde{X}^2E$ emission spectrum of 1-chloropenta-1,3-diyne, recorded from a supersonic free jet [138].

Because of their cylinder symmetry, $C_{\infty v}$ or $D_{\infty h}$, the radical cations of halogen-substituted (poly)acetylenes are ideal systems to study the influence of spin-orbit coupling on the energies of their doublet states $^2\Phi_j$. In this connection, it should be mentioned that PE band-splits due to spin-orbit coupling, persist in lower symmetry alkyl-halides, as can be seen in *Fig. 43*. The typical evolution of the band shape, due to the increasing competition between spin-orbit coupling and hyperconjugation, is well accounted for by a HMO treatment incorporating spin-orbit coupling parameters [139].

C) ‘*Aromatic*’ *Molecules*. An obvious field for PE spectroscopic investigations was the determination – always within *Koopmans’* theorem (5) – of the electronic structure of aromatic hydrocarbons, *e.g.*, in 1972, of the acenes [140]. Surprisingly, it was found that simple HMO treatments account perfectly well for the observed π -band positions. Later work dealt with the PE spectra of annulenes, such as *E. Vogel’s* bridged [14]annulenes **14**

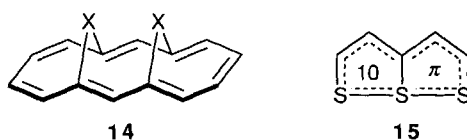


Fig. 42

138. Spectroscopic Characterization of Open-Shell Cations: Emission and Laser Excitation Spectra of Rotationally Cooled $\text{CH}_3\{\text{C}\equiv\text{C}\}_2\text{X}^+$, $\text{X} = \text{Cl}, \text{Br}$

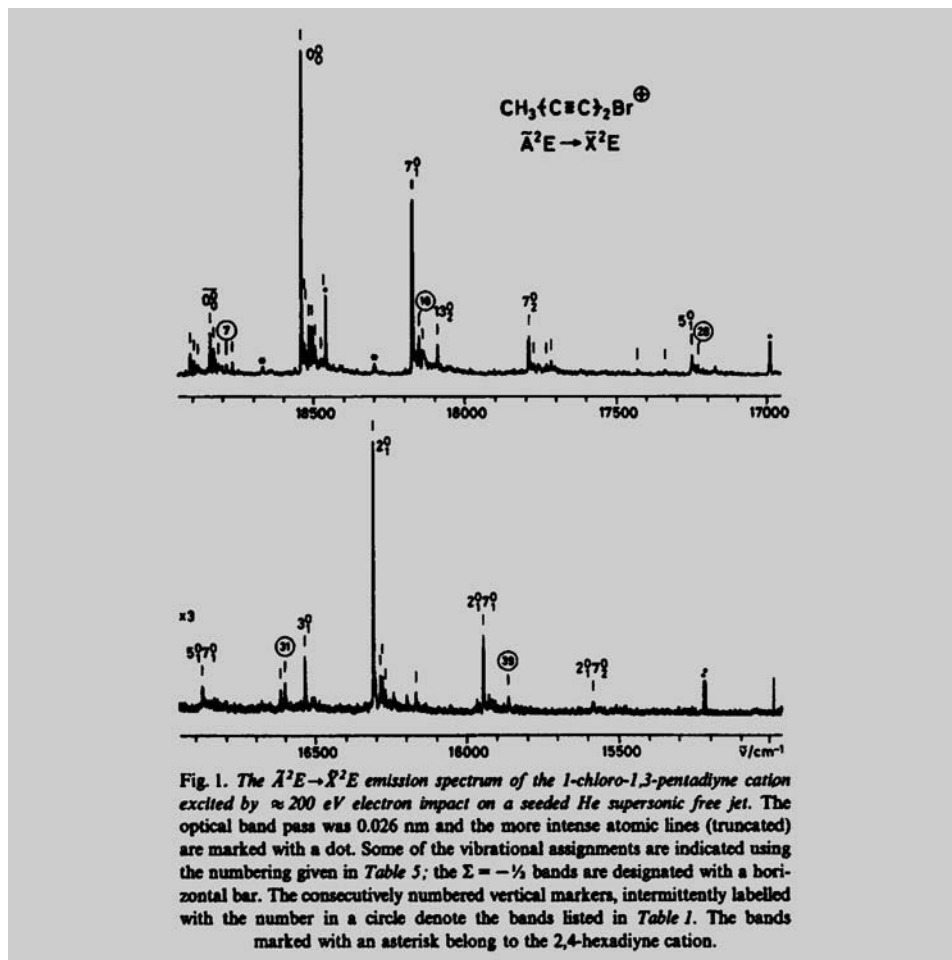
by Dieter Klapstein, Robert Kuhn, John P. Maier*, Lubomir Misev and Martin Ochsner

Physikalisch-Chemisches Institut der Universität Basel, Klingelbergstrasse 80, CH-4056 Basel

(11.V.84)

Summary

Gas phase emission and laser excitation spectra of the $\tilde{A}^2E \leftrightarrow \tilde{X}^2E$ ($\Sigma = +\frac{1}{2}, -\frac{1}{2}$) transition of rotationally/vibrationally cooled 1-chloro- and 1-bromo-1,3-pentadiyne cations have been obtained. The emission was excited by electron impact on a seeded helium supersonic free jet and the fluorescence by laser excitation of cations produced by *Penning* ionization and collisional relaxation. From these two sets of data the origin bands of the spin-orbit systems are located and for the bromo species this leads to better values of the spin-orbit splittings in the two electronic states and of the first adiabatic ionization energy. The vibrational frequencies of many of the fundamentals of these cations in the \tilde{X}^2E and \tilde{A}^2E states have been obtained to within $\pm 2 \text{ cm}^{-1}$.



[141]. As an example of an annulene PE spectrum, we reproduce in Fig. 44 the spectrum of [18]annulene, obtained by H. Baumann, J.-C. Bünzli, and J. F. M. Oth [142].

The group of non-alternant aromatic hydrocarbons has also been studied extensively by UPS. From the large number of such PE spectra, we reproduce in Fig. 45 those of the two isomeric π systems azuleno[1,2,3-*cd*]phenalene and azuleno[5,6,7-*cd*]phenalene,

146. The Competition between Spin Orbit Coupling and Conjugation in Alkyl Halides and its Repercussion on their Photoelectron Spectra¹⁾

by F. Brogli and E. Hellbronner

Physikalisch-Chemisches Institut der Universität Basel

(17. V. 71)

Fig. 43

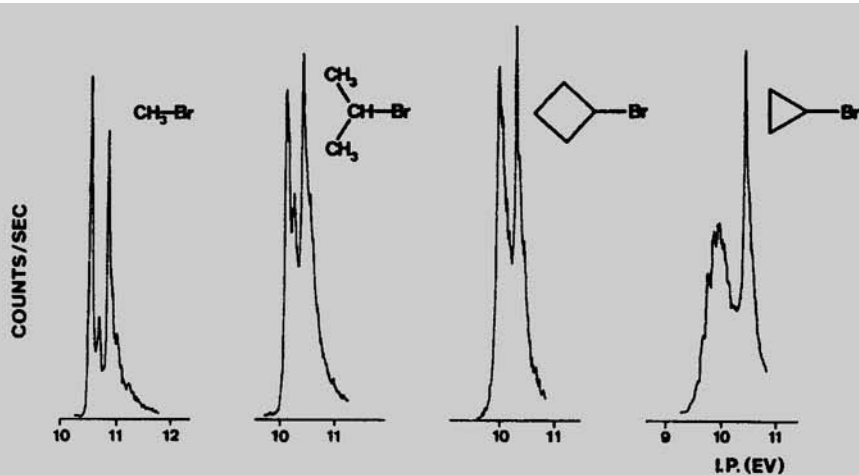


Fig. 1. "Lone pair" bands in the PE.-spectra of methyl bromide, isopropyl bromide, cyclobutyl bromide and cyclopropyl bromide

Fig. 44

58. The Photoelectron Spectrum of [18]Annulene

by Harold Baumann, Jean-Claude Bünzli¹⁾ and Jean François Michael Oth

Laboratorium für Organische Chemie der Eidgenössischen
Technischen Hochschule, Universitätstr. 16, CH-8092 Zürich

(3. II. 82)

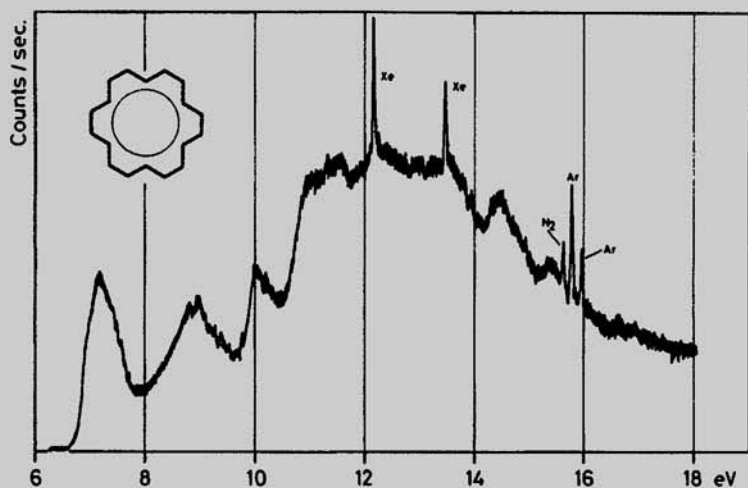


Fig. 1. Overall PE. spectrum of [18]annulene

155. The Electronic Structure of Azuleno[1,2,3-*cd*]phenalene and Azuleno[5,6,7-*cd*]phenalene, a Comparison

by Rolf Gleiter¹⁾, Jens Spanget-Larsen¹⁾, Erik W. Thulstrup^{1,2)},
Ichiro Murata³⁾, Kazuhiro Nakasuj¹⁾ and Christian Jutz¹⁾

Institut für Organische Chemie der Technischen Hochschule D-61 Darmstadt (West-Germany);

Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560 (Japan);

Organisch Chemisches Institut der Technischen Universität D-8 München (West-Germany).

(18. III. 76)

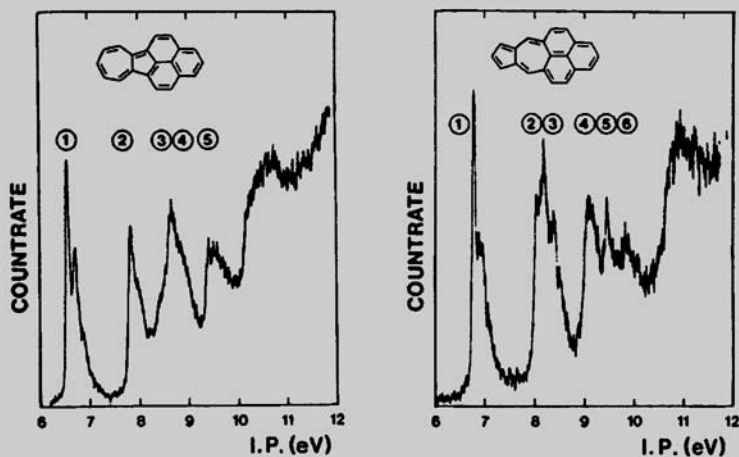


Fig. 1. Photoelectron spectra of azuleno[1,2,3-*cd*]phenalene (1) and azuleno[5,6,7-*cd*]phenalene (2)

which were recorded by Rolf Gleiter and his coworkers [143]. The same author also discussed the PE spectra of π systems related to thiathiophene (15) which provided useful information about the peculiar electronic structure of this molecule [144].

D) *Saturated Hydrocarbons*. The study of the PE spectra of saturated hydrocarbons [145] proved to be unexpectedly rewarding. This is particularly true for hydrocarbons containing small rings, because of the strong interactions between Walsh orbitals of three-membered [146] or of four-membered rings [147] with other p-type orbitals. Of the saturated hydrocarbons containing four-membered rings, we reproduce as typical examples the PE spectra of cubane [148] and of pentaprismane [149] in Fig. 46.

195. The Electronic Structure of Pentaprismane (C₁₀H₁₀), as Revealed by its Photoelectron Spectrum

by Evi Honegger¹⁾, Phillip E. Eaton²⁾, B.K. Ravi Shankar²⁾ and Edgar Heilbronner¹⁾

Physikalisch-Chemisches Institut der Universität Basel, Klingelbergstrasse 80, CH-4056 Basel

and Department of Chemistry, The University of Chicago, 5735 South Ellis Avenue,
Chicago, Illinois 60637, U.S.A.

(24. VI. 82)

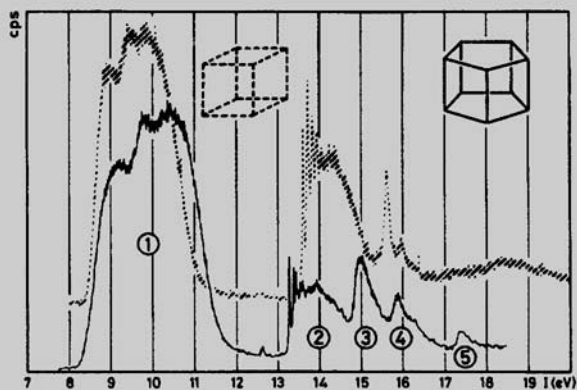
Fig. 46
(cont.)

Fig. 1. He(I) PE. spectra of pentaprismane (3) (solid line) and of cubane (2) (dashed line) [1]

A rather unexpected feature of the electronic structure of large, polycyclic, saturated hydrocarbons – as revealed by UPS – was the presence of so-called ‘ribbon orbitals’ [150], with orbital energies well above those of other σ orbitals. In the case of perhydroperylene, these ribbon orbitals, shown on top of Fig. 47, lead to a well detached first band in the PE spectrum, separated from the remaining manifold by about 1 eV [151].

E) *Comparison of UV/VIS with PE Spectra.* Naive molecular-orbital pictures, especially those of the *Hückel*-type, suggest that the difference $I_2 - I_1$ between the positions of the first two bands in the PE spectrum of a molecule M should correspond to the difference $\nu_{\max}(2) - \nu_{\max}(1)$ between the corresponding first two maxima in its UV/VIS

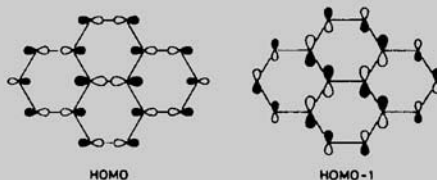
Fig. 47

196. The Persistence of Ribbon Orbitals in Polycyclic Alkanes¹⁾

by Edgar Heilbronner*, Evi Honegger, and Werner Zambach
 Institut für Physikalische Chemie, Klingelbergstrasse 80, CH-4056 Basel

and Peter Schmitt and Harald Günther
 Fachbereich 8, OC II, Universität GH Siegen, D-5900 Siegen

22.VIII.84



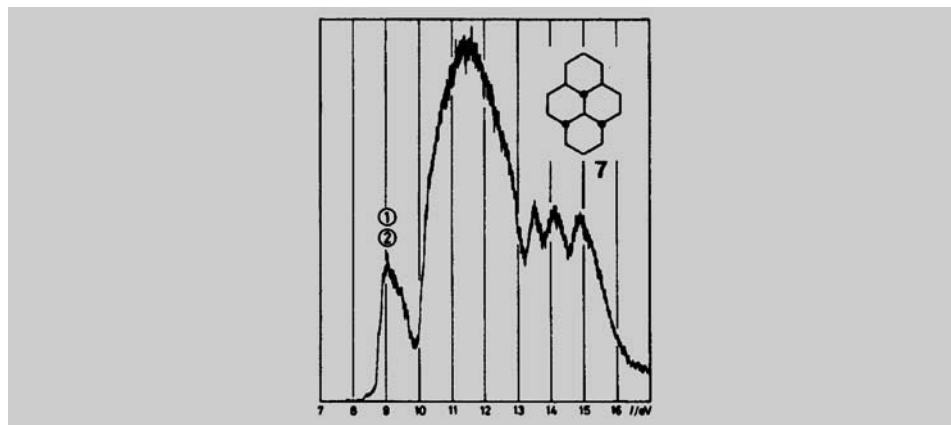


Fig. 47
(cont.)

spectrum. Unfortunately, this is an artefact of independent electron models. However, as shown by *Edwin Haselbach* and *Andreas Schmelzer* [152], simple rules can be derived, which allow a qualitative (or sometimes a semiquantitative) correlation of excitation and ionization-energy differences, if electron-electron interaction is taken into account. They yield useful information about the changes in structure and/or electron population which accompany the ionization and excitation processes, as for instance in the case of pyrazine [153], cf. Fig. 48.

299. On the Correlation between Ionization Potentials and Excitation Energies, Part III: Pyrazine¹

by **Edwin Haselbach, Zuzanna Lanyiova and Michel Rossi**
Physikalisch-Chemisches Institut der Universität Basel, Switzerland

(5. VII. 73)

Fig. 48

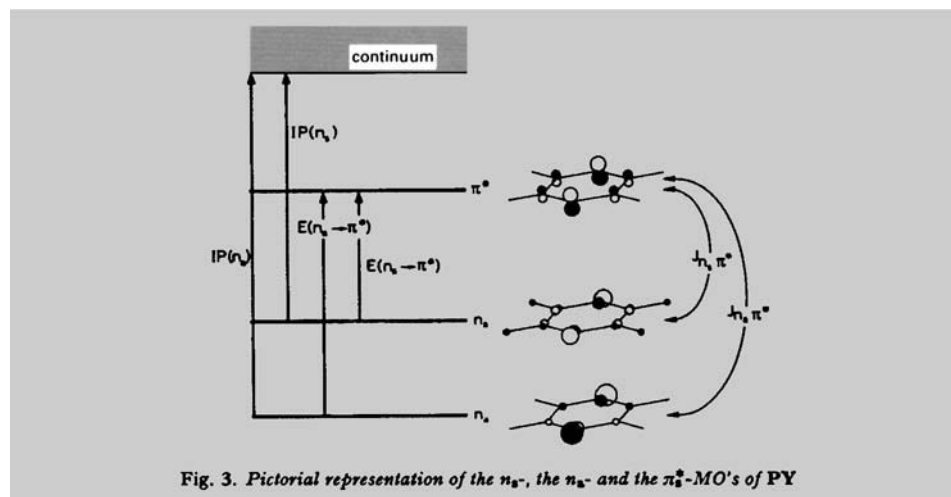


Fig. 3. Pictorial representation of the n_s -, the n_s^+ - and the π_s^+ -MO's of PY

A closely related problem concerns the matching of the PE spectrum of a molecule M with the UV/VIS spectrum of the corresponding radical cation M^+ , the latter usually contained in a solid matrix at low temperatures. In contrast to the above comparison, mis-matches between the two types of spectra are due to structural changes only. As in the example reproduced in *Fig. 49*, taken from work by *Haselbach et al.* [154], where the PE spectrum of [3]radialene (**16**) is matched with the UV/VIS spectrum of its radical cation, it is possible to draw important conclusions about the structure of the relaxed radical

Fig. 49

236. Studies on Radical Cations I.
Molecular and Electronic Structure of [3]Radialene Cation Produced
by γ -Irradiation in Condensed Phase¹

by **Thomas Bally, Edwin Haselbach²** and **Zuzana Lanyiova**
 Physikalisch-Chemisches Institut der Universität Basel, Klingelbergstrasse 80,
 CH-4056 Basel

and **Peter Baertschi**
 Eidg. Institut für Reaktorforschung (EIR),
 CH-5303 Würenlingen

(17.VIII.78)

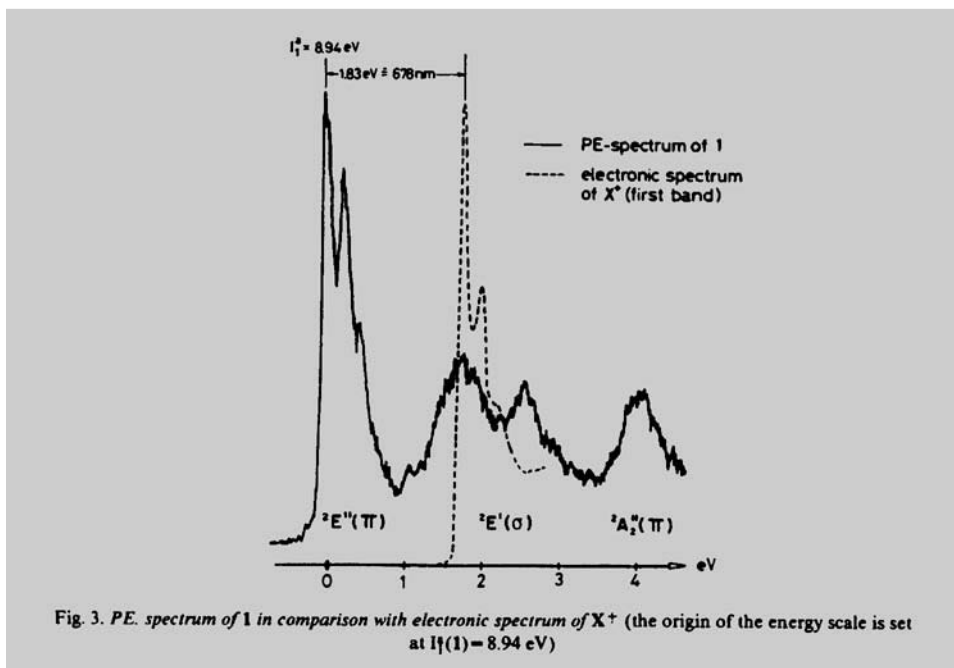
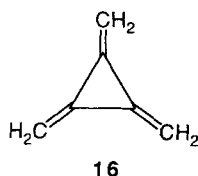


Fig. 3. PE. spectrum of **1** in comparison with electronic spectrum of X^+ (the origin of the energy scale is set at $I_1^+(1) = 8.94$ eV)



cations. In this connection, work from the same group on ‘non-Koopmans’ states, and their importance in UPS studies should be mentioned [155].

F) *Miscellaneous PE Spectroscopic Work.* UPS has been used, in conjunction with ion cyclotron resonance (ICR) measurements of gas-phase basicities (GB), to gain quantitative insight into the substituent-induced charge dispersal in substituted quinuclidines, postulated by Cyril Grob [156]. The trend in lone-pair ionization energies I_1 for quinuclidines substituted by CH_3 , Cl, or CN at C(2), C(3), or C(4), is shown in Fig. 50, together with the corresponding Δ GB values from the ICR measurements [157], obtained by Raymond Houriet (see also [158] for similar measurements on furans and diols). These results, taken in conjunction with $\text{p}K$ measurements in solution by C. Grob, M. G. Schlageter, and B. Schaub [159], allow to draw conclusions about steric inhibition of solvation in the 2-substituted derivatives.

224. Charge Dispersal in the Quinuclidine Radical Cation and in the Quinuclidinium Ion, as Revealed by PE and ICR Spectroscopy

by Edgar Hellbrunner*, Evi Honegger, and Jacques Lecoultre

Institut für Physikalische Chemie der Universität Basel, Klingelbergstr. 80, CH-4056 Basel

and Cyril A. Grob*

Institut für Organische Chemie der Universität Basel, St. Johannis-Ring 19, CH-4056 Basel

and Raymond Houriet* and Eric Rolli

Institut de Chimie Physique, Ecole Polytechnique Fédérale de Lausanne, Ecublens, CH-1015 Lausanne

(2.X.86)

Fig. 50

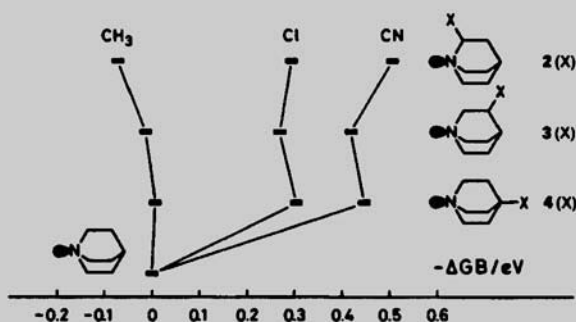
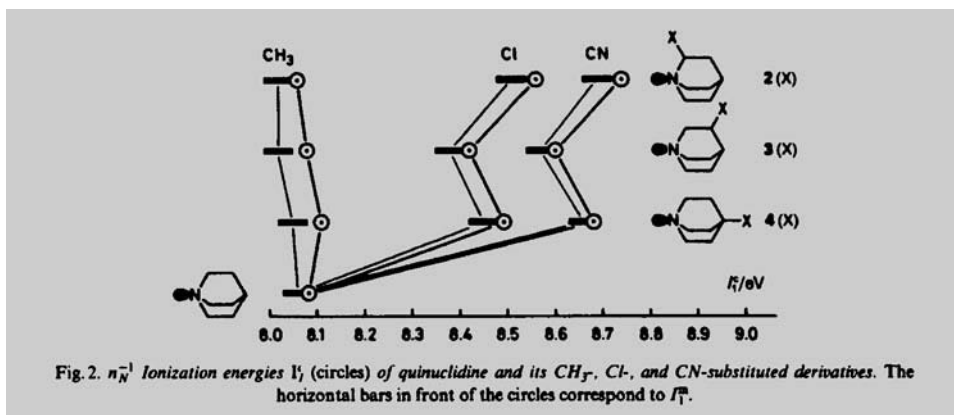


Fig. 3. Shifts ΔGB of the gas-phase basicities $\text{GB}(X)$ of 2(X), 3(X), and 4(X) relative to the gas-phase basicity $\text{GB}(1)$ (cf. Table 2)

Fig. 50
(cont.)

UPS has been widely used by *Hans Bock* and his group at the University of Frankfurt, as an analytical tool to follow and monitor gas-phase reactions. As an example of such work, we show in *Fig. 51* the PE spectrum of the parent compound di(*tert*-butyl)-azomethane and of the decomposition products obtained at 710 K [160].

Finally, we mention the assessment of the fragmentation pathways accessible to a radical cation M^+ in a given electronic state ${}^2\Phi_j$. This can be observed in a photoelectron-photoion coincidence experiment. As an example, we show in *Fig. 52* the results for the strained radical cation of bicyclobutane, due to *R. Bombach, J. Dannacher, J.-P. Stadelmann, and R. Neier* [161]. The same technique has also been applied to study the fragmentation of the penta-1,3-diyne radical cation [162].

G) *Related Topics*. The investigation of PE spectra, especially of the *Frank-Condon* envelopes of their bands, necessarily raised the question about the structure of the radical cations, in particular in their electronic ground state. In this connection, one should mention *Haselbach* and his group who investigated radical cations and their photophysi-

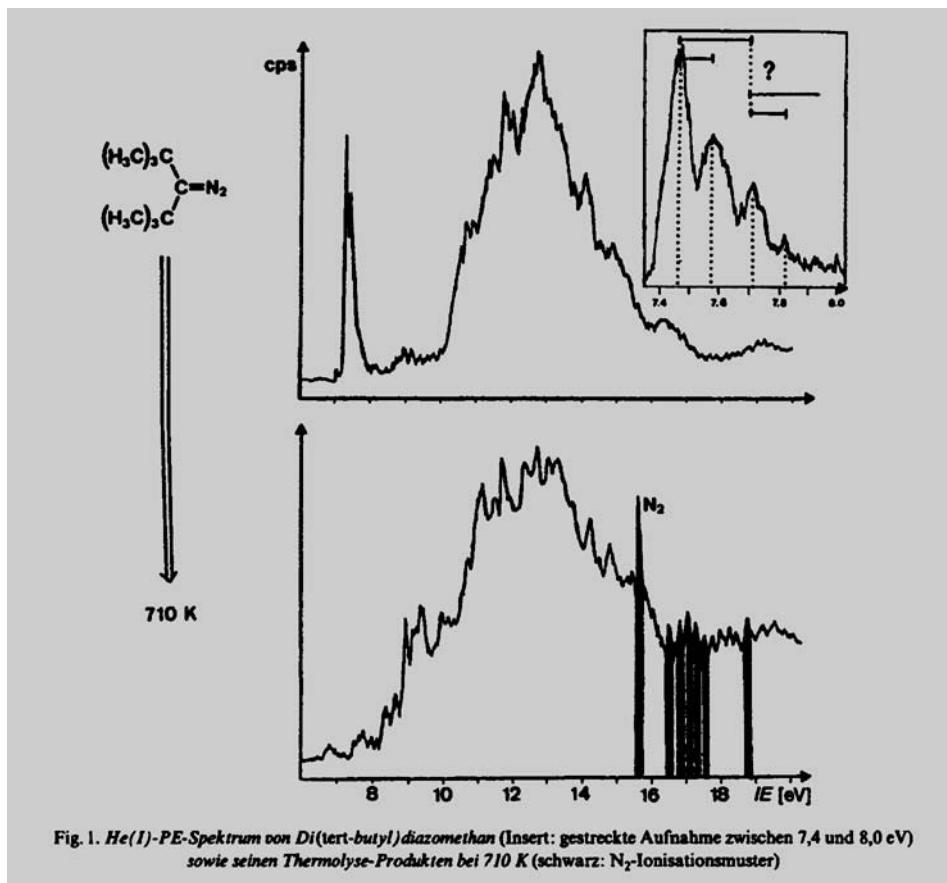
Fig. 51

137. Di(*tert*-butyl)diazomethan: Thermische Zersetzung und Einелектрон-Redox-Reaktionen¹⁾

von *Hans Bock*^{*}, *Bodo Berkner*²⁾, *Bernhard Hierholzer*²⁾ und *Dieter Jacult*²⁾

Institut für Anorganische Chemie der Universität Frankfurt, Niederurseler Hang,
D-6000 Frankfurt (Main) 50

(10.VI.92)



66. Fundamental Aspects of Ionic Dissociations: The Fragmentation Pathways of Excited Bicyclobutane Cations

by Rolf Bombach, Josef Dannacher and J.-P. Stadelmann

Physikalisch-Chemisches Institut der Universität Basel, Klingelbergstrasse 80, CH-4056 Basel

and Reinhard Neier

Institut de chimie organique, Université de Fribourg, Pérolles, CH-1700 Fribourg

In memorial of Henry M. Rosenstock (1927-1982)

(22. XI. 82)

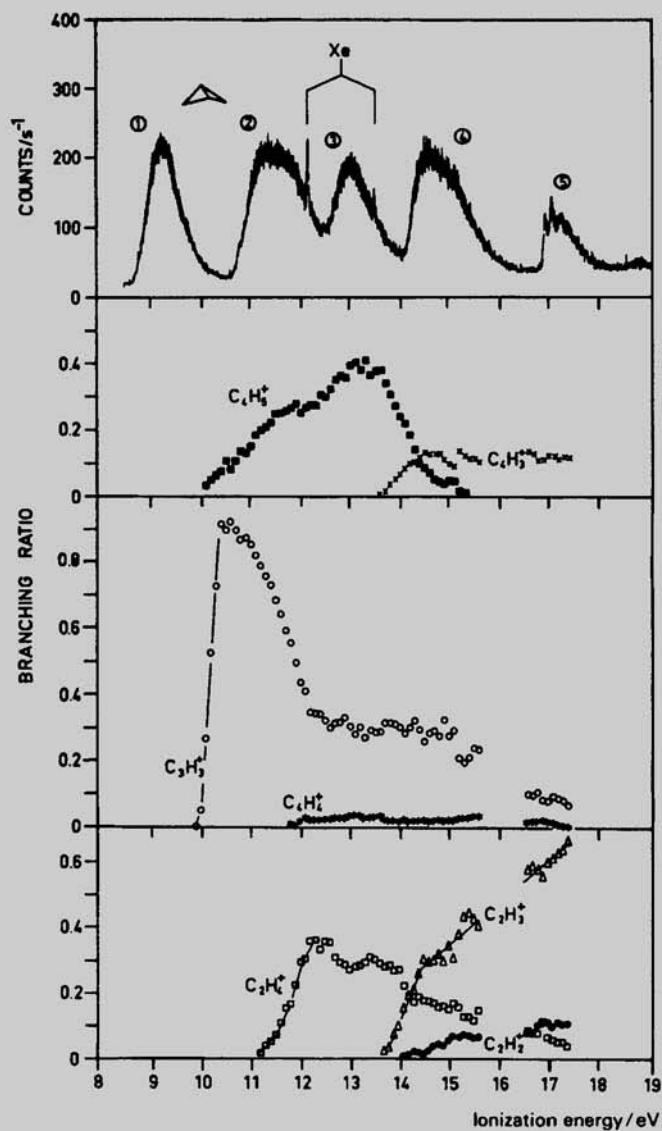
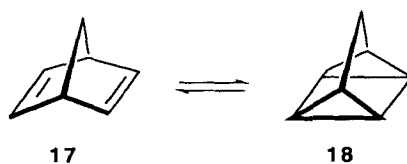
Fig. 52
(cont.)

Fig. 1. The photoelectron spectrum of bicyclobutane and the experimentally determined breakdown diagram of its radical cation. As a consequence of the very low electron intensity, coincidence measurements around $I = 16$ eV are not feasible.

cal behavior in solid matrices at low temperature, *e.g.* the pair norbornadiene radical cation/quadricyclane radical cation, **17/18**, and their conversion, or the determination of the structure of the oxirane molecular cation [163].



ESCA has been used to determine the structure of protonated azo groups. It has been shown that they prefer the classical structure over the non-classical, symmetric one, *i.e.* that the proton is linked to only one of the two N-atoms [164].

Photoionization thresholds of alkali-metal atom clusters have been determined in the course of the pioneering work by *Ernst Schumacher* and *Samuel Leutwyler* at the Institute of Inorganic and Physical Chemistry of the University of Berne, of which we show an example in *Fig. 53* [165].

Fig. 53

38. On Metal-Atom Clusters IV. Photoionization Thresholds and Multiphoton Ionization Spectra of Alkali-Metal Molecules¹⁾
 by *André Herrmann, Samuel Leutwyler, Ernst Schumacher²⁾, and Ludger Wöste*
 Institute for Inorganic and Physical Chemistry, University of Berne, 3000 Bern 9, Switzerland

In memory of Professor *Heinrich Labhart*
 (18.XI.77)

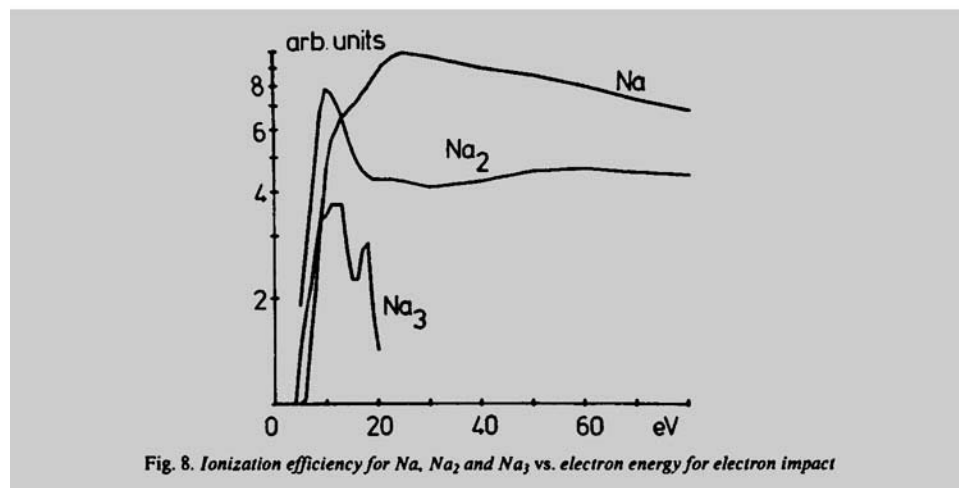


Fig. 8. Ionization efficiency for Na, Na₂ and Na₃ vs. electron energy for electron impact

To conclude this section, we show in *Fig. 54* a sample of the work by *Michael Allan* of the Institut de Chimie Physique de l'Université de Fribourg [166], who has measured forbidden electronic transitions by forward electron scattering, and the energies of negative ion states, *i.e.* electron affinities of organic molecules.

Fig. 54

198. Forward Electron Scattering in Benzene; Forbidden Transitions and Excitation Functions

by Michael Allan

Institut de chimie physique de l'Université, CH-1700 Fribourg

(6. VIII. 82)

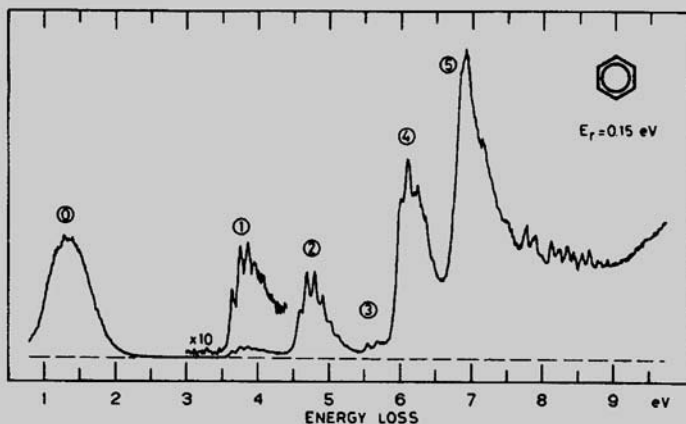


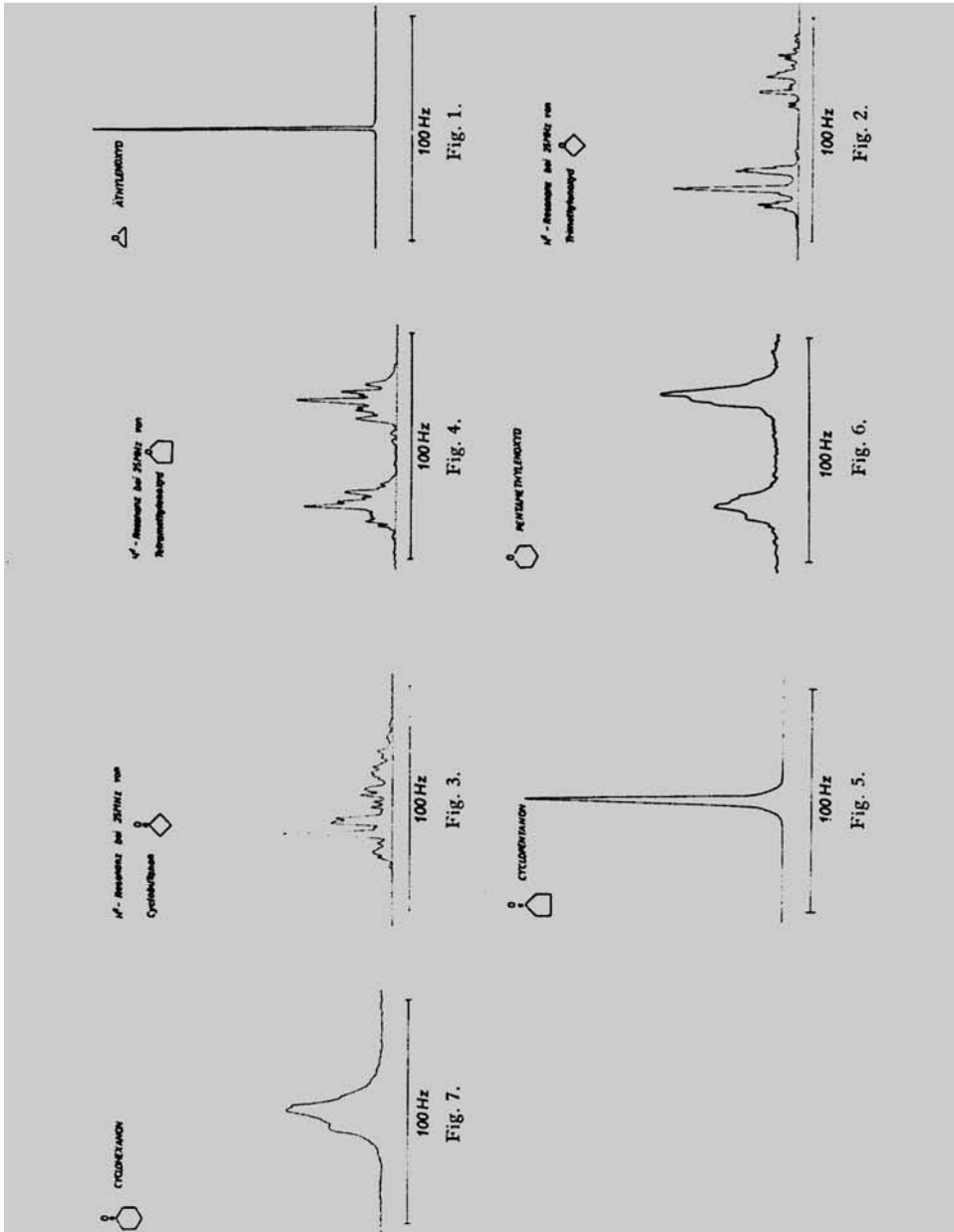
Fig. 4. Global energy-loss spectrum (Region 0 is pure vibrational excitation, regions 1–5 are predominantly valence, at this residual energy mostly singlet-triplet transitions. Rydberg transitions cause the structure above region 5)

1.4. Nuclear Magnetic Resonance (NMR) and Electron Spin Resonance (ESR, ENDOR) Spectroscopy. NMR is certainly the most powerful method used routinely for the elucidation of the structure of organic and inorganic molecules in solution, and – in some special cases – in the solid state. This is documented in *HCA* by innumerable publications. In the following overview, we shall restrict ourselves only to NMR work published in the early, pioneering period of the 1950s, or to papers dealing with problems of spectroscopic interest. However, it should be realized that this will not do justice to fundamental NMR work performed in Switzerland, since some of the most active research groups – for instance that of *Richard Ernst* – did not publish their results in *HCA*.

6. Protonenresonanzspektren einfacher cyclischer Äther und Ketone I

von H. Primas, K. Frei und Hs. H. Günthard.

(1. XI. 57.)



The first paper in *HCA* dealing with NMR is due to *Hans Primas, Karl Frei, and Hans H. Günthard*. It appeared in 1958 [167]. As shown in *Fig. 55*, the authors presented the high-resolution proton resonance spectra of the lower cyclic ketones and ethers, taken with a home-built high-resolution spectrometer²²⁾ [168]. It was shown that the proton signal of cyclopentanone consisted, surprisingly, of a single line.

Already in 1961, *H. A. Christ, P. Diehl, H. R. Schneider, and H. Dahn* published an extensive list of ¹⁷O chemical shifts, measured with a commercial instrument [169]. From about this time, NMR instruments became readily available, and were routinely used for structure determinations in the course of organic-chemical research.

Fig. 56

62. Deuteronen-Kernresonanzspektroskopie

von P. Diehl und Th. Leipert

(11. I. 64)

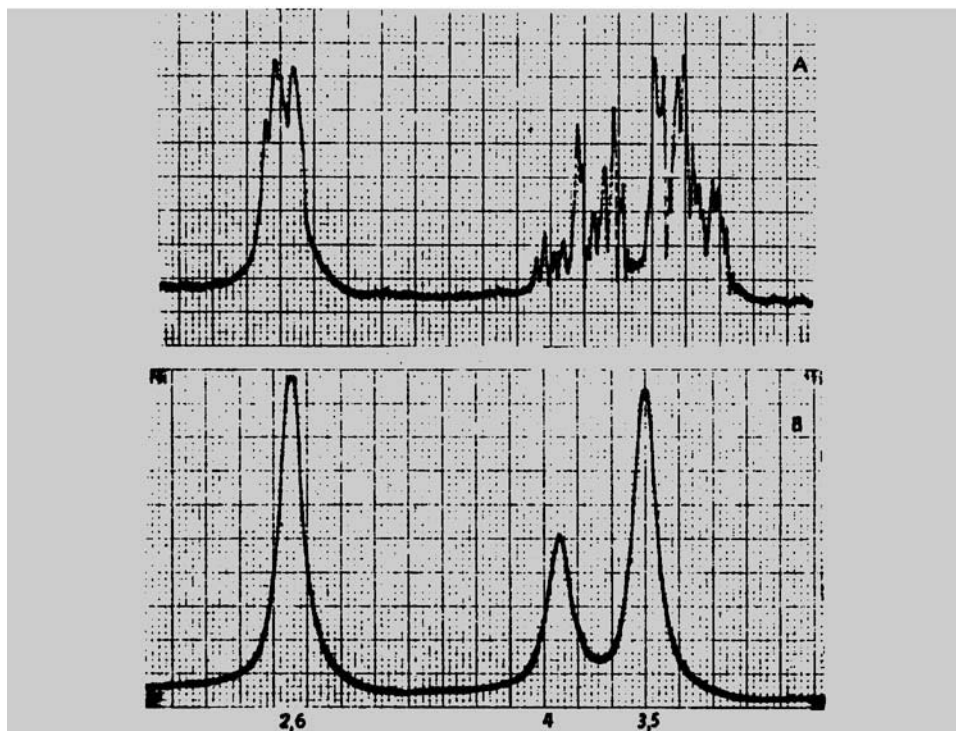


Fig. 2. Protonen- (A) und Deuteronen-Spektren (B) von Pyridin bzw. voll deuteriertem Pyridin

Resonanzfrequenz: Protonen: 56,4 MHz

Deuteronen: 7,65 MHz



$\delta_4 - \delta_2 = 1,16$ ppm

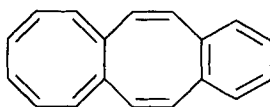
$\delta_5 - \delta_6 = 0,37$ ppm

²²⁾ This instrument became the prototype for a commercial NMR spectrometer produced by *Trueb-Täuber & Co.* in Switzerland. *Bruker Physics* took over *Trueb-Täuber NMR* to form *Spectrospin AG*, which is presently a flourishing company.

An early attempt to break down proton shifts, observed in the spectra of substituted benzenes, has been reported by *Peter Diehl* [170]. The same author published papers on the theoretical analysis of NMR spectra of simple molecules [171] and on the DMR spectra of deuterium-enriched organic compounds [172], as documented in *Fig. 56*.

A further important contribution from the Basle group headed by *Diehl*, concerned the NMR spectra of oriented molecules, using nematic liquids as solvents [173]. This contribution was followed by further publications on the same subject [174].

The potentialities of ^1H - and ^{13}C -NMR for the determination of kinetic and dynamic processes was demonstrated by *J.F.M. Oth*, *K. Müllen*, and their coworkers, using bullvalene (**10**) [175], benz[*c*]octalene (**19**) [176], and organolithium compounds [177] (see *Fig. 57*) as substrates. The same group also published methods for the kinetic analysis of temperature-dependent (decoupled) NMR spectra [178].

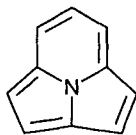
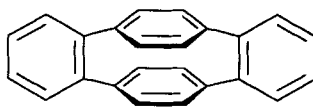
**19**

The use of the nuclear *Overhauser* effect (NOE) for the determination of $^{31}\text{P}/^1\text{H}$, and of T_1 relaxation times in palladium-phosphine complexes has been reported by *W. Bosch* and *P.S. Pregosin* [179].

Finally, the use of solid-state magic angle spinning (MAS) in a ^{13}C - and ^1H -NMR study of species adsorbed on aluminium oxide, or on silicates, has been reported by *Harald Günther* and his coworkers [180], as shown in *Fig. 58*.

In analogy to what has been said about NMR at the beginning of this section, much of the work on electron spin resonance (ESR) spectroscopy carried out in Switzerland (almost all of it at X-band frequency) has been submitted to other journals. However, some of the research groups most active in this field – in particular the one of *Fabian Gerson*, first at ETH-Zurich, then at the University of Basle – have published extensively in *HCA*.

The first ESR paper in *HCA* (in 1963), due to *F. Gerson* and *J.D. W. van Voorst* [181], describes the spectra of the radical anions of cycl[3,2,2]azine (**20**) and its 1,4-deuterated derivative, as shown in *Fig. 59*.

**20****21**

This paper marked the beginning of a long series of studies by *Gerson*'s Basle group, of radical ions in solution, obtained *e.g.* by reduction with sodium or potassium of a wide range of polycyclic molecules possessing extended π systems. Both radical cations and anions were investigated, and it was shown that the ESR spectra could be satisfactorily

Fig. 57

193. Quantitative Line-Shape Analysis of Temperature- and Concentration-Dependent ^{13}C -NMR Spectra of ^6Li - and ^{13}C -Labelled Organolithium Compounds

Kinetic and Thermodynamic Data for Exchange Processes in Dibromomethylithium, (Phenylthio)methylithium, and Butyllithium

by **Josef Heinzer, Jean F.M. Oth, and Dieter Seebach***

Laboratorium für Organische Chemie der Eidgenössischen Technischen Hochschule, ETH-Zentrum,
Universitätstrasse 16, CH-8092 Zürich

(19.VII.85)

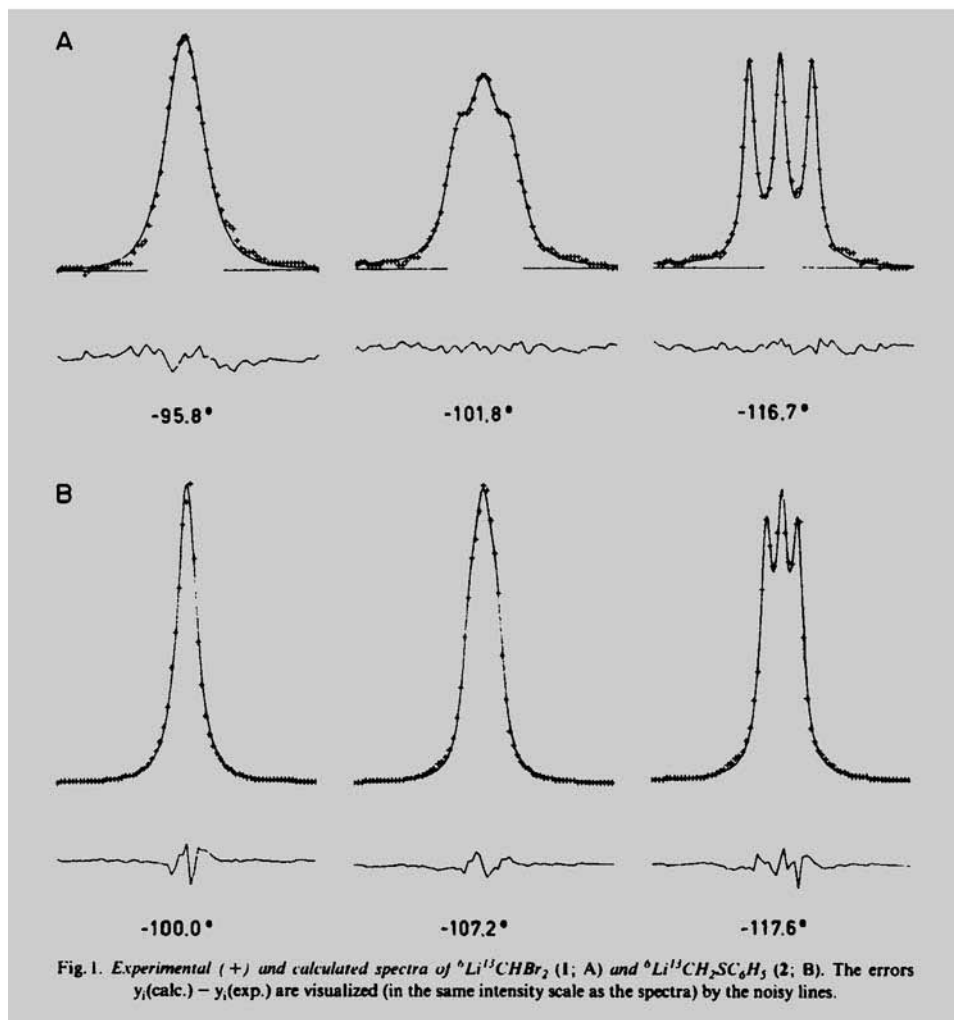


Fig. 1. Experimental (+) and calculated spectra of $^6\text{Li}^{13}\text{CHBr}_2$ (1; A) and $^6\text{Li}^{13}\text{CH}_2\text{SC}_6\text{H}_5$ (2; B). The errors $y(\text{calc.}) - y(\text{exp.})$ are visualized (in the same intensity scale as the spectra) by the noisy lines.

126. High-Resolution Solid-State MAS ^{13}C - and ^1H -NMR Spectra of Benzenoid Aromatics Adsorbed on Alumina and Silica: Successful Applications of 1D and 2D Pulse Experiments from Liquid-State NMR

by Michael Ebener, Gero von Fircks, and Harald Günther*

Fachbereich 8, OC II, Universität Siegen, Postfach 10 12 40, D-5900 Siegen

Dedicated to Prof. Edgar Heilbronner on the occasion of his 70th birthday

(12. VIII. 91)

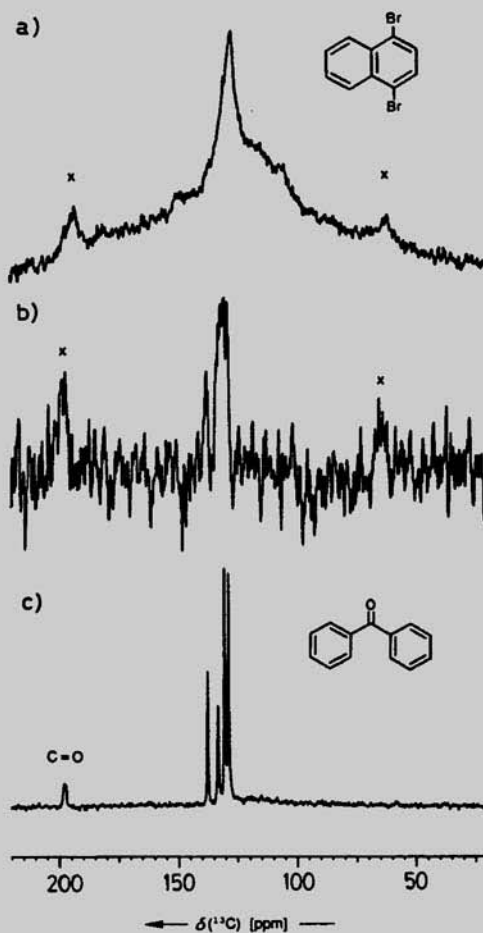


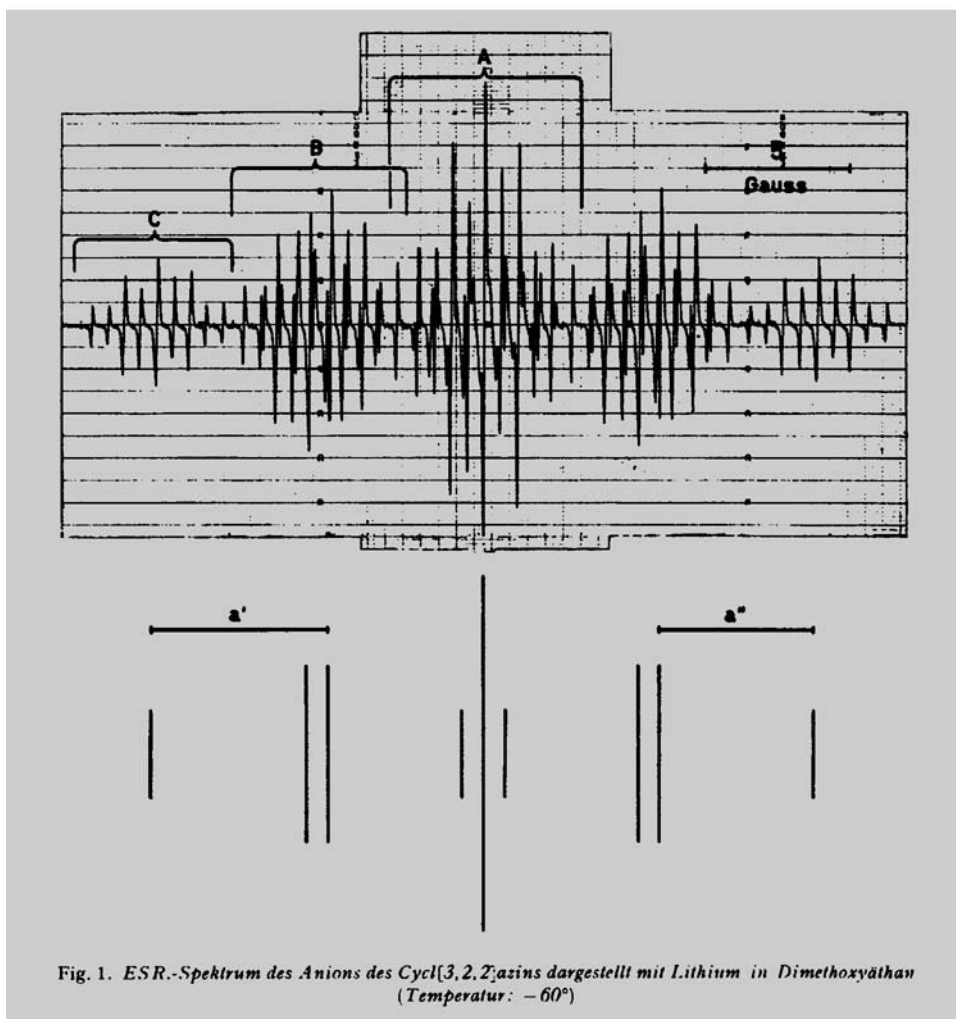
Fig. 1. 75.5-MHz Solid-state ^{13}C -NMR spectra of 1,4-dibromonaphthalene (a) and benzophenone (b). CP/MAS experiments with the pure solids, 4450 and 5700 transients, respectively, spinning rate 4 kHz, high-power ^1H decoupling; x indicates sidebands. c) MAS experiment for benzophenone adsorbed on aluminum oxide. 670 transients, other conditions as above; δ scale refers to TMS as reference.

Fig. 59

251. Tieftemperatur - Elektronspinresonanz-Spektren der Anionen des Cycl[3,2,2]azins und des 1,4-Dideutero-cycl[3,2,2]azins

von F. Gerson¹⁾ & J. D. W. van Voorst²⁾

(24. VIII. 63)



interpreted using HMO-type molecular-orbital models. We mention as typical examples work on the radical ions of bridged annulenes [182], or of bridged annulenyls [183] (see Fig. 60). These molecules are of special interest because of the non-planarity of their perimeter π systems. More often than not, the use of ENDOR spectroscopy is needed to assign their complicated ESR spectra.

283. The Radicals and Radical Dianions of Bridged [11]- and [15]Annulenylyls as Compared with Those of Benzotropyyl and 2,3-Naphthotropyyl

by Fabian Gerson and Walter Huber

Physikalisch-Chemisches Institut der Universität Basel, Klingelbergstrasse 80, CH-4056 Basel

and Klaus Müllen

Organisch-Chemisches Institut der Universität Köln, Greinstrasse 4, D-5000 Köln 41

Herrn Professor Dr. Edgar Heilbronner zu seinem 60. Geburtstag gewidmet

(14.IX.81)

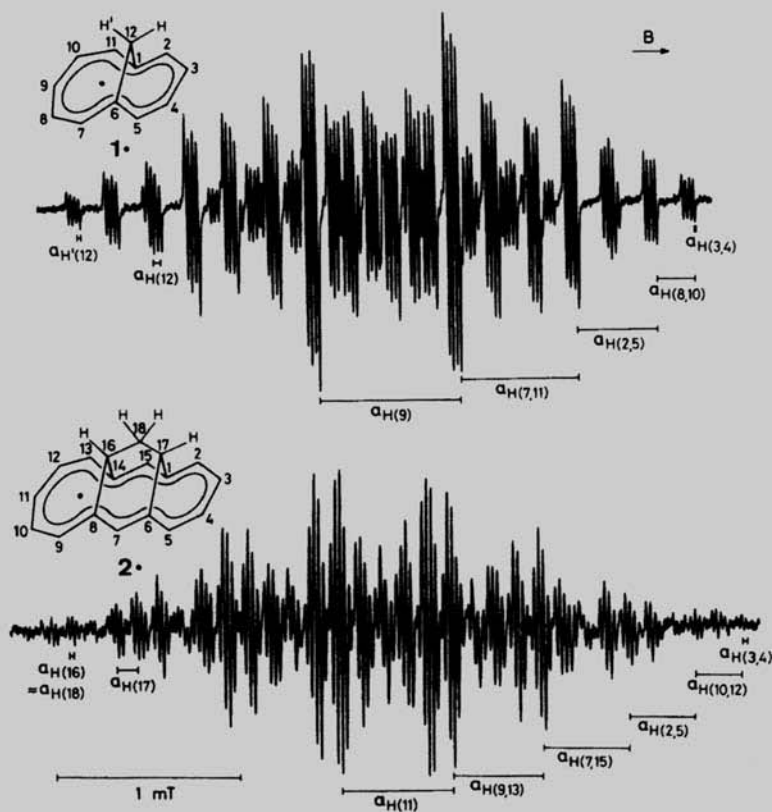


Fig. 1. ESR. spectra of the 1,6-methano[11]annulenylyl (1•) and 1,6:8,14-propane-1,3-diylidene[15]annulenylyl (2•) radicals (Solvent: high-boiling oil; temperature: 383 (1•) and 353 K (2•))

Other examples of important contributions by *Gerson's* group concern the ESR, ENDOR, and triple-resonance spectra of radical ions derived from cyclophanes, *e.g.* 1,2:9,10-dibenzo[2.2]paracyclophane (**21**) [184], shown in *Fig. 61*, or the ESR spectra of non-alternating aromatic systems, such as 1,3,5-tri(*tert*-butyl)pentalene [185], shown in

Fig. 61

**9. The Radical Anion of 1,2:9,10-Dibenzo[2.2]paracyclophane¹).
An ESR, ENDOR, and TRIPLE Resonance Study**

by Fabian Gerson^{*} and William B. Martin, Jr.²)

Institut für Physikalische Chemie der Universität Basel, Klingelbergstrasse 80, CH-4056 Basel

and Henry N. C. Wong and Chia Wing Chan

Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong

(30.X.86)

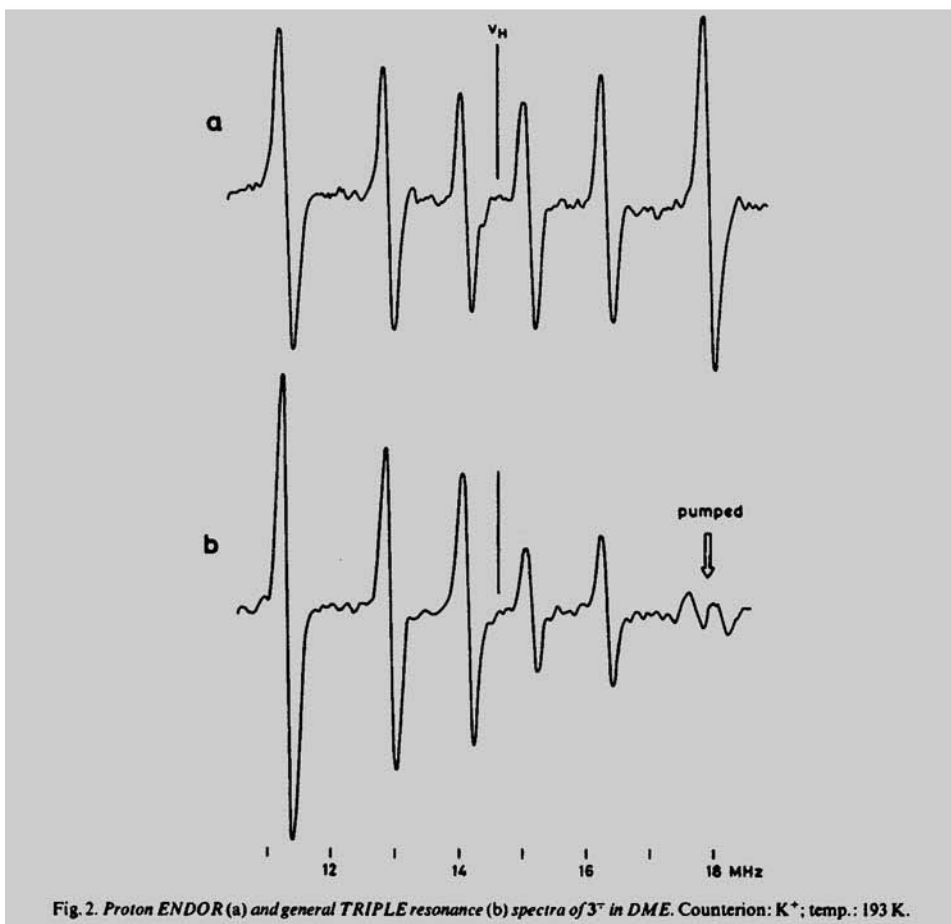


Fig. 62, which is of particular interest in connection with the phenomenon of fluctuating double-bond localization.

Fig. 62

281. Radical Ions in the Pentalene Series. Part I. 1,3,5-Tri-*t*-butylpentalene

by Peter Fürderer and Fabian Gerson

Physikalisch-chemisches Institut der Universität Basel, Klingelbergstrasse 80, CH-4056 Basel

and Klaus Hafner

Institut für Organische Chemie der Technischen Hochschule Darmstadt, Petersenstrasse 22,
D-6100 Darmstadt

(29.IX.78)

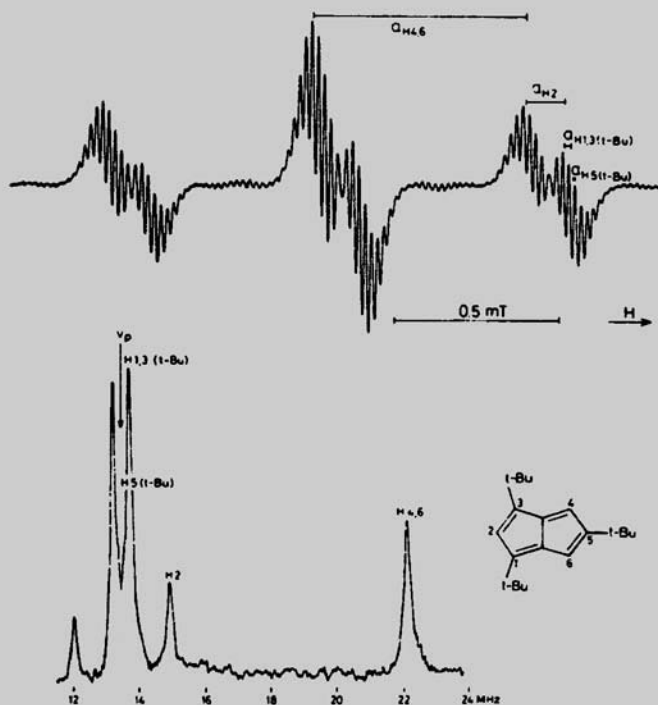


Fig. 1. ESR. and ENDOR. spectra of the radical anion of 1,3,5-tri-*t*-butylpentalene (II). Solvent: MTHF; counterion: Na^{\oplus} ; temp.: 273 (ESR.) and 203 K (ENDOR.). ν_p = frequency of the free proton.

Further nice examples of the use of ESR spectroscopy are Gerson's studies of the electron transfer, *i.e.* the electron delocalization between aromatic moieties separated by alicyclic groups [186], or the ESR and ENDOR investigation of radical cations isolated in solid freon matrices at low temperature [187] (see Fig. 63).

Fig. 63

162. Applications of ENDOR Spectroscopy to Radical Cations in Freon Matrices

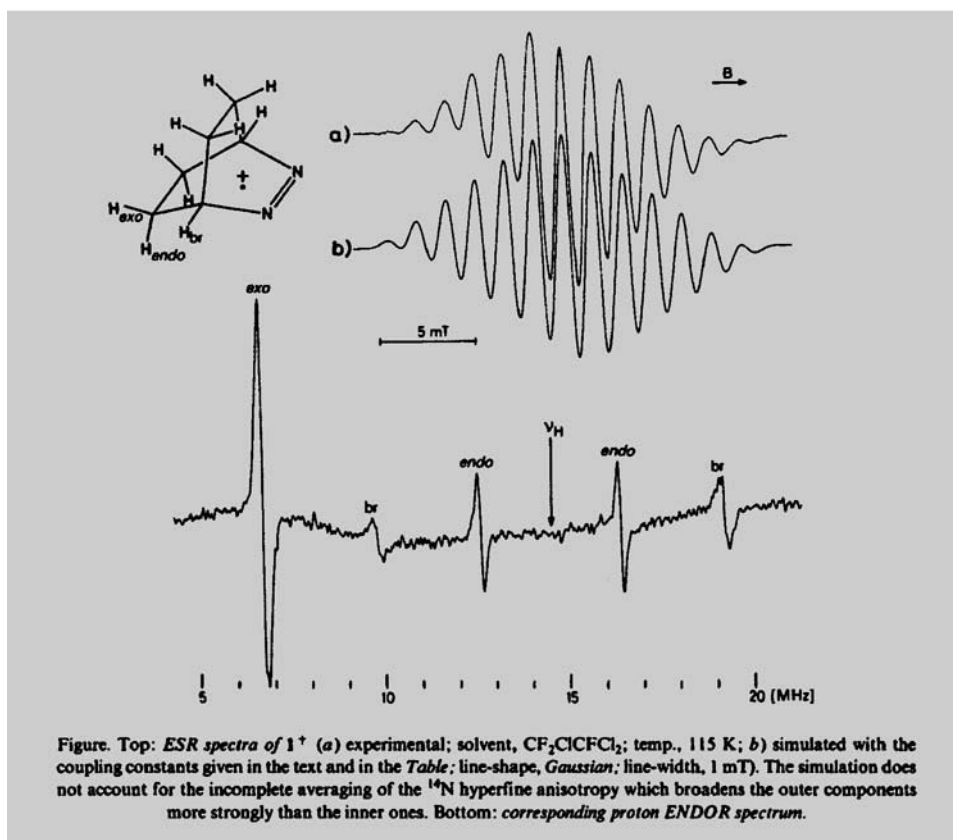
Part 2¹⁾

The Radical Cation of 2,3-Diazabicyclo[2.2.2]oct-2-ene

by Fabian Gerson* and Xue-Zhi Qin

Institut für Physikalische Chemie der Universität Basel, Klingelbergstrasse 80, CH-4056 Basel

(3. VII. 88)



Necessarily, quantum-chemical calculations of ESR coupling constants are often included in papers of this type, as for instance in a study by *H. Baumann* and *J. F. M. Oth* on the [18]annulene radical anion [188], where these constants have been computed by semi-empirical methods.

The use of ESR as a detector of radicals which occur as photoproducts, has been reported by *K. Heusler* and *H. Ladiger* for the light-induced decomposition of lead

carboxylate [189], by *F. Graf, K. Loth, and Hs. H. Günthard* for the determination of chlorine coupling constants in photochemically generated, Cl-substituted phenoxy radicals [190], and by *K. Loth and F. Graf* for the determination of the parameters for the description of intramolecular dynamic processes involving symmetrical and unsymmetrical H-bonds in systems derived from diacetyl and α -aminoxy radicals [191].

The application of ESR spectroscopy to the structural analysis of complexes was first reported in *HCA* by *K. Wüthrich* for VO^{2+} complexes in aqueous solution [192], as shown in *Fig. 64*.

**83. Elektronenspinresonanz-Untersuchungen
von VO^{2+} -Komplexverbindungen in wässriger Lösung**

von **K. Wüthrich**¹⁾

(27. III. 65)

Fig. 64

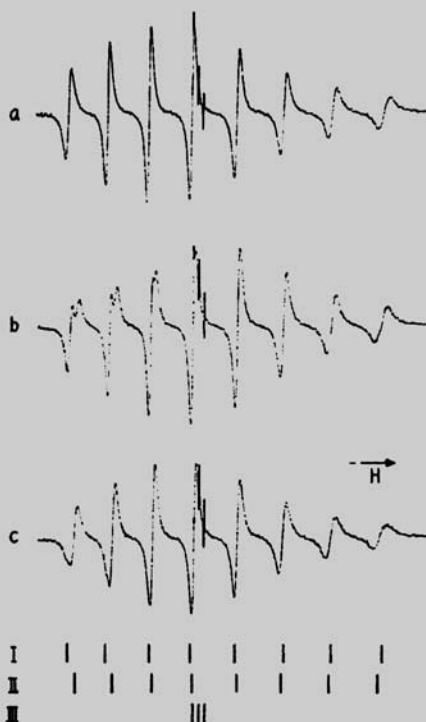


Fig. 3. ESR-Spektren von $VO(NTA)^-$ -Lösungen bei hohen pH-Werten.

$[VO_2O_4] = 2 \cdot 10^{-3} M$; $[NTA] = 2 \cdot 10^{-3} M$; pH = a) 4,5, b) 7,5, c) 9,5. Die Strichdiagramme I–III geben die Lage der HFS.-Linien für $VO(NTA)^-$, $VO(NTA)(OH)_2^-$ und FRÉMY-Salz ($g_0 = 2,0055$, $a = 13,0$ Gauss) an.

Other examples of this type are the single crystal spectra obtained by *W. Schneider* and *A. von Zelewsky* for Cu^{2+} -pyridine complexes [192], as can be seen from *Fig. 65*.

Fig. 65

**166. ESR.-Spektren von CuN_4 -Chromophoren:
Komplexe des zweiwertigen Kupfers mit Pyridin und Pyridinderivaten**
von *W. Schneider* und *A. v. Zelewsky*
(16. VII. 65)

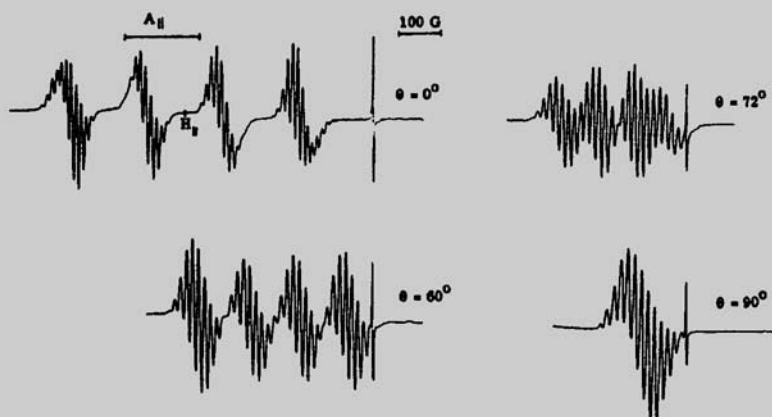


Fig. 1. ESR.-Spektren von $\text{Cu}(4\text{-NC-C}_6\text{H}_4\text{N})_4^{2+}$; Wirtsgitter *Cdcp*
Aufnahmen an Einkristall mit magnetisch äquivalenten Komplexen in der Elementarzelle;
Winkel θ zwischen Magnetfeld und tetragonaler Achse der chromophoren Gruppe CuN_4 .

ESR data for the triplet ground state of a metal complex with radical ligands have been reported by *P. Clopath* and *A. von Zelewsky* [194]. *A. von Zelewsky* and *M. Zobrist* studied planar Cu^{II} and low-spin Cu^{II} complexes in nematic phases and in single crystals [195] (*Fig. 66*). They observed that, in the liquid crystal host, orientation of the complex takes place only if it is sufficiently non-isotropic in its mean molecular plane.

Fig. 66

**209. EPR. Spectroscopic Investigations of Planar $\text{Cu}(\text{II})$ - and
Low-Spin $\text{Co}(\text{II})$ -Complexes in Nematic Phases and in Single Crystals**

by *Alex von Zelewsky* and *Markus Zobrist*¹⁾

Institute of Inorganic Chemistry, University of Fribourg, Pérolles, CH-1700 Fribourg

(7. VII. 81)

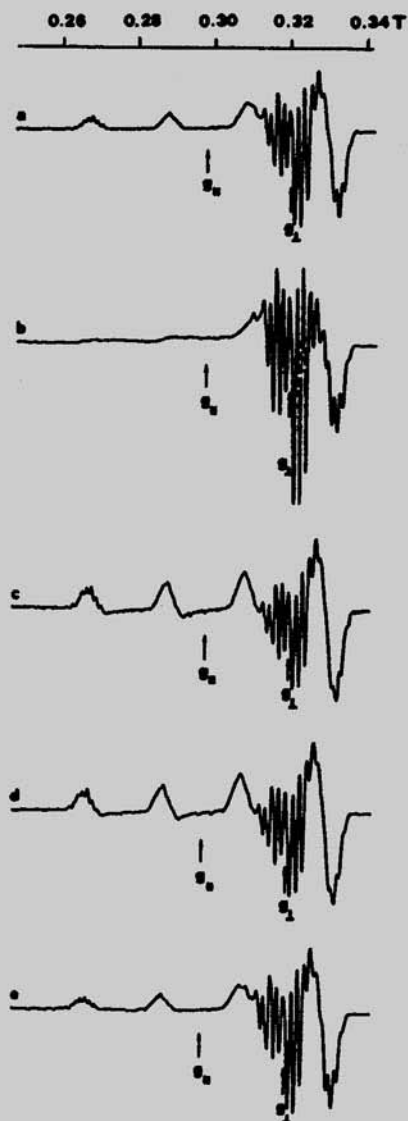


Fig. 1. EPR spectra of $\text{Cu}(\text{acacen})$ in nematic phase 7A at 77 K, X-band frequency (a) Non-oriented sample, b) \vec{H}_{meas} parallel to \vec{H}_{orient} , c) \vec{H}_{meas} perpendicular to \vec{H}_{orient} , d) \vec{H}_{meas} parallel to \vec{E}_{orient} , e) \vec{H}_{meas} perpendicular to \vec{E}_{orient})

The structural *Jahn-Teller* distortion of orbitally degenerate sandwich complexes, incorporated in diamagnetic host crystals, was investigated by *J. H. Ammeter, N. Oswald, and R. Bucher* [196] (see Fig. 67). They found that the distortions depend sensitively on the structure of the host crystal.

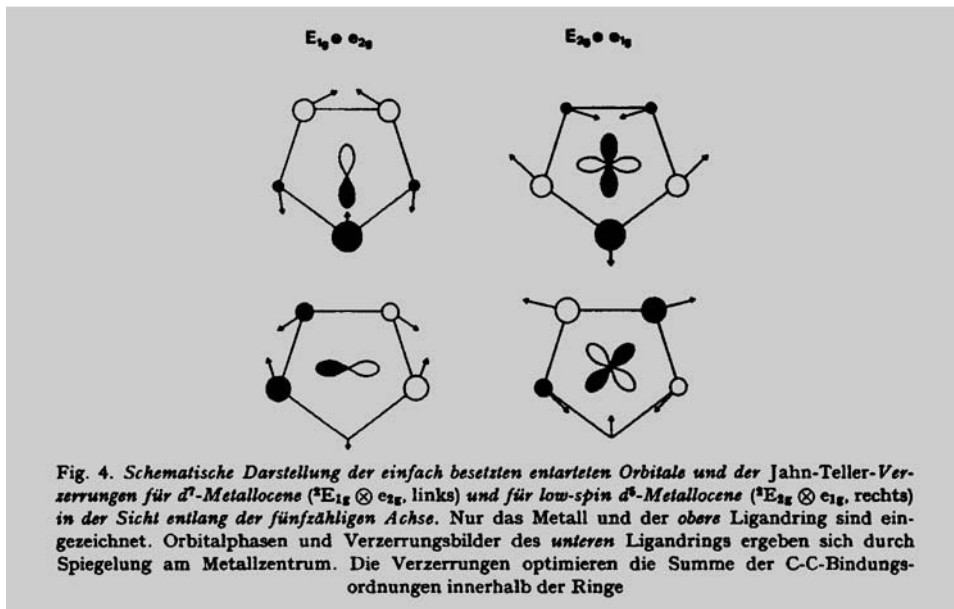
Fig. 67

78. Dynamische Jahn-Teller Verzerrungen und chemische Bindungsverhältnisse in orbitalentarteten Sandwichkomplexen¹⁾

von J. H. Ammeter, N. Oswald und R. Bucher

Institut für Anorganische Chemie, ETH Zürich

(19. XI. 74)



Only a single paper of an ESR study of radicals generated by irradiation was published in *HCA*. *M. Geoffroy* and *A. Llinares* observed that two different radicals are generated, when dimethyl arsinato single crystals are irradiated by X-rays [197].

1.5. Spectroscopy at Radiofrequencies: Nuclear Quadrupole Resonance and Microwave Spectroscopy. The first papers in *HCA* devoted to solid-state nuclear quadrupole resonance (NQR) spectroscopy were published in 1971. They stemmed from the research groups headed by *E. A. C. Lucken* and by *H. Labhart*, both groups using home-built superregenerative oscillators. In the publication by *S. Ardjomand* and *E. A. C. Lucken* [198], the NQR resonances of polycrystalline adducts of BCl_3 with a variety of organic nitrogen and oxygen compounds were studied and interpreted in terms of the *Townes-Dailey* theory (cf. Fig. 68).

15. The ^{35}Cl Nuclear Quadrupole Resonance Frequencies of Complexes of Boron Trichloride

by *S. Ardjomand* and *E. A. C. Lucken*

Département de Chimie Physique. Section de Chimie, de l'Université de Genève, Sciences II,
30, Quai de l'Ecole de Médecine, 1211 Genève 4

(24 XI 70)

Résumé. Les fréquences de résonance quadripolaire du noyau ^{35}Cl dans les complexes du trichlorure de bore avec une variété de donneurs organiques ont été mesurées à 77 K. Quoique ces fréquences dans l'accepteur soient assez peu sensibles à la nature du ligand, la tendance observée est en accord avec d'autres mesures du pouvoir donneur des ligands. Certains des ligands étudiés ici contiennent un atome de chlore et les changements de fréquence amenés par la complexation sont également en accord avec les résultats prévus. Le trichloroacétonitrile et le dichloroacétonitrile réagissent avec le trichlorure de bore pour donner un composé d'addition sur la triple liaison du groupement $-\text{C}\equiv\text{N}$ plutôt qu'un complexe donneur-accepteur. Ce comportement est clairement mis en évidence par la spectroscopie de résonance quadripolaire.

Fig. 68

The publication by *P. Gerber*, *H. Labhart*, and *E. Kloster-Jensen* [199] (Fig. 69) contains the ^{35}Cl -NQR data of chloroacetylenes in the polycrystalline state and makes use of a modified *Townes-Dailey* treatment for the analysis of the observed quadrupole coupling constants.

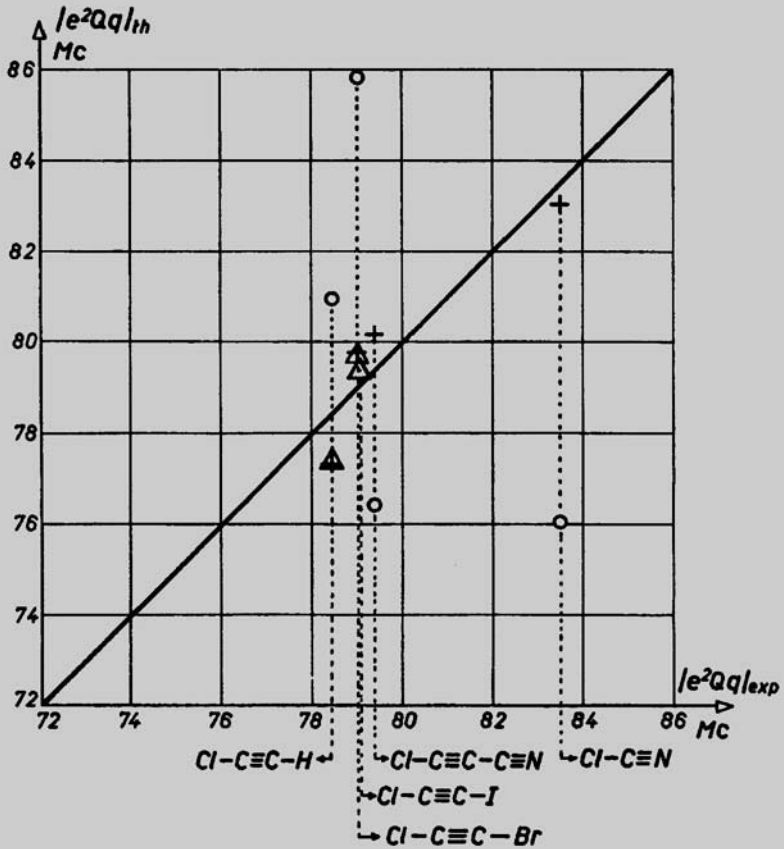
218. Kernquadrupolresonanz von ^{35}Cl in Chloracetylenen

von *P. Gerber*¹⁾, *H. Labhart*¹⁾ und *Else Kloster-Jensen*²⁾

Physikalisch-Chemisches Institut der Universität Zürich und
Physikalisch-Chemisches Institut der Universität Basel

(23. VII. 71)

Fig. 69

Fig. 69
(cont.)Fig. 2. Korrelation von berechneten und experimentellen ^{35}Cl -Quadrupolkopplungskonstanten

- Townes-Dailey-Näherung (Gl. 1)
- + Townes-Dailey-Näherung mit Korrektur nach Gleichung 2
- △ Ab-initio-Berechnung Straub [3]

Microwave spectroscopy of molecules in the gas phase was an outgrowth of the enormous progress in radio and microwave electronics during the second world war. Only a single paper from this field has been published in *HCA* [200]. In it, *A. Bauder, F. Tank, and Hs. H. Günthard* describe the microwave spectrum of cyclobutanone, measured with home-built X- and K-band spectrometers, and the structure of the molecule, as shown in Fig. 70.

Fig. 70

162. Mikrowellenspektrum, Dipolmoment und Struktur von Cyclobutanon¹⁾

von *A. Bauder, F. Tank und Hs. H. Günthard*

(23. II. 63)

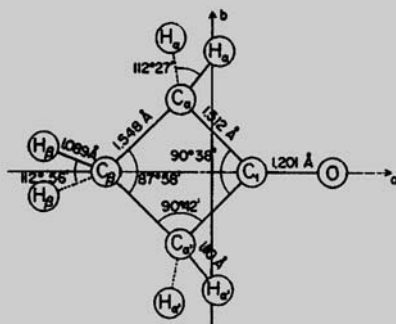
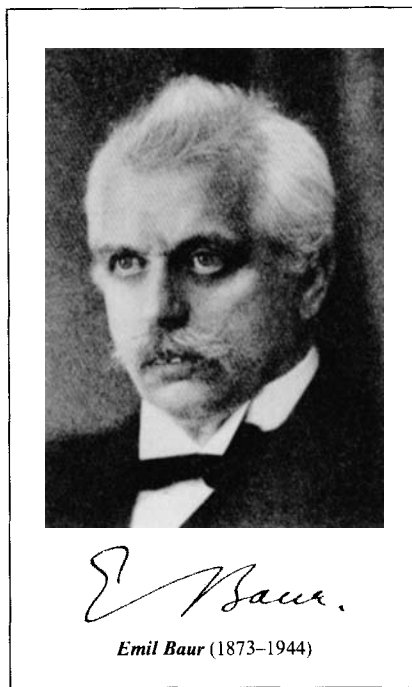


Fig. 3. Struktur von Cyclobutanon

2. Photochemistry. – Over the years, a considerable number of publications on photochemistry have appeared in *HCA*. However, the major part of them must be classified as ‘Organic Chemistry’, because photons are only used as ‘educts’ in the preparation of compounds not easily accessible by ground-state reactions. This is particularly true for the synthesis of molecules in configurations which are determined by excited-state mechanisms, *i.e.* governed by the *Woodward-Hoffmann* rules [125]. In such publications, the accent is either on the synthetic potentialities of photochemical reactions or on the elucidation of the structure of the photoproducts, rather than on the reaction mechanism itself. Unfortunately – from the point of view of this review – quite a number of publications hover on the borderline between organic and physical chemistry, which makes it difficult to draw the line. Not to overload our review, we have chosen to concentrate on two examples of the early history of photochemistry in *HCA*, and only on a few selected examples from more recent times. We hasten to add that this does not reflect the importance of work not mentioned in what follows.

The first paper on photochemistry published in *Vol. 1* of *HCA* (see below) stems from *Emil Baur* (1873–1944)²³ [201], professor of Physical Chemistry at the ETH-Zurich. In his research, he pursued many diverse ideas, some of them well in advance of their time, and some rather wild. He was one of the first to work on fuel cells, tried to convert graphite into diamond at high pressures and high temperatures, studied the gold content of the oceans, and proposed that energy should be stored in the form of hydrogen,

²³) *Emil Baur* was born in 1873 in Ulm. He studied Chemistry in Munich and in Berlin, where he obtained his Ph.D. in Physical Chemistry. In 1901, he became ‘Privatdozent’ in Munich. After having worked at the ‘Kaiserliche Gesundheitsamt’ in Berlin, he was elected, in 1907, as Extraordinarius for Physical Chemistry at the Technische Hochschule in Braunschweig. In 1911, he became the successor of *G. Bredig* and director of the Laboratorium für Physikalische Chemie at the ETH-Zurich, a post which he occupied until his retirement. He died in Zurich in 1944.



obtained by either electrolysis²⁴⁾ [202], or by photochemical processes [203]. On the other hand, he tried to show that the second law of thermodynamics is not generally valid²⁵⁾.

His photochemical studies began with the proposal of a theoretical model, linking the properties of the excited state of a molecule – which he called its ‘Lichtzustand’ – with those arising during electrolysis [204], as shown in *Fig. 71*.

Fig. 71

Photolyse und Elektrolyse

von

Emil Baur.

(3. VI. 18.)

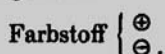
²⁴⁾ He writes in 1921 (!) [202]: ‘*In den Alpenländern ist es eine vielbesprochene Frage, wie die überschüssigen Sommer- und Abfallwasserkräfte zweckmässig gespeichert werden könnten*’.

²⁵⁾ One of the authors remembers his sometimes confusing lectures because of some quaint definitions, e.g. explaining the crystal lattice: ‘*Das Kristallgitter ist dreidimensional. Dreidimensional heisst, so nach vorn und hinten*’.

Fig. 71
(cont.)

Unter dem Lichtzustand haben wir also nichts anderes zu verstehen, als die Ausbildung einer elektrischen Polarisation im Molekül.

Wenn nun der positive Pol die Eigenschaften einer Anode, der negative aber die Eigenschaften einer Kathode besitzt, erlangt hiermit das Molekül gleichzeitig oxydierendes und reduzierendes Vermögen. Somit werden wir nicht fehlgehen, wenn wir den Lichtzustand z. B. eines Farbstoffes durch das Auftreten einer Volta'schen Potentialdifferenz innerhalb des Moleküls bestimmen. Dieser Zustand der photochemischen Polarisation sei durch das Symbol dargestellt:



Indem eine eintretende chemische Lichtwirkung in der Ver-
nichtung dieser Ladungen besteht, erkennt man die Photolysen
als molekulare Elektrolysen.

These ideas were then applied, in a series of theoretical and experimental studies, to the important problem of the photolysis of carbon dioxide, of which we show the title of the first paper [205] on top of Fig. 72. This was followed by a number of later contributions, finally collected in the book '*Erforschung der Photolyse der Kohlensäure*', published a year before his death [206]²⁶⁾.

Of Baur's later papers, dealing with photolysis, we quote the one on the photolysis of uranyl oxalates and uranyl acetates [207], of the influence of light on dissolved silver salts in the presence of zinc oxide [208], and a theoretical paper [209], the beginning of which is reproduced in the lower part of Fig. 72²⁷⁾.

Another important photochemical investigation, which covered close to 30 years, was the study, by Hans von Halban [11] [27], of the behavior of tetrabenzoyl ethylene under the influence of light. He began these studies in 1920, when he was still at the University of Würzburg [210], but the first paper on this topic published in HCA, by H. Keller and H. v.

Fig. 72

Über Versuche zur Photolyse der Kohlensäure

von

Emil Baur und A. Rebmann.

(28. VII. 22.)

²⁶⁾ The book ends with the following statement, showing where Baur's sympathies lied in the then raging world war II: 'Übrigens sehe ich kommen, dass die Menschheit des technischen Fortschritts überdrüssig wird, während die Lust an der Erkenntnis der Natur, *obwohl von Ost und West bedroht, solange der Drachentöter standhalten mag, wohl lebendig bleibt*' (our italics).

²⁷⁾ The Footnote 1 to this paper (cf. Fig. 72) documents another side of Baur's idiosyncrasies, namely the use of words at odds with current usage. As can be seen, the editors of HCA lost the battle.

Fig. 72
(cont.)**Formeln für die sensibilisierte Photolyse**

von Emil Baur.

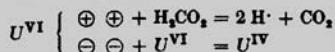
(28. V. 29.)

Unter sensibilierter¹⁾ Photolyse verstehe ich eine solche, bei der die vom Lichtempfänger gespeicherte Lichtenergie in einem Oxydations-Reduktionsprozess — also durch Abgabe und Wiederaufnahme von (negativen) Ladungen — verausgabt wird. Die alsdann für die Umsatz-Zeit-Kurve in Betracht kommenden Gleichungen sollen nachfolgend abgeleitet werden.

I. Aufstellung der Gleichungen.

Ich lege der Ableitung ein Beispiel zugrunde und wähle hiezu die von E. C. Hatt²⁾ (1917) sehr ausführlich und genau untersuchte Photolyse des Uranylformates.

Wir schreiben die Umsatzgleichung nach der von mir³⁾ (1918) gegebenen Theorie in der Gestalt:



¹⁾ Auf ausdrücklichen Wunsch des Verf. drucken wir „sensibilisiert“, „Sensibilisator“ und „Desensibilisierung“, obgleich weder *Duden* noch *Jansen* diese Formen kennen, und obgleich wir der Ansicht sind, man sollte nicht der Kürze zuliebe richtig gebildete Wortformen verändern. *Red.*

Halban [211], appeared only in 1940. In *Fig. 73*, we reproduce the beginning of part IV of this series [212], in which the originally assumed photochemical process of the transformation of tetrabenzoyl ethylene (Verbindung A) into the unknown, yellow photoproduct B is shown. However, as further studies revealed, the processes involved were much more complex than surmised, and this is illustrated by the revised scheme reproduced at the bottom of *Fig. 73*.

Fig. 73

8. Über die Photochemie des Tetrabenzoyl-äthylens IV¹⁾

von H. Keller und H. v. Halban.

(24. XI. 44.)

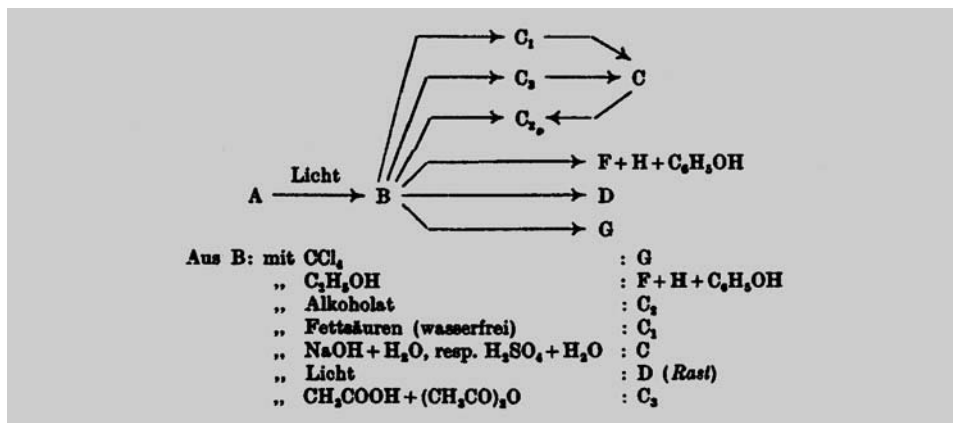
A. Andres²⁾ hatte festgestellt, dass das farblose, bei 185° schmelzende Tetrabenzoyl-äthylen sich im Licht gelb bis orange färbt, und dass diese Färbung auch beim Auflösen erhalten bleibt; auch beim Belichten der Lösungen selbst werden diese gelb gefärbt. Bei der Lösung in Eisessig verschwindet die Färbung im Dunkeln allmählich, rascher beim Erwärmen und tritt beim Belichten wieder auf.

Andres schloss daraus auf eine umkehrbare Lichtreaktion. Im folgenden wird der Kürze halber Tetrabenzoyl-äthylen mit A, die im Lichte entstehende gelbe Verbindung mit B bezeichnet.



Es gelang ihm nicht, die gelbe Verbindung zu isolieren.

Fig. 73
(cont.)



As it turned out, the unravelling of the intricate interplay between the primary and secondary processes, which follow the formation of compound B, was beyond the scope of simple UV/VIS spectroscopic observations. It needed the help of a competent organic chemist – in this instance of *Hans Schmid* – to establish the structures of the various molecules present in the mixture of photoproducts. The solution of this problem was reported in two publications by *H. Schmid*, *M. Hochweber*, and *H.v. Halban* [213], of which we reproduce part of the proposed reaction scheme in Fig. 74.

Fig. 74

146. Über die Photochemie des Tetrabenzoyl-äthylens VIII
 von *H. Schmid*, *M. Hochweber* und *H. von Halban*.
 (6. VI. 47.)

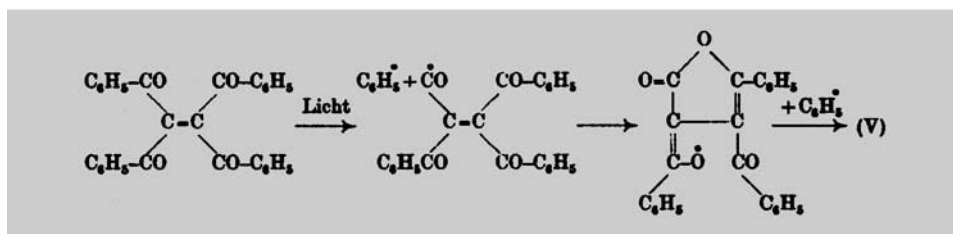
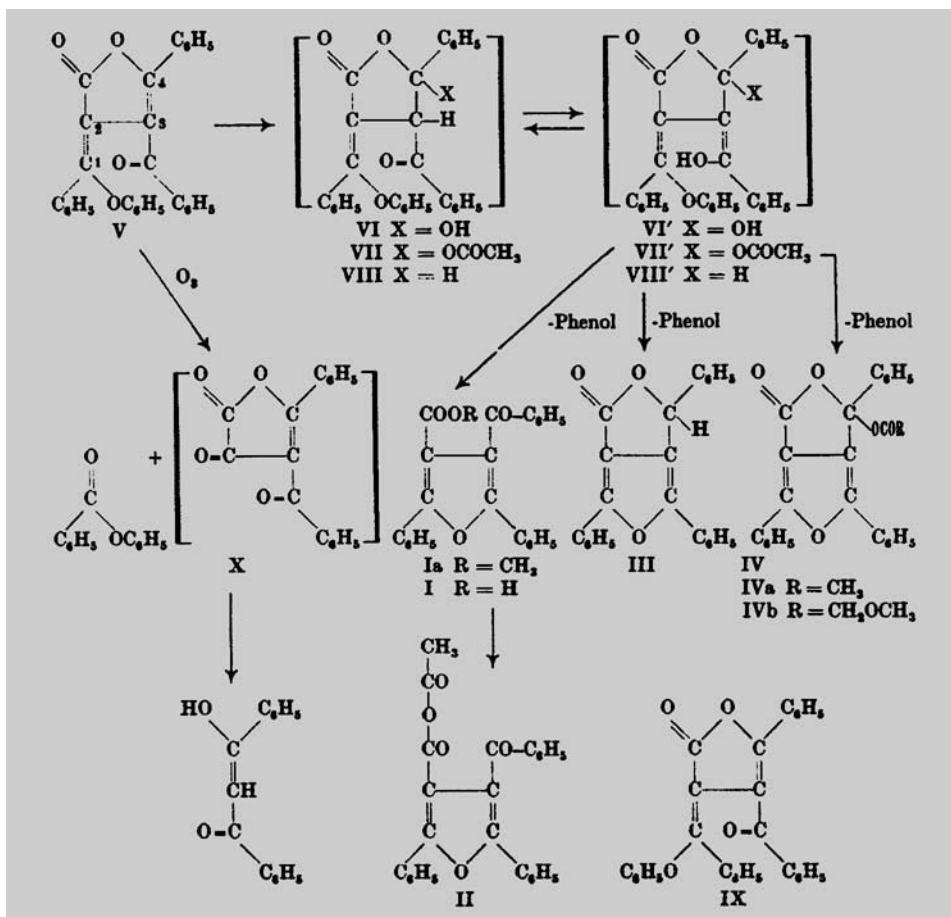


Fig. 74
(cont.)

We conclude this section with a small, random selection of papers, which we believe documents the variety of photochemical work of a more physico-chemical nature, published in *HCA*.

In 1971, *Werner Schmidt* studied a remarkable, photoinduced valence isomerization [214] (Fig. 75), in which a bridged annulene is converted into a metacyclophane by a *Woodward-Hoffmann*-forbidden process.

A fair number of photochemical and photophysical investigations published in *HCA* stems from the group of *Hans Jakob Wirz* at the University of Basle. Earlier examples concern the photohydrolysis of trifluoromethyl-substituted phenols and naphthols [215], or the photolysis of the azo precursors of 2,3- and 1,8-naphthoquinodimethane (**22** and **23**, respectively) [216]. Only **22** was obtained in a rigid matrix at 77 K, whereas **23** reacted immediately to yield acenaphthene.

86. Die Valenzisomerisierung des *trans*-15,16-Dimethyl-dihydropyrens - Ein Beitrag zur Frage nach der Aktivierungsenergie Symmetrie-verbotener Prozesse

Vorläufige Mitteilung¹⁾

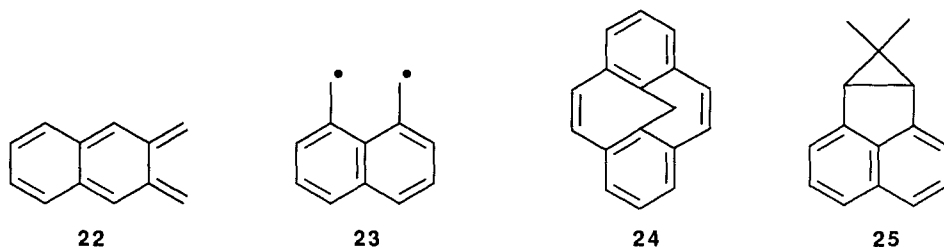
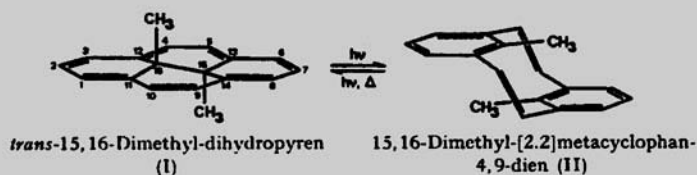
von **W. Schmidt**

Physikalisch-chemisches Institut der Universität Basel

(18. II. 71)

Summary. Concerted electrocyclic processes which are forbidden according to the symmetry conservation rules of *Woodward & Hoffmann*, may nevertheless take place at low activation energies. The necessary conditions are exemplified by the unique case of the *trans*-15,16-dimethyl-dihydropyrene \rightleftharpoons 15,16-dimethyl-[2.2]metacyclophane-4,9-diene system.

trans-15,16-Dimethyl-dihydropyren (I) [1] lagert sich beim Belichten mit sichtbarem Licht ($\lambda \geq 365$ nm) in 15,16-Dimethyl-[2.2]metacyclophan-4,9-dien (II) um [2]²⁾. Durch Einstrahlen von Licht der Wellenlänge 313 nm wird das thermodynamisch stabilere Ausgangsprodukt vollständig zurückgebildet.



In Fig. 76 are shown the mechanism and the correlation diagram for the photoenolization of 2-methylacetophenone [217]. From the same group stem detailed studies of the photoisomerization pathways of 8,16-methano[2.2]metacyclophane-1,9-diene (**24**) [218],

255. The Photoenolization of 2-Methylacetophenone and Related Compounds

by **Roland Haag and Jakob Wirz**¹⁾

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Klingelbergstrasse 80, CH-4056 Basel, Switzerland

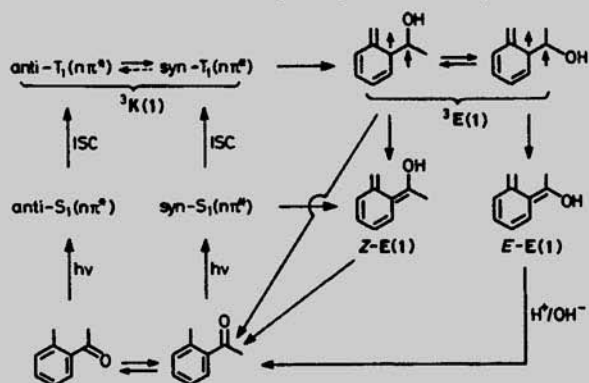
and **Peter J. Wagner**

Department of Chemistry, Michigan State University, East Lansing, Michigan 48824, U.S.A.

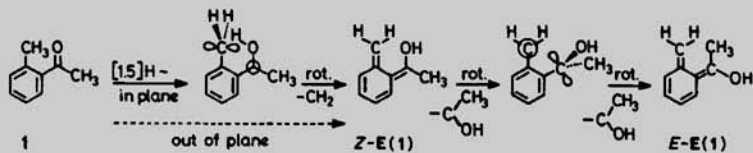
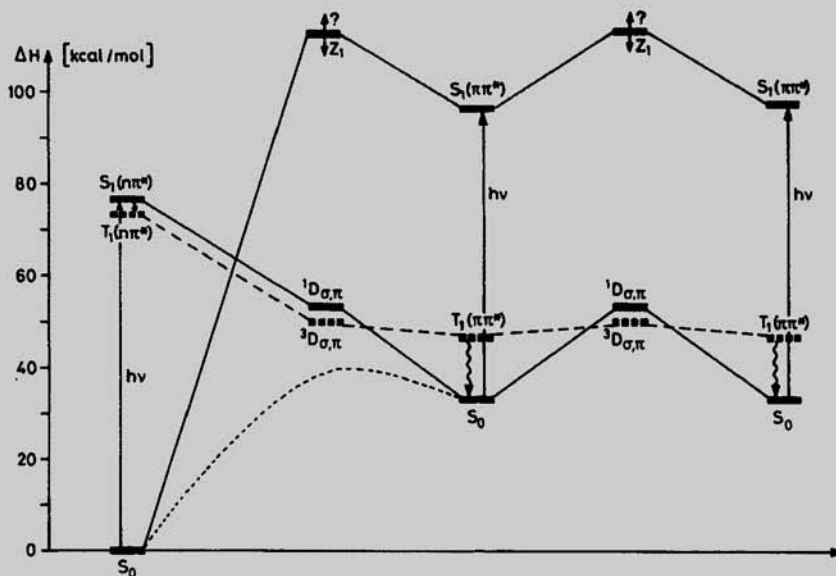
(30. VIII. 77)

Fig. 76
(cont.)

Scheme 1. Mechanism for the photoenolization of 1



Scheme 2. State correlation diagram for the photoenolization of 1



and of the conjugated biradical intermediates obtained from 2,2-dimethyl-1,3-perinaphthadiyl (**25**) [219].

Edwin Haselbach reported on the laser-flash photolysis of the *p*-chloranil/naphthalene system [219], and later on the free-energy dependence of the ion yield of photo-

Fig. 77

10. Free-Energy Dependence of the Ion Yield of Photo-Induced Electron-Transfer Reactions in Solution

by Eric Vauthey*, Paul Suppan, and Edwin Haselbach

Institute of Physical Chemistry, University of Fribourg, CH-1700 Fribourg

(28. IX. 87)

A study of photo-induced electron-transfer reactions in MeCN with 9,10-dicyanoanthracene as acceptor and 21 electron donors with transient photoconductivity measurements is reported. The free-ion yield and the rate constant of back electron transfer are determined. For exergonic reactions, the 'Marcus-inverted' region is observed. The fit with the theory is best, when a nearly solvent-independent *Coulomb* term is used in the calculation of the energy balance.

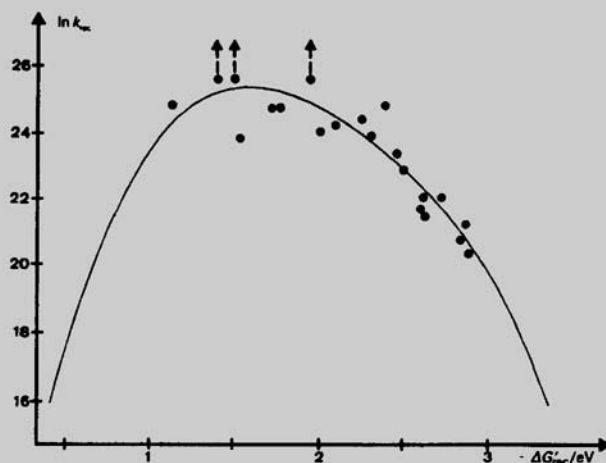


Fig. 4. Rates of back electron-transfer reactions as a function of the exergonicity. The points with the arrows represent lower bound values, see the Table.

induced electron-transfer reactions in solution [220] (Fig. 77), an interesting contribution to the theory developed by *R. A. Marcus*.

In 1979, *Jean-Marie Lehn* and his coworkers discussed in the paper shown in Fig. 78 [221] (see also [222]) an approach to the photochemical conversion and storage of solar

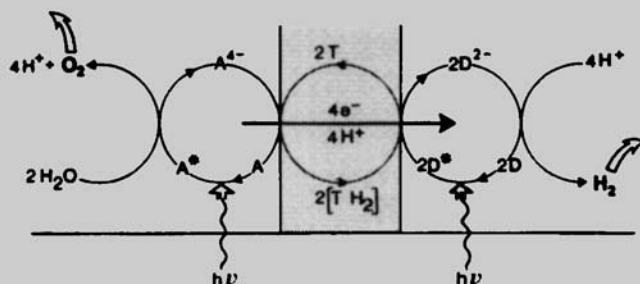
Fig. 78

142. Hydrogen Generation by Visible Light Irradiation of Aqueous Solutions of Metal Complexes. An Approach to the Photochemical Conversion and Storage of Solar Energy¹⁾

by Michèle Kirch, Jean-Marie Lehn and Jean-Pierre Sauvage

Institut Le Bel, Université Louis Pasteur, 4, rue Blaise Pascal, F-67000 Strasbourg, France²⁾

(20.III.79)



OXIDATIVE PROCESS TRANSPORT REDUCTIVE PROCESS
4 electron Acceptor Carrier 2 electron Donor

Fig. 1. Schematic representation of a membrane separated photochemical water splitting system. A is a photoactive species which is a strong oxidant in its excited state and a four-electron acceptor. T is a redox carrier rendering the membrane permeable to electrons and protons. D is a photoactive species which yields a reduced state capable of forming hydrogen from water in a dielectronic process. This is of course only one possible variant of such a system; several other schemes may be imagined

energy. At the same time, the group around *Michael Grätzel* published a paper on the same subject [223], as evidenced in *Fig. 79*.

Photochemical work by *J. R. Huber* and his coworkers on the light-induced rearrangement of nitrosooxy compounds and nitrosamines has already been mentioned [115] (*Fig. 37*). Finally, attention should be drawn to the photochemical studies, carried out by *André Braun* and his research group at the Ecole Polytechnique Fédérale à Lausanne [224].

247. Towards the Construction of a Complete Cyclic Water Decomposition System, Design and Operation of an Oxygen Producing Half Cell

by Kuppaswamy Kalyanasundaram, Olga Mitik, Edmondo Pramauro and Michael Grätzel

Institut de Chimie-Physique, Ecole Polytechnique Fédérale, CH-1005 Lausanne

(3.IX.79)

Summary

Oxygen is generated when aqueous solution of iron(III) tris(2, 2'-bipyridyl), $Fe(bipy)_3^{3+}$, are brought in contact with catalytic amounts of powdered or colloidal RuO_2 . The oxygen yield depends strongly on the pH, reaching a maximum between pH 7 and 8 where it corresponds to the stoichiometry of the reaction:



The rate of the reaction is so fast that it occurs practically upon dissolution of $Fe(bipy)_3^{3+}$ in the aqueous phase. In acidic media (pH 4), no O_2 evolution is observed. Instead, $Fe(bipy)_3^{3+}$ is converted to an intermediate which in the presence of RuO_2 yields O_2 upon neutralization.

The pH profile of the O_2 evolution occurring upon illumination of $Ru(bipy)_3^{2+}$ in the presence of the cobalt complex $[Co(NH_3)_5Cl]^{2+}$ was also investigated.

The surprisingly low energy losses (160 mV) in reaction (1) makes the construction of four quanta water splitting systems feasible.

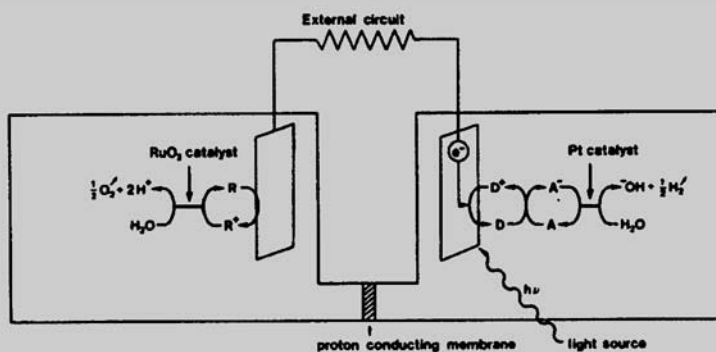
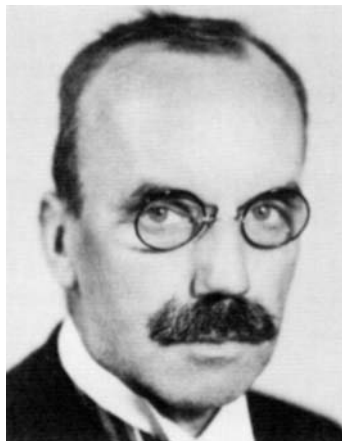


Fig. 1. Cell device for cyclic water decomposition by visible light (see text for explanation)

3. Theoretical Chemistry and Quantum Chemistry. – Traditionally, the birthdate of Quantum Chemistry is given as 1927, the year in which were published *Oyvind Burrau's* solution of the *Schrödinger* equation for the ground state of the hydrogen molecule ion H_2^+ [225] and the treatment of the electron-pair bond of the hydrogen molecule H_2 by *Walter Heitler* and *Fritz London* [226]. However, if one wants to put the accent on 'Chemistry', quantum chemistry got its start in the early 1930s, mainly through the work of *Linus Pauling* [227] and of *Erich Hückel* [228]. Later, important steps in making quantum chemistry a useful tool for the practicing chemist were a five-part publication by *Michael J.S. Dewar* in 1952 [229], the formulation of the *Woodward-Hoffmann* rules in 1965 [125], and the availability of semi-empirical and *ab initio* procedures in computer-ready form, due to a large extent to *M. J. S. Dewar* and to *John Pople* [230].

As far as *HCA* is concerned, the first quantum-chemical contribution appeared as late as 1948, in the form of *Hans Kuhn's* proposal of the 'electron-in-a-box model' for cyanine dyestuffs [231], to which we shall come back later. Of course, the electronic structure of molecules and its relevance to their properties had been discussed before in *HCA*, albeit on a purely qualitative level, and without (explicit) use of quantum mechanics.

Already the first volume of *HCA* contains two papers [232] that qualify as 'Theoretical Chemistry'. They are due to *August Leonhard Bernoulli* (1879–1939)²⁸) [8], professor



August Leonhard Bernoulli (1879–1939)

²⁸) *August Leonhard Bernoulli*, born in 1879 in Basle, first studied Chemistry at the University of Basle before moving to the University of Munich, where he devoted himself mainly to physics. He did his doctoral work with *W. C. Röntgen*, and obtained his Ph. D. in Physics in 1903. After a short stay at the University of Bonn, he became, in 1907, 'Privatdozent' for Physics at the Technische Hochschule Aachen. In 1912, he came to the University of Basle, first as a.o. Professor of Physical Chemistry, and then, from 1917 on, as o. Professor. He assumed the directorship of the newly founded 'Physikalisch-chemische Anstalt' in 1920, the same year in which the official chair in Physical Chemistry was created. His early research concerned problems of Theoretical Physics, but his work in Basle dealt, among other things, with optical and thermal properties of metals, reaction kinetics, thermodynamic properties of multiphase systems, and photochemistry. Another noteworthy contribution was the development of calorimeters for precision micro-calorimetry. *Bernoulli* died in Basle in 1939.

of Physical Chemistry of the University of Basle. These papers deal with a proposal to refine *Einstein's* formula for the specific heat of crystals, by linking its characteristic frequency to spectroscopically observed frequencies, *e.g.* those derived from IR spectra. In the second of the two papers, *Bernoulli* proposed to use such IR data, *e.g.* those obtained by *Rubens* for alkali halides, to calibrate the characteristic frequency of the *Nernst-Lindemann* formula for the specific heat of ionic crystals. Although, in retrospect, this work did not have the expected impact, it is noteworthy that it constitutes the first try to link observed optical data with the thermodynamic properties of a substance, a method which is now routinely used as a convenient means to compute thermodynamic data of molecules.

In a third contribution [233], *Bernoulli* described a procedure, aimed at calculating heats of formation on the basis of observed IR band positions. In the light of present-day knowledge, this is a rather curious publication. To obtain the desired results, *Bernoulli* had to make the following two assumptions: *a*) that the frequency of light emitted by an atom or a molecule is equal to the frequency of the 'periodic motion' (rotation) of its electrons, and *b*) that the forces acting on an electron or an atom within a molecule are equal, *i.e.* that the ratio ν_{el}/ν_{vib} of the frequencies of electronic transitions and vibrational frequencies equals the ratio $m_{atom}/m_{electron}$ of the atom and electron masses.

We mention in passing two papers by *H. Decker* [234], in which are derived simple formulae connecting the number of C- and H-atoms in hydrocarbons of different degree of unsaturation.

In 1928 and 1929, *Friedrich Ebel* and *Egon Bretscher* discussed the concept of 'Haftfestigkeit' (between two atoms and/or groups) in two publications [235] [236]. As mentioned in the introduction to their first paper (see *Fig. 80*, taken from [235]), the authors realized that this was a rather vague concept. The difficulty they faced (and which they could not resolve at the time) was that they lacked experimental information and a clear-cut definition which would have allowed them to discriminate between – what we now call – bond enthalpies, dissociation energies, and activation energies. The typical example for vastly different sizes of 'Haftfestigkeit', *e.g.* between two C-atoms, was 'hexaphenylethane' (which, as we now know, has a different formula from the one assumed in *Fig. 80*).

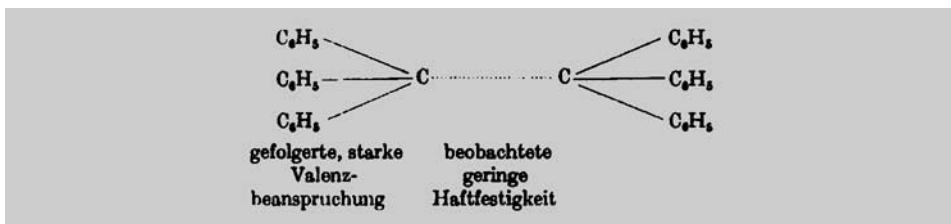
Über die Grundlagen der Haftfestigkeitslehre (I)

von **Friedrich Ebel** und **Egon Bretscher**.

(12. XII. 27.)

Haftfestigkeit ist kein scharf umrissener Begriff. Man schuf damit zunächst nur einen Ausdruck¹⁾ für die in der organischen Chemie oft beobachtete Tatsache, dass zwei in der Molekel verbundene Atome ihrer Trennung einen von Fall zu Fall wechselnden Widerstand entgegenzusetzen.

Fig. 80

Fig. 80
(cont.)

The arguments of *Ebel* and *Bretscher* were commented upon by *Gerold Schwarzenbach*²⁹⁾ [237] who made the important point – *cf. Fig. 81* – that one should distinguish between bond enthalpies and dissociation energies, the latter being mainly determined by the stability of the dissociation products.

Fig. 81

**Bemerkungen zur Arbeit von Fr. Ebel und E. Bretscher über
„Die wirksamen Bindungsfestigkeiten in mehratomigen Molekeln“**

von G. Schwarzenbach.

(5. VI. 29.)

Es ist mit keinerlei Schwierigkeiten verbunden, die C-C-Bindung des Hexaphenyl-
äthans als nahezu so stark anzusehen wie diejenige im Äthan selber. Wir müssen nur
annehmen, dass die Bindungsstärken der Phenylreste an den Methyl-Kohlenstoff im
freien Radikal viel fester sind als im assoziierten Ausgangsprodukt. Der Grund der
scheinbaren Lockerheit der Äthanbindung im Hexaphenyläthan liegt in der Stabilität
des Triphenylmethyls. Die drei Phenylreste des freien Radikals geben den freigelegten
Elektronen, welche zur Bindung der Reste dienen, eine Gelegenheit, anderweitig unter-
zukommen. Es bietet sich eine Möglichkeit der Bildung eines ganz neuen Systems.

Chemical Department, University College, London.

Two rather intriguing papers concerning the constitution of boron hydride B_2H_6 were published in 1928 by *Fritz Ephraim* [238] and in 1929 by *Egon Wiberg* [239]. *Fig. 82* shows the title and an excerpt from the discussion in *Ephraim's* paper [238], where a formula – based on the *Lewis-Kossel* octet theory – is proposed for B_2H_6 . This proposition has been commented upon and reformulated by *E. Wiberg* [239], as shown in *Fig. 83*. It is postulated that an electron pair can bond more than two atoms, *i.e.* that we could have a

Fig. 82

Über die Konstitution der Borwasserstoffe

von Fritz Ephraim.

(15. X. 28.)

²⁹⁾ For a portrait of *Schwarzenbach* and an appreciation of his work, see the review by *Venanzi* [16].

Der hypothetische Borwasserstoff BH_3 müsste ein Gebilde mit sechs Aussenelektronen sein, deren drei aus dem Boratom, drei von den drei Wasserstoffatomen stammen. Dieses Gebilde kann ebenso wenig beständig sein, wie ein einzelnes Sauerstoffatom, das ebenfalls sechs Aussenelektronen hat und sich daher, wie Fig. 1 zeigt, zur Molekel polymerisiert.

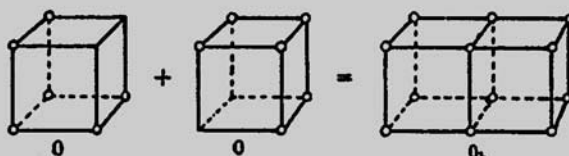


Fig. 1.

Im O_2 ist durch sog. Kovalenz von vier Elektronen ein Gebilde entstanden, das aus zwei vollkommenen Oktetten besteht. Ganz analog kann nun die Polymerisation des BH_3 zu B_2H_6 gedacht werden, wie Fig. 2 zeigt:

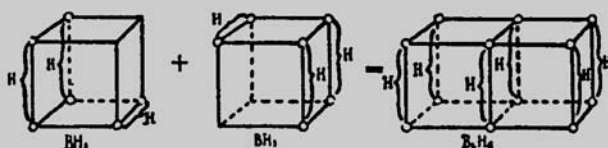


Fig. 2.

three-centre bond, as shown in *Ephraim's* formula. If the two central H-atoms in the latter had been placed up and down, instead of in the plane of the remaining four H-atoms, one would have predicted the correct structure of B_2H_6 already in 1929.

Probably the most important series of theoretical papers before the appearance of quantum chemistry in *HCA* are the investigations of resonance systems by *Schwarzenbach* and his coworkers. Fig. 84 shows the title of the first contribution [240] and a short excerpt which draws attention to the conceptual difficulties with which chemists not acquainted with the principles of quantum mechanics had to cope. Thus, resonance between 'limiting structures' is discussed in terms of a chemical equilibrium. (Note that *Schwarzenbach's* paper was published seven years after *Pauling's* seminal valence-bond publications, on which the qualitative resonance theory is based).

Notwithstanding such difficulties, a large body of observations could be rationalized and systematically compared. The following two papers of the series [241] report the preparation and investigation of substituted 'aniline sulfon-phthaleins' **26**, the absorption spectra of which have then been studied by *Schwarzenbach* in collaboration with *Hermann Mohler* and *Forster* [54], as already discussed in Sect. 1.1, cf. Fig. 10. A noteworthy feature of this work is that *Schwarzenbach's* treatment led him to expect a strong dependence of the spectral band pattern on the symmetry of the resonating π system of the molecule, and not on that of the σ frame in which it is embedded, or on differences in charge, an expectation fully confirmed by the experimental results.

Fig. 83

Über die Konstitution der Borwasserstoffe

(Bemerkung zu der Arbeit von Fritz Ephraim).

von Egon Wiberg.

(16. I. 29.)

Im Band 11, S. 1094 ff. dieser Zeitschrift veröffentlicht *F. Ephraim* eine Formel für das Diboran. Dieser Formel liegt die von mir zur Lösung des Borwasserstoffproblems vorgeschlagene Hypothese der Mehratombindung zugrunde, welche besagt, dass ein Elektronenpaar auch mehr als zwei Atomen gleichzeitig angehören kann¹⁾. In der von mir gewählten *Knorr'schen* Schreibweise haben unsere Diboranformeln folgendes Aussehen:

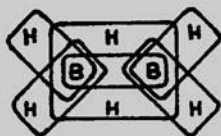


Fig. 1.

Formel von *Wiberg*

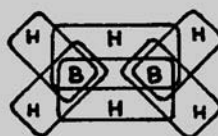


Fig. 2.

Formel von *Ephraim*

In der von *Ephraim* gewählten *Lewis'schen* Schreibweise werden sie durch folgende Bilder wiedergegeben:



Fig. 3.

Formel von *Wiberg*



Fig. 4.

Formel von *Ephraim*

Beide Formeln nehmen also an, dass die zwei Protonen, welche nach Anlagerung von vier Protonen an die vier freien Elektronenpaare der aus dem *Grimm'schen* Hydridverschiebungssatz hervorgehenden B_2 -Elektronenhülle verbleiben, zur Bindung ein Elektronenpaar benutzen, welches bereits zur Bindung zweier Boratome dient. Der Unterschied ist dabei der, dass nach meiner Formel beide Protonen ein- und dasselbe Elektronenpaar wählen, während nach der *Ephraim'schen* Formulierung, die übrigens bereits von *M. v. Stackelberg*²⁾ und in gewissem Sinne auch schon von *A. F. Core*³⁾ vorgeschlagen worden ist, jedes von ihnen gesondert ein solches Elektronenpaar beansprucht.

¹⁾ Z. anorg. Chem. 173, 199 (1928). Vergl. auch die Kritik von *E. Müller*, Z. anorg. Chem. 176, 205 (1928), sowie meine gleichzeitig mit vorliegender Bemerkung in der Zeitschrift für anorganische und allgemeine Chemie erscheinende Erwiderung.

²⁾ Z. El. Ch. 34, 443 (1928).

³⁾ J. Soc. chem. Ind. 46, 642 (1927). *Core* schreibt zwar: „Each of the inner hydrogen atoms shares one electron with one boron atom and one with the other boron atom“; aber die Bemerkung: „Both electrons of either of these hydrogen atoms are under the attractive influence of both boron nuclei“ zeigt, dass er der *Ephraim'schen* Auffassung sehr nahe steht.

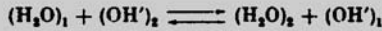
Fig. 84

66. Molekulare Resonanzsysteme. I. Allgemeines

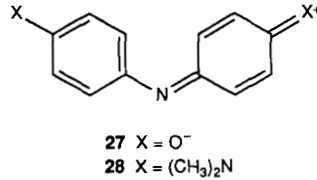
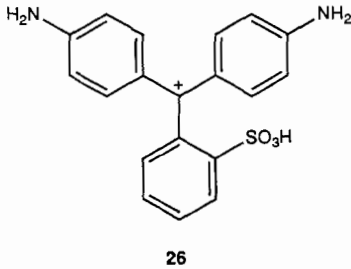
von G. Schwarzenbach, M. Brandenberger, G. H. Ott und O. Hagger.

(I. IV. 37.)

Die Resonanz ist als eine rasch verlaufende intramolekulare Reaktion aufzufassen. Genau wie etwa in einer wässrigen Lösung von Hydroxylionen ein ständiger Austausch von Protonen mit den Wassermolekeln stattfindet:



so findet innerhalb der Carboxylgruppe ein ständiger Austausch der reaktionsfähigen Doppelbindung statt ($I \rightleftharpoons I'$).



Further papers in this series deal with the UV/VIS spectra of phthaleins [242], of indophenols 27, and indamines 28 [243]. Finally, as shown in Fig. 85, a classification of

68. Die Absorptionsspektren der allereinfachsten „Farbstoffe“
von G. Schwarzenbach, K. Lutz und E. Felder.
(17. III. 44.)

Wir glauben nun, dass es zweckmässig ist, die Farbstoffe nach der Zahl ihrer gleichberechtigten Normalformeln einzuteilen, so dass wir die Zusammenstellung der Tabelle I erhalten. Zwischen den in dieser angeführten Grenztypen gibt es alle möglichen Übergänge. Bei den typischen Cyaninen sind die beiden Normalzustände a und b energetisch vollkommen gleichwertig. Lassen wir nun b gegenüber a langsam energiereicher werden, so werden wir langsam zum Polyentyp kommen, sobald b als stark angeregte Grenzstruktur zu betrachten sein wird.

Tabelle I.

Zahl der gleichberechtigten Grenzformeln	Typ
1 a	Polyen-Typ
2 $[X - \text{span style="display: inline-block; border: 1px solid black; border-radius: 10px; padding: 2px 10px;">a - X \leftrightarrow X - \text{span style="display: inline-block; border: 1px solid black; border-radius: 10px; padding: 2px 10px;">b - X]$	Cyanin-Typ
3 $[\begin{array}{ccc} X & X & X \\ & & \\ X = \text{span style="display: inline-block; border: 1px solid black; border-radius: 50%; padding: 2px 5px;">a - X & \leftrightarrow & X - \text{span style="display: inline-block; border: 1px solid black; border-radius: 50%; padding: 2px 5px;">b = X & \leftrightarrow & X - \text{span style="display: inline-block; border: 1px solid black; border-radius: 50%; padding: 2px 5px;">c = X \\ & & \\ X & X & X \end{array}]$	Fuchsin- und Auramin-Typ

the electronic spectra of the simplest chromophores was derived with reference to the number of equivalent resonance structures [244].

As mentioned at the beginning of this section, the first quantum chemical publication in *HCA* was, in 1948, *Hans Kuhn's* treatment of cyanine dyes, using the electron-in-a-box model [231]. (In the same volume of *HCA*, *Werner Kuhn* published a theoretical treatment of polyenes, to which we shall come back below.) *Hans Kuhn's* paper has already been discussed in some detail by *Zollinger* on pp. 1739 and 1740 of his review [22]. In this model, the linear π system of a cyanine dye, e.g. of the *Brooker* dye shown in *Fig. 86*, is approximated by a linear 'box' of length L containing the π electrons, where L is either equal to the distance between the terminal N-atoms, or includes a correction ΔL at both ends of the π system, to take care of the 'overshooting' of the π electrons. Depending on the former or latter choice of L , *Kuhn* obtained the theoretical values listed under Gl. (17) or Gl. (19) in the Table of *Fig. 86*. As can be seen, the corrected values agree almost perfectly with the observed band positions. In particular, the model accounted for the

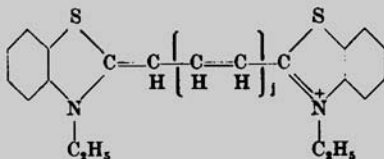
Fig. 86

**194. Elektronengasmodell zur quantitativen Deutung
der Lichtabsorption von organischen Farbstoffen I¹⁾**

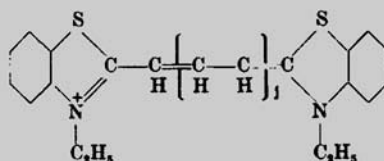
von **Hans Kuhn.**

(22. VI. 48.)

und



IIIa



IIIb

Cyanin IIIa, IIIb

Z	N	j	λ_1 (theor. nach Gl. (17)) Å	λ_1 (theor. nach Gl. (19)) Å	λ_1 (exp. nach <i>Brooker</i>) Å
5	6	0	3280	4050	4250
7	8	1	4530	5320	5550
9	10	2	5790	6570	6500
11	12	3	7060	7870	7600
13	14	4	8340	9160	8700 ¹⁾
15	16	5	9590	10 400	9950 ¹⁾

observation that the wavelength λ_{\max} of the first band in the cyanine-dye spectra is a linear function of the (corrected) length L of the π system: $\lambda_{\max} \propto L$.

The model was extended by *Hans Kuhn* to branched π systems, by introducing continuity conditions for the wave functions at the branch centres [245]. This meant that the partial free electron wave functions Ψ_j , valid within the segments j meeting at a branch center, must have the same value and the same slope at this point. As can be seen from

Fig. 87

292. Quantenmechanische Behandlung von Farbstoffen mit verzweigtem Elektronengas

von Hans Kuhn.

(1. IX. 49.)

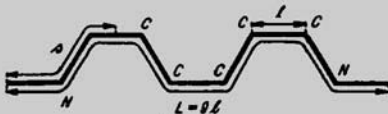


Fig. 1a.

Dipirydiviolet (Strukturformel II). Nicht verzweigtes Modell. Es wird angenommen, dass sich die neun π -Elektronen, welche den Atomen angehören, die in der Strukturformel II mit kräftigen Strichen verbunden sind, als eindimensionales Elektronengas entlang diesen Atomen ausbreiten.

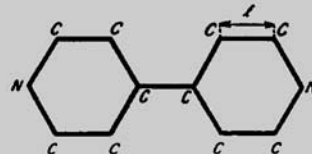


Fig. 1b.

Verzweigtes Modell. Sämtliche dreizehn π -Elektronen der Molekel breiten sich als eindimensionales Elektronengas entlang der angedeuteten verzweigten Bahn aus. Potentielle Energie entlang der gesamten Bahn konstant.

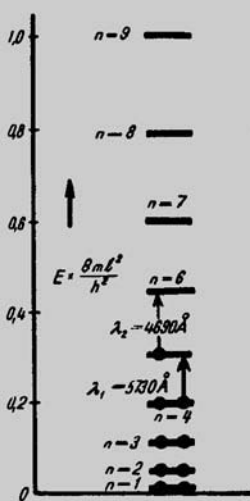


Fig. 2a.

Nicht verzweigtes Modell.

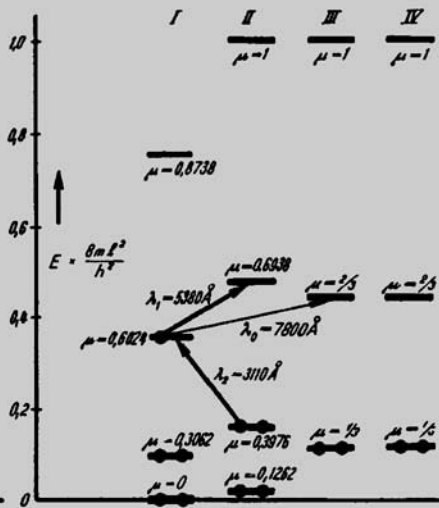
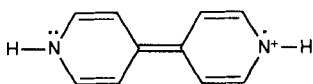


Fig. 2b.

Verzweigtes Modell.

Dipirydiviolet. Energieniveaus, in welchen sich ein π -Elektron des Elektronengases aufhalten kann.

Fig. 87 (taken from [245]) vastly different and much improved results are obtained by applying this model to *e.g.* dipyrindyl violet (**29**), as compared to those derived from the (unrealistic) linear model. (Slightly different branching conditions were later introduced by *K. Ruedenberg* [246], who re-investigated the model in great detail; see below.)



29

Fig. 88 is a typical example of *Hans Kuhn's* 'hands-on'-way to deal with theoretical problems. It concerns the 'experimental' determination of the size and direction of the transition moment, and thus of the intensity, associated with the electronic long-wave transition of a linear cyanine dye [247].

Fig. 88

158. Elektronengasmodell zur quantitativen Deutung der Lichtabsorption von organischen Farbstoffen II.

Teil A. Ermittlung der Intensität von Absorptionsbanden

von Hans Kuhn.

(21.V. 51)

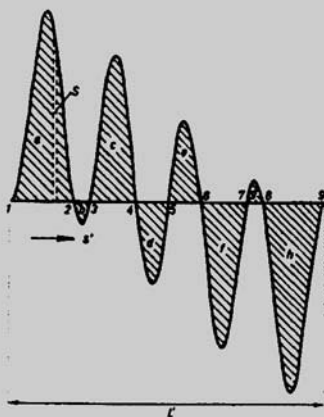


Fig. 6.

Kartonstücke a bis h, umgrenzt durch Abszissenachse s' und durch Kurve, die der Funktion $(\sin 4 \pi s'/L')$ $(\sin 5 \pi s'/L')$ entspricht.

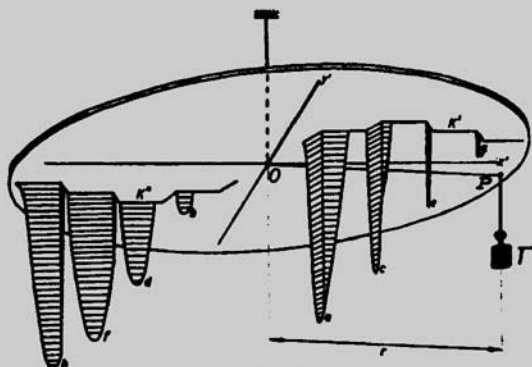


Fig. 7.

Scheibe mit aufgeklebten Kartonstücken a bis h (Fig. 6), in ihrem Mittelpunkt O an einem Faden aufgehängt. Das Gewicht Γ hält die Scheibe in horizontal schwebender Lage. Die Grösse des Gewichts Γ bestimmt die Intensität (den f-Wert) der Absorptionsbande. Die Richtung OP des Hebelarms des Gewichts Γ entspricht der Richtung des Übergangsmoments des Elektronensprungs.

A further refinement introduced by *Hans Kuhn* into the ‘electron-in-a-box’ model consisted in taking variations of the potential function into account *via* a perturbation treatment [248]. In the particular example shown in *Fig. 89*, the perturbation, due to the

291. Elektronengasmodell zur quantitativen Deutung der Lichtabsorption von organischen Farbstoffen II.

Teil B. Störung des Elektronengases durch Heteroatome¹⁾

von Hans Kuhn.

(13. X. 51.)

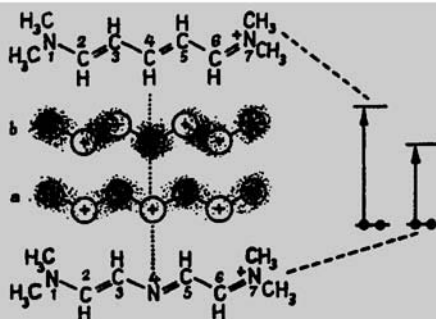


Fig. 2.

Symmetrisches Polymethin und Azaderivat, bei welchem die mittlere CH-Gruppe des Polymethins durch ein N-Atom ersetzt ist. Fall $j = 3$.

Ladungswolke des für die Absorption verantwortlichen Elektrons im Normalzustand (Wolke a) und im angeregten Zustand (Wolke b). Der Ersatz der CH-Gruppe durch ein N-Atom führt zu einer Stabilisierung des angeregten Zustandes (nicht aber des Normalzustandes) und daher zu einer Verschiebung des Absorptionsmaximums nach längeren Wellen.

replacement of the central C-atom by an N-atom, leads to a lowering of the LUMO, but leaves the HOMO invariant, the latter orbital having a node at the centre of replacement. As a result, one expects a bathochromic shift of the absorption band corresponding to the HOMO-LUMO transition.

Nowadays, the major attraction of the free-electron model are its didactic potentialities. Apart from allowing to introduce most quantum-chemical concepts in a transparent fashion, as nicely demonstrated by *H.-D. Försterling* and *H. Kuhn* in their book on Physical Chemistry [249], the wave functions derived from the model yield sometimes useful trial approximations for the solutions of the *Schrödinger* equation, if the lengths L_x , L_y , and L_z of the box are used as adjustable parameters within a variational treatment [250]. Otherwise – with a few exceptions – the model is now obsolete, and this for mainly three reasons: *a*) it was tailor-made for analogue rather than digital computers; *b*) introducing electron-electron interaction, as has been tried by *Labhart* [251] and by *Ruedenberg* [246], needs either unrealistic *ad hoc* assumptions, or leads to involved computations; *c*) it has been shown by *Ruedenberg* that the free-electron model of branched π systems is completely equivalent to the *Hückel* treatment [246], which is very much easier to handle.

We mention briefly the description, by *Labhart* [252], of a purely mechanical device for solving the *Schrödinger* equation for the ‘electron-in-a-box’ model.

In the same volume of *HCA*, in which *Hans Kuhn* introduced the ‘electron-in-a-box’ model for cyanine dyes, *Werner Kuhn* presented a model [253] (*cf. Fig. 90*), aimed at explaining the electronic spectra of linear polyenes, which had been recorded by *Richard Kuhn*³⁰) and his coworkers [35] [37]. The model is a semi-classical one, consisting, for a polyene with n double bonds, of n coupled oscillators (‘Ersatzresonatoren’). The computation leads to a secular determinant, shown in *Fig. 90*, which is formally equivalent to that obtained from a *Hückel*-type treatment using two-centre π orbitals as basis functions.

Fig. 90

236. Über das Absorptionsspektrum der Polyene¹⁾

von **Werner Kuhn.**

(3. IX. 48.)

$$\begin{vmatrix}
 k_0 - \varkappa_1 & k' & 0 & 0 & \dots & 0 \\
 k' & k_0 - \varkappa_1 & k' & 0 & \dots & 0 \\
 0 & k' & k_0 - \varkappa_1 & k' & \dots & 0 \\
 \dots & \dots & \dots & \dots & \dots & \dots \\
 0 & 0 & 0 & 0 & k' & k_0 - \varkappa_1 & k' \\
 & & & & & k' & k_0 - \varkappa_1
 \end{vmatrix} = 0 \quad (16)$$

The standard *Hückel* treatment appears in *HCA* for the first time in a paper by *Linus Pauling* [254] dealing with the stability of (*Z/E*)-isomerized polyenes (*cf. Fig. 91*).

³⁰⁾ *Richard Kuhn*, *Hans Kuhn*, and *Werner Kuhn* – the latter two working in the same Institute of Physical Chemistry of the University of Basle – are not related to each other.

291. Zur *cis-trans*-Isomerisierung von Carotinoiden

von Linus Pauling.

(16. VI. 49.)

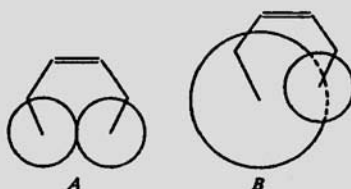


Fig. 1.

Schematische Darstellung der inneren sterischen Einwirkung von
 (A) $-\text{CH}-\text{CR}=\text{CR}'-\text{CH}-$ und
 (B) $-\text{C}(\text{CH}_3)-\text{CR}=\text{CR}'-\text{CH}-$ Gruppen auf die *cis*-Konfiguration an der Doppelbindung.

Um eine, in erster Annäherung richtige Voraussage betr. die Grössen zu machen, können wir die einfache molekular-orbitale Behandlung vornehmen¹⁾, die im vorliegenden Falle im wesentlichen zu den gleichen Ergebnissen führt, als die Wertigkeitsbindung-Behandlung²⁾). Es wurde von *Hückel*¹⁾ gezeigt, dass, wenn das Wechselintegral β für die einfachen Bindungen 2, 3 usw. den gleichen Wert besitzt wie für die Doppelbindungen 1, 2 usw., so beträgt die Resonanzenergie für ein linear konjugiertes System mit n Doppelbindungen und $n - 1$ einfachen Bindungen:

$$E_{\text{Resonanz}}(n) = 4\beta \left\{ \sum_{r=1}^n \cos \frac{\pi r}{2n+1} - n/2 \right\} \quad (1)$$

Beginning in 1949, *O. Klement*, professor of Physical Chemistry at the University of Fribourg, published a series of papers in which the standard valence bond treatment of hydrocarbon π systems, in the form originally introduced by *Pauling* and his group [227], has been applied to a number of aromatic molecules [255]. The method, involving the 'superposition' of canonical structures, was used to derive relative charge distributions in naphthalene [256], benzene, anthracene, and phenanthrene [257], but the results, obtained with restricted sets of basis functions – and before the availability of computing facilities – were of limited significance. The same procedure was used by *W. Heitler* – of *Heitler-London* fame [226] – to discuss the electronic structure of small hydrocarbons [258], in particular their 'Bindungsenergien'. Unfortunately, *Heitler*'s criticism of the well-tried additivity of bond increments for the estimation of enthalpies of formation is based on the confusion of such increments with bond dissociation energies.

Publications, in which the HMO technique was applied systematically for the study of aromatic hydrocarbons, in particular of non-alternant ones, began in 1952 with a discussion of the basic properties of azulenes [259], as reported in some detail by *Heimgartner*

and Hansen on pp. 415 and 416 of their review [41] (where a *Hückel* matrix is shown in Fig. 74). An amusing application concerned the azulene aldehyde lactarviolin, the structure of which was determined by a combination of spectroscopic measurements and HMO calculations [260], as summarized in Fig. 92. To our knowledge, this was the first time that the structure of a natural compound was elucidated by using quantum-chemical calculations.

Fig. 92

238. Zur Kenntnis der Sesquiterpene und Azulene.

113. Mitteilung¹⁾.

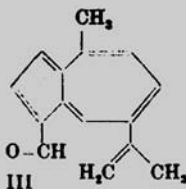
Azulenaldehyde und Azulenketone: Die Struktur des Lactarviolins²⁾

von E. Heilbronner und R. W. Schmid.

(2. X. 54.)

SUMMARY.

Using the LCAO-MO theory in its usual approximation, it is shown that the spectroscopic, polarographic and chemical evidence concerning the azulenealdehyde lactarviolin is only compatible with structure III. The correlation between the carbonyl stretching



frequency $\tilde{\nu}_{\text{CO}}$ and the characteristic half-wave potential $E_1^{(1)0}$ of aromatic aldehydes is discussed.

In the early 1950s, the only computing facility available at ETH-Zurich consisted of a Zuse Z4 computer – now at the Deutsches Museum in Munich – which worked with electric telephone relays, had a mechanical storage for 64 numbers (of which one was broken), and allowed only linear programs, with a single subroutine, which had to be punched on old movie films. To perform HMO calculations, it was, therefore, necessary to first compute the secular polynomials by hand. To this end, an algebraic method was developed [261], which yielded the polynomial for a large, composite system, starting from the polynomials of its components, as shown in Fig. 93.

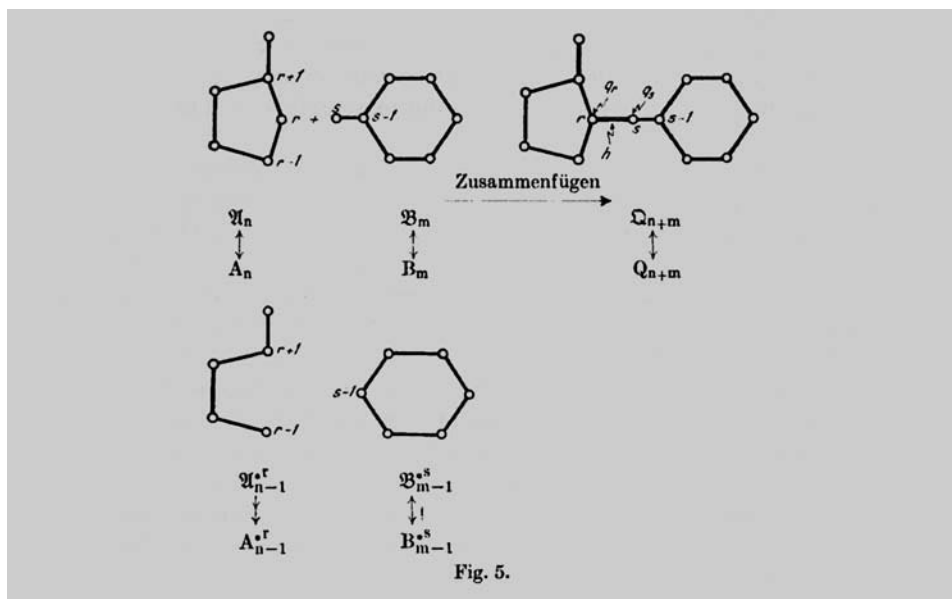
Fig. 93

24. Das Kompositions-Prinzip: Eine anschauliche Methode zur elektronen-theoretischen Behandlung nicht oder niedrig symmetrischer Molekeln im Rahmen der MO-Theorie

von E. Heilbronner.

(10. XII. 52.)

Fig. 93
(cont.)



In a similar vein, and for the same reasons, graphical methods were proposed for the factorization of secular determinants [262] and for the calculation of large systems consisting of repeating units [263]. In some special cases, the latter method allowed to obtain the eigenvalues of the *Hückel* determinant, *i.e.* the orbital energies, in closed form.

In 1956, it was shown by *Günthard* and *Primas* [264] that the results of the standard HMO treatment, *i.e.* using only the *Coulomb* integral α and the resonance integral β as adjustable parameters, were purely topological in nature (see *Fig. 94*). Linking the results of such a HMO calculation to the properties of the graph representing the connectivity of the π system, in particular to its adjacency matrix, opened the way for the large number of graph-theoretical investigations of molecules that have appeared since.

Fig. 94

197. Zusammenhang von Graphentheorie und MO-Theorie von Molekeln mit Systemen konjugierter Bindungen

von Hs. H. Günthard und H. Primas.

(28. VII. 56.)

Relations between the simple form of MO-theory (two parameter theory) and the theory of spectra of graphs are investigated. By the use of some theorems of graph theory it is shown that the spectra of energy eigenvalues given by the simple MO-theory are determined besides of scale factors by the topology of the conjugated systems. Furthermore bond orders and charge orders are completely determined by the topology. A procedure for the calculation of the characteristic polynomial and the characteristic vectors directly from the graph is given.

Taking advantage of the symmetry properties of a molecule leads to a considerable simplification of quantum-chemical calculations. In a series of three communications, it was shown how symmetry-adapted linear combinations of s-type [265] or p-type [266] atomic orbitals can be formed, using the irreducible representations of the point group in matrix form.

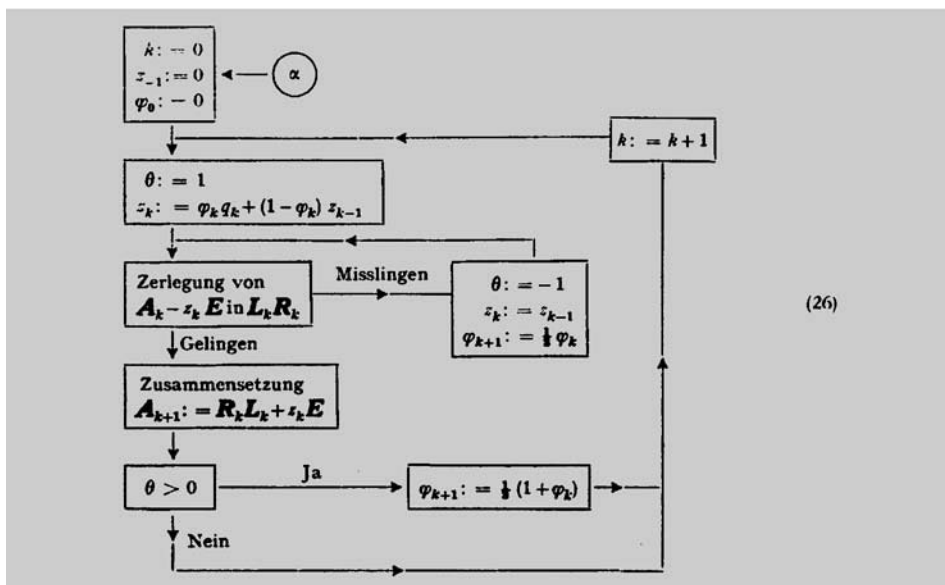
A quite general problem in quantum chemistry consists in solving the *Schrödinger* equation for the movement of a particle, e.g. an electron, in a one-dimensional potential $V(x)$. In 1956, the authors, in collaboration with *Raymond Gerdil* [267], proposed a variational method for the particular case that $V(x)$ is given as a polynomial of degree n . It consists of writing the wave function as a linear combination of $N \gg n$ harmonic oscillator eigenfunctions. The advantage of this procedure is that the matrix elements can be given in closed form, i.e. perfectly adapted for computer generation. The disadvantage was that N must be rather large to ensure a good approximation. It was a lucky coincidence that *Heinz Rutishauser* of the Institute for Applied Mathematics of the ETH, one of the fathers of the programming language ALGOL – which later became PASCAL – and one of the foremost applied mathematicians of his time, had invented the so-called **LR**-algorithm [268] for obtaining the eigenvalues and eigenfunctions of band-matrices, such as those arising in the above problem. This provided *HCA* with its first computer flow-chart, shown in *Fig. 95* [269].

Fig. 95

249. Verfahren zur programmgesteuerten Berechnung der Eigenwerte eindimensionaler Molekel-Modelle!

von E. Heilbronner, H. Rutishauser und F. Gerson

(4. VII. 59)



As an example for the application of this procedure, we reproduce in *Fig. 96* the results obtained by *Fabian Gerson* for a symmetric double-minimum potential [270].

We skip the many applications of simple independent electron models, such as the HMO treatment, to chemical, physico-chemical, and spectroscopic problems, to turn to the use of semi-empirical and *ab initio* calculations [230], which appeared in *HCA* after the corresponding computer programs became generally available. In almost all publications of this kind, such calculations are used only as a tool, the fundamental papers dealing with the development of the methods, and the programs having been published before in other (specialized) journals.

An extension of the HMO model to encompass both the σ and the π systems of a molecule is *Roald Hoffmann's* extended *Hückel* model (EHT) [271]. This was used, for

58. Der eindimensionale Oszillator 6^{ter} Potenz als Basis für ein symmetrisches Doppelminimum-Problem¹⁾

von F. Gerson

(18. I. 61)

Fig. 96

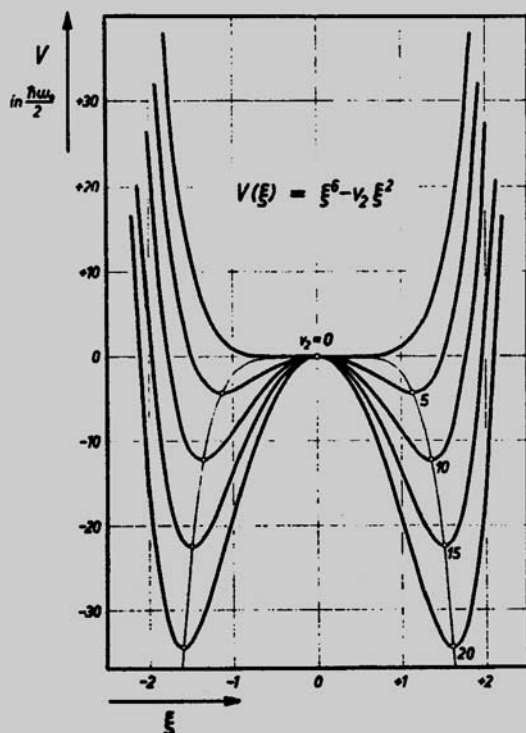
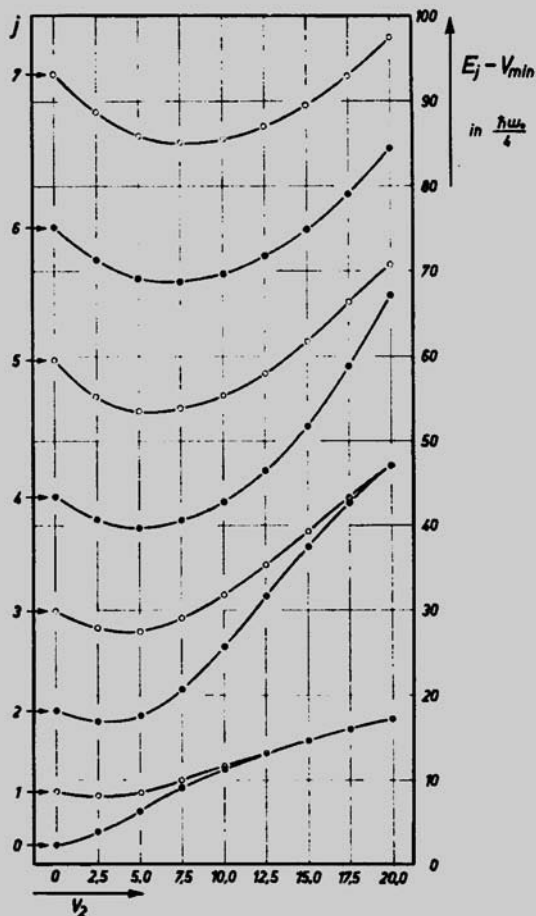


Fig. 1. Potentialkurven $V(\xi) = \xi^6 - v_2\xi^2$; $v_2 = 0, 5, 10, 15$ und 20
Potentialeinheit ist $\hbar\omega_0/2$

Fig. 96
(cont.)Fig. 2. Differenzen $E_j - V_{min}$ als Funktion von v_2
Energieeinheit ist $h\omega_0/4$

example, by Rolf Gleiter and Rolf Seeger to predict the structure of the ferrocenyl-methyl cation shown in Fig. 97 [272].

Fig. 97

124. The Structure of the Ferrocenyl-methyl Cation

Preliminary Communication¹⁾

by Rolf Gleiter and Rolf Seeger

Physikalisch-Chemisches Institut der Universität Basel

(11. III. 71)

Summary. Using a modified Extended Hückel (S.C.C.) procedure the structure of the ferrocenyl-methyl cation has been calculated. The result is a structure (V) with about equal overlap population between all Fe–C bonds. The methylene group is bent towards the iron atom and both rings are tilted.

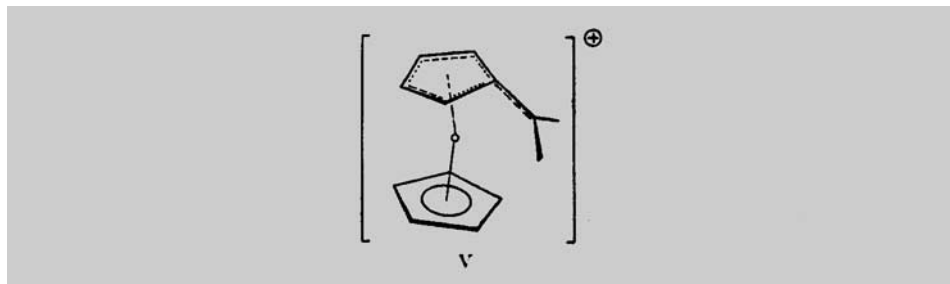


Fig. 97
(cont.)

The same procedure underlies the detailed discussion of the electronic mechanism of the *Grob* fragmentation, given by *Rolf Gleiter*, *Wolf-Dietrich Stohrer*, and *Roald Hoffmann* [273], from which we reproduce the correlation diagram in Fig. 98.

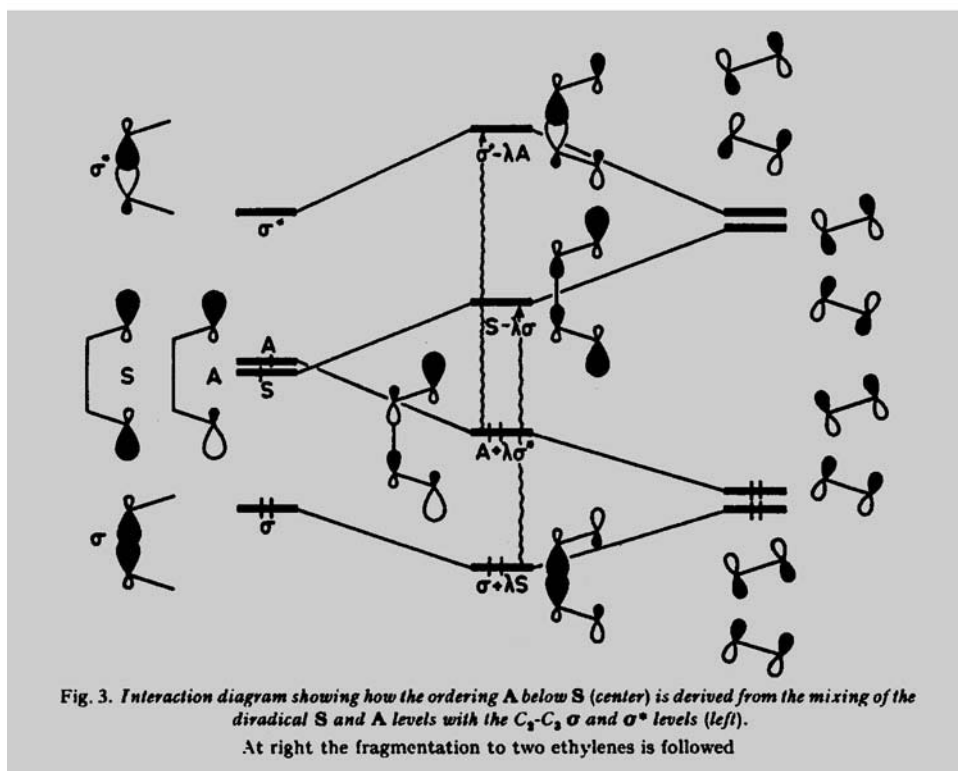
92. Orbital Theory of Heterolytic Fragmentation and Remote Effects on Nitrogen Inversion Equilibria

by *Rolf Gleiter*, *Wolf-Dieter Stohrer* and *Roald Hoffmann*

Department of Chemistry, Cornell University, Ithaca, N. Y.

(7. I. 72)

Fig. 98



Another, very successful semi-empirical procedure was the MINDO/2 procedure developed by *Michael J.S. Dewar* and *Edwin Haselbach* [274]. As an example, we present in *Fig. 99* the predicted structure of the 1,2-benzyne molecule, as obtained, according to the MINDO/2 procedure, by *Haselbach* [275]. (For further examples, see [276].)

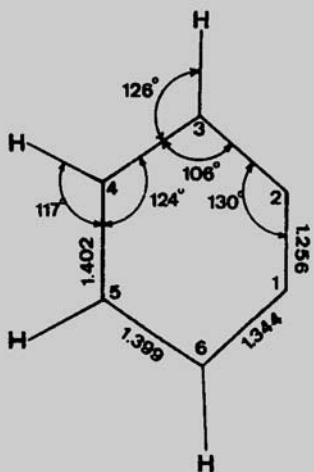
Fig. 99

211. Theoretical Study of the Structure and the Physico Chemical Properties of 1,2-Benzyne

by **E. Haselbach**

Physikalisch-Chemisches Institut der Universität Basel

(6. VII. 71)



Structural data of 1,2-benzyne

In this connection, a useful program, written by *E. Haselbach* and *A. Schmelzer* should be mentioned, which allows the transformation of computed orbitals into easily read graphical representations [277], such as those shown in *Fig. 100* for the interaction of the p orbital of a methylene group with the *Walsh* orbitals of a cyclopropyl moiety.

Fig. 100

132. Computer-Drawn Molecular Orbitals: An Aid for the Users of MO-programs

by **E. Haselbach** and **A. Schmelzer**

Physikalisch-Chemisches Institut der Universität Basel

(4. V. 71)

Summary. A computer program is described, which generates a simplified pictorial representation of computed molecular orbitals. As examples, the highest occupied MO's of the two C_4 -rotamers of the cyclopropylcarbinylcation ($C_4H_7^+$), of pyridine and of barrelene (bicyclo[2.2.2]octatriene) are given.

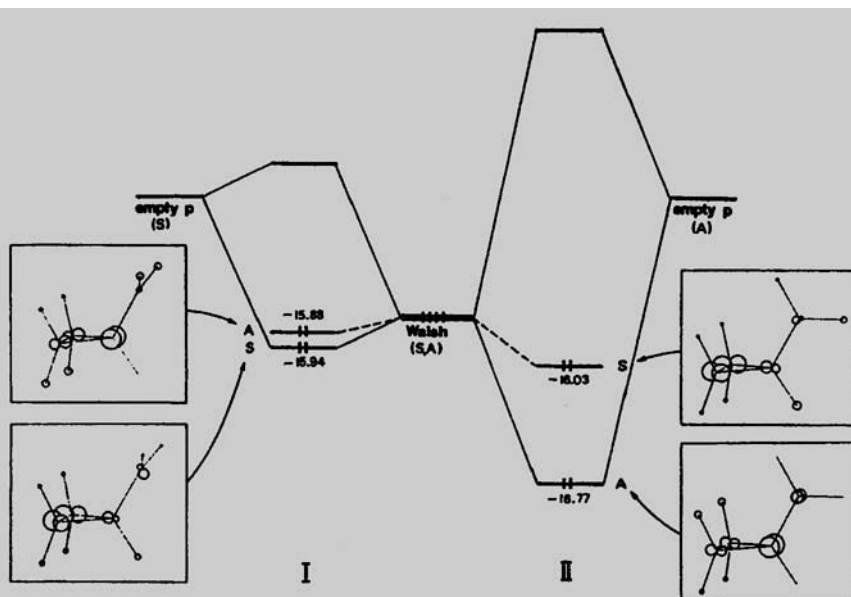


Fig. 1. Correlation diagram for the interaction of the p-orbital of a CH_2^+ -group with the Walsh orbitals of cyclopropane

Given are the computer drawn MO's and their orbital energies (in eV; obtained by MINDO/2 calculations)

The heuristically useful, albeit artificial dissection of orbital interactions into 'through-space' and 'through-bond' terms, as proposed by *Ronald Hoffmann* [128], has been re-examined within the framework of different semi-empirical methods, using localized molecular orbitals [278]. This provided insight into the built-in biases of the different methods.

After *W. Kuhn* and *R. Rometsch* had discussed different theoretical approaches for the interpretation of optical activity [279] (see also [75] and *Fig. 17*), semi-empirical methods were used to deal with this problem. Examples are the work by *Urs P. Wild* and his coworkers [280], and the treatment of optically active oligopeptides by *Georges Wagnière* and his group [281], shown in *Fig. 101*.

13. MO-Calculation of the Optical Activity of Oligopeptides.

II. Open-Chain Conformations.

Comparison with Some Cyclic Systems.

by *Max Iseli*, *Rudolf Geiger*¹⁾ and *Georges Wagnière*

Physikalisch-Chemisches Institut der Universität Zürich

Rämistrasse 76, CH-8001 Zürich

In Memory of Professor *Heinrich Labhart*

(14.XI.77)

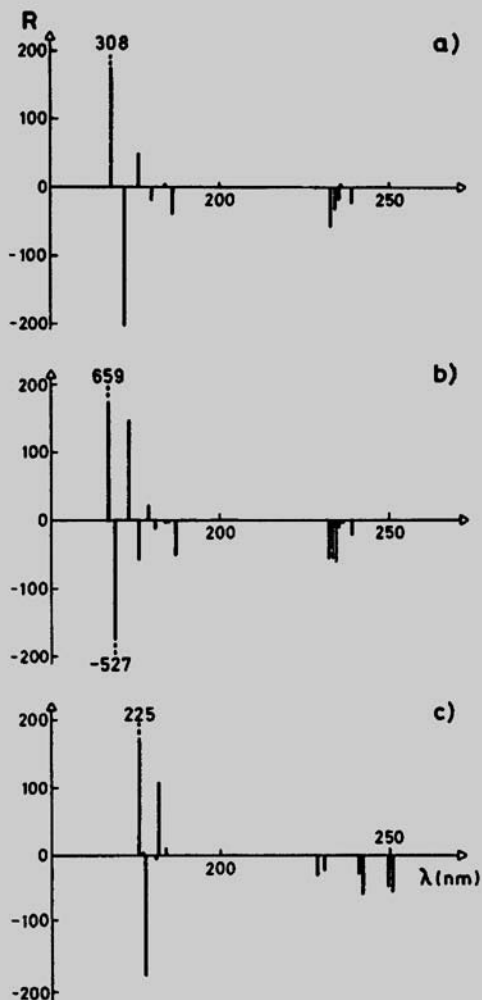
Fig. 101
(cont.)

Fig. 2. R : Computed rotatory strengths (in cgs units $\times 10^{40}$) for a) a hexamer in the PC pleated sheet conformation, with $\varphi = -119^\circ$, $\psi = 113^\circ$, $\omega = 180^\circ$; b) a nonamer in the PC pleated sheet conformation; c) a cyclohexamer in the conformation described by Table VII of [15]. Parameters are $\Lambda = 0.5$ eV for all amide groups, $I_n = 26.80$ eV. The transitions above 200 nm are $n-\pi^*$

To document the usefulness of semi-empirical methods for the interpretation of UV/VIS spectra, we mention the results obtained by *H. Baumann* and *J. F. M. Oth* for [18]annulene [282] (see also Fig. 44), and by *M. Gisin* and *J. Wirz* for conjugated biradicals in their lowest triplet state [283].

To conclude this section, we present some selected examples of the many applications of *ab initio* methods. Thus, *Martin Jungen* calculated the electronic reorganisation energies of radical cations in their *Koopmans'* states [284], which are of prime importance for the interpretation of the PE spectra of the corresponding molecules. A theoretical study

of complex formation has been published by *Tae-Kyu Ha*, *Urs P. Wild*, and their coworkers [285], of which we show an electron density difference plot in *Fig. 102*.

Ab initio methods have also proved useful for the study of the interaction of ionophores with cations, e.g. with Ca^{2+} or Mg^{2+} , as depicted in *Fig. 103*, taken from work by *Wilhelm Simon* in collaboration with *M. Wehrli*, *E. Pretsch*, and *E. Clementi* [286].

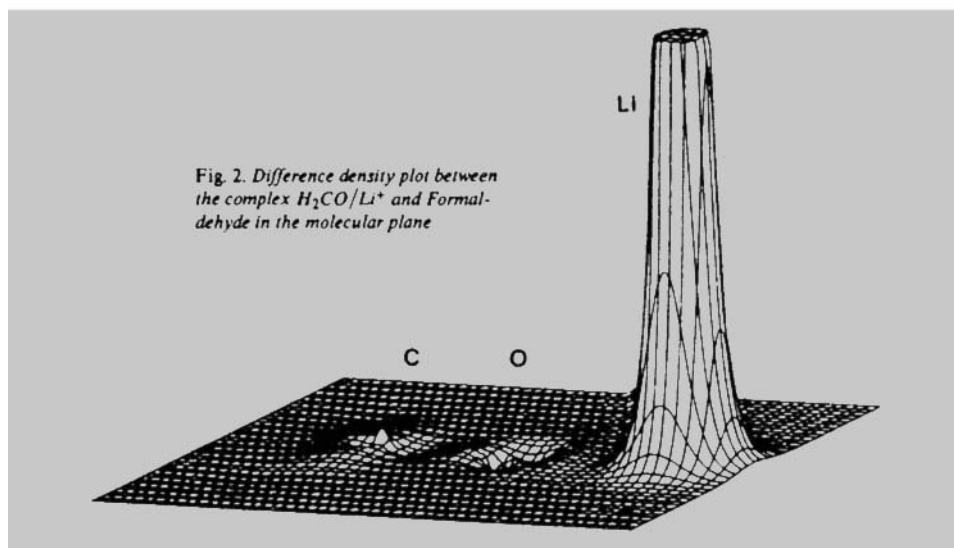
115. A Theoretical Study of Complex Formation between Formaldehyde and Lithium

by *Tae-Kyu Ha*, *Urs P. Wild*, *René O. Kühne*, *Charles Loesch*,
Thierry Schaffhauser, *Johanna Stachel* and *Alexander Wokaun*

Laboratory of Physical Chemistry, Swiss Federal Institute of Technology,
Zurich, Switzerland

(14. III. 78)

Fig. 102



197. Interaction of Ca^{2+} and Mg^{2+} with Ionophores Studied by Using a Pair-Potential Model Based on *Ab Initio* Calculations

by *Martin Wettli*, *Ernö Pretsch*, *Enrico Clementi*^{*)} and *Wilhelm Simon*

Laboratorium für Organische Chemie, Eidgenössische Technische Hochschule Zürich, CH-8092 Zürich

^{*)} IBM Data Processing, Product Group, Poughkeepsie, New York 12602, USA

(21. VII. 82)

Fig. 103

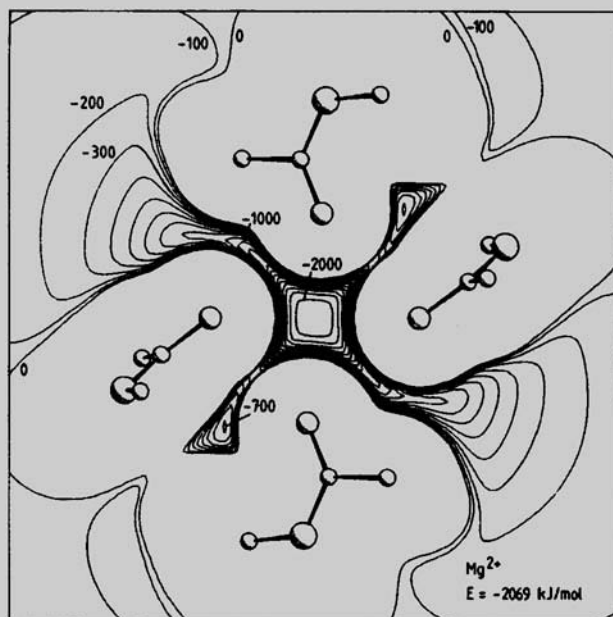
Fig. 103
(cont.)

Fig. 5. Isoenergy contour map for the interaction of six *N*-methylacetamide molecules in octahedral arrangement with Mg^{2+} (two molecules are not depicted). The arrangement of the ligands corresponds to the structure of the Mg^{2+} -complex of *N*-methylacetamide $[MgCl_2(C_3H_7ON)_6]$ [33] (see text). The net atomic charges calculated for a single *N*-methylacetamide molecule were used. The N-atoms were described by class 18. The plane of the diagram is defined by the four O-atoms (and the optimal location of the Mg^{2+} -ion). The contour-to-contour interval is 100 kJ mol^{-1} . The figure maps an area of 1200 pm^2 square.

Furthermore, such calculations serve as a sound basis for the derivation of reaction mechanisms, as exemplified by the investigation of hydrogen migration in metal complexes, due to *J. Silvestre* and *Roald Hoffmann* [287], from which *Fig. 104* has been taken.

Finally, the results of *ab initio* calculations are integrated routinely into organic-chemical work, sometimes in conjunction with semi-empirical ones, *e.g.* those published by *Hanspeter Huber* in collaboration with *M. Nikles*, *D. Bur*, and *U. Séquin* [288], shown in *Fig. 105*.

Fig. 104

154. Hydrogen Migration in Transition Metal Alkyne and Related Complexes

by Jérôme Silvestre and Roald Hoffmann*

Department of Chemistry and Materials Science Center, Cornell University, Ithaca, NY 14853

(23.V.85)

Fig. 104
(cont.)

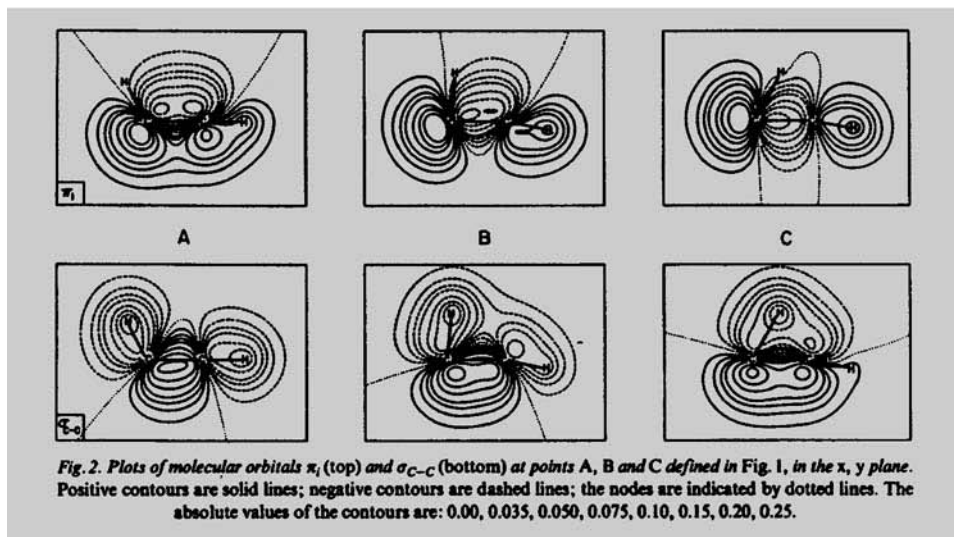
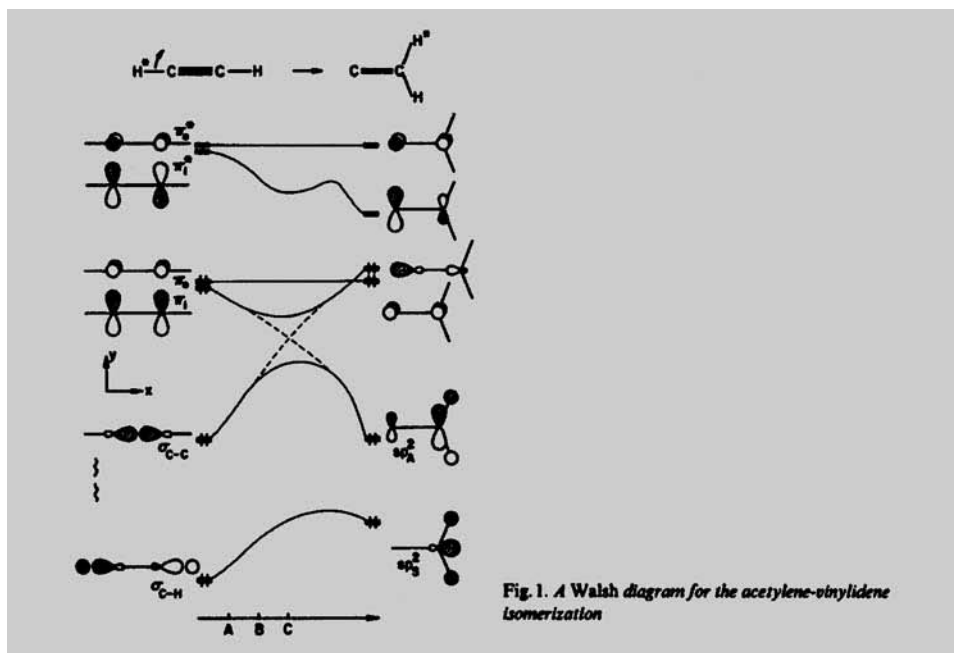


Fig. 105

127. Conformational Analysis of 1,2:3,4-Diepoxides: *Ab Initio* and Semiempirical Molecular-Orbital Calculations

by Martin Nikles¹⁾, Daniel Bur, and Urs Séquin*

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and Hanspeter Huber*

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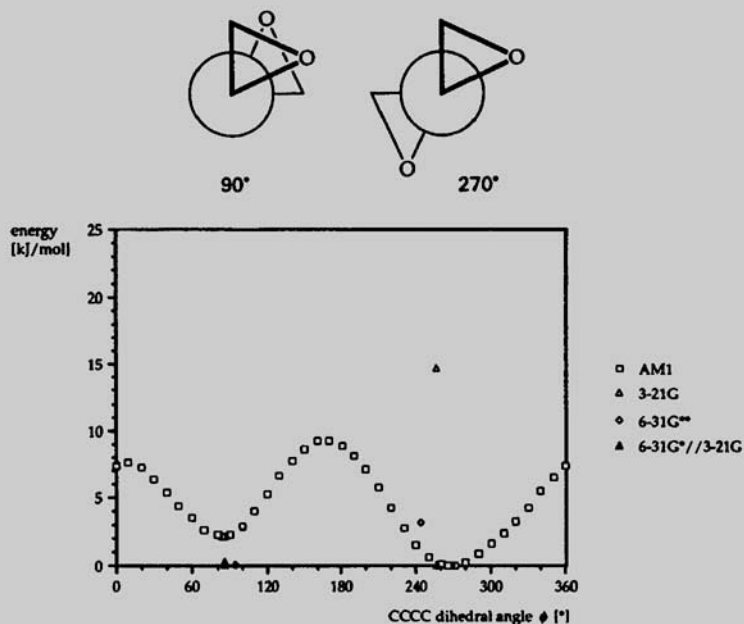


Fig. 1. Energy profiles of **3** as calculated by different methods. The points for 3-21G and 6-31G** show local minima on the profiles. Note that the point for 3-21G at 84° is nearly hidden by the one for 6-31G**//3-21G.

4. Thermodynamics, Kinetics, and Statistical Mechanics. – 4.1. Polymers and Micelles. Polymer chemistry, as documented by publications in *HCA*, is essentially tied to four names: *Hermann Staudinger*, *Kurt H. Meyer*, *Rudolf Signer*, and *Werner Kuhn*. Although the first two were organic chemists, mainly interested in the structure elucidation and the synthesis of polymeric compounds, they had to concern themselves – by necessity – with the physico-chemical properties of these materials. This resulted in important contributions to physical chemistry of polymers. On the other hand, both *R. Signer* and *W. Kuhn* were physical chemists, and their work, especially that of *Kuhn*, belongs to the highlights of Swiss Physical Chemistry.

In his publication ‘*Über Polymerisation*’ [289], which appeared in 1920, **Hermann Staudinger** (1881–1965)³¹⁾ coined the name ‘macromolecule’, which implied a radical departure from the then assumed structure of such molecules. An important tool in his investigations was the study of the relationship between the specific viscosity η_{sp} of solutions of macromolecules and their molecular mass M , that lead him to the following ‘Viskositätsgesetz’,

$$\eta_{sp}/(cM) = K_m \quad (6)$$

which was going to play a central role in his research on this class of compounds. In collaboration with *W. Heuer*, he applied the relationship (6) to solutions of paraffins, and obtained thereby an estimate of the constant $K_m \approx 3 \cdot 10^{-4}$ [290]. *Fig. 106* shows the title and the conclusion of a publication by *H. Staudinger* and *R. Nodzu*, [291], in which the

Fig. 106

Über Isopren und Kautschuk.
27. Mitteilung¹⁾.
**Über Beziehungen zwischen Viskosität und Molekulargewicht
bei Hydrokautschuken**
von **H. Staudinger** und **R. Nodzu.**
(25. X. 30.)

Da die Konstante K_m in der Poly-prenreihe den gleichen Wert wie in der Poly-prenreihe besitzt, so kommt man zu dem interessanten Ergebnis, dass für die Viskosität der Lösung von homöopolaren Molekelkolloiden wesentlich die Länge der Molekel eine Rolle spielt.

viscosity law (6) was applied to solutions of ‘Hydrokautschuk’, *i.e.* hydrogenated rubber, the molecules of which are homologous paraffins with methyl side chains.

Staudinger’s views about the geometry of such molecules is summarized in *Fig. 107*, taken from his 59th contribution to the field [292]. He assumed that the molecules were

Fig. 107

Hochpolymere Verbindungen
59. Mitteilung¹⁾.
Viskositätsgesetze bei hochpolymeren Verbindungen
von **H. Staudinger.**
(1. I. 1932.)

³¹⁾ *Hermann Staudinger* studied chemistry in Halle, where he obtained his Ph. D. in 1903. After having occupied the chair of Organic Chemistry at the University of Karlsruhe, he accepted, in 1912, to become the head of the Laboratorium für Organische Chemie at the ETH-Zurich, a post he occupied until 1926. He left Zurich for the University of Freiburg im Breisgau, where he founded the world-famous Institute of Macromolecular Chemistry. He retired in 1950 and died in 1965 in Freiburg. His seminal views on the structure of what we now call polymers earned him in 1953 the Nobel Prize in Chemistry, with the laudatio: ‘for his discoveries in the field of macromolecular chemistry’. *Staudinger*’s contributions towards the creation of *HCA* have been mentioned in a previous review [5].

Fig. 107
(cont.)

Folgende Tabelle II zeigt das Anwachsen des Eigenvolumens und des Wirkungsbereiches von Fadenmolekeln bei gleichbleibendem Durchmesser mit zunehmender Kettenlänge.

Tabelle II.

Länge = l	Fadenmolekeln vom Durchmesser d = 5 Å			
	Eigenvolumen einer Molekel = $\left(\frac{d}{2}\right)^2 \pi \times l$ in Å ³	Wirkungsbereich einer Molekel = $\left(\frac{l}{2}\right)^2 \pi \times d$ in Å ³	Zahl der Molekeln in 1 cm ³	
			ber. Eigenvolumen	ber. Wirkungsbereich
5 Å	10 ³	10 ³	10 ²²	10 ²²
50 Å	10 ³	10 ⁴	10 ²¹	10 ²⁰
500 Å	10 ⁴	10 ⁶	10 ²⁰	10 ¹⁸
5000 Å	10 ⁵	10 ⁸	10 ¹⁹	10 ¹⁶

Bei einer Fadenmolekel, die 1000mal länger als breit ist, ist also der Wirkungsbereich 1000mal grösser als ihr Eigenvolumen.

more or less linear, albeit undergoing bending motions, that their thickness was about $d = 5$ Å, and that their zone of influence – the ‘Wirkungsbereich’ – was equal to the volume generated, when the molecule rotates about a perpendicular axis through its midpoint. (The assumption of a rod-like structure of the macromolecules was successfully challenged by *Werner Kuhn*, as we shall see below.)

The general reluctance to accept the idea of a macromolecule – whatever its detailed shape – is nowadays difficult to understand. As told by *Robert Signer* [293]: After *Staudinger* had held his last public lecture in Zürich, before moving to the University of Freiburg, the famous ETH crystallographer *Paul Niggli* gave him the following advice: ‘*Herr Staudinger, wenn Sie Ihr Polystyrol genügend reinigen würden, würde es kristallisieren wie Naphthalin oder Benzoesäure.*’ And Nobel Prize winner *Heinrich Wieland*, who had attended *Staudinger*’s first lecture in Freiburg, slapped him afterwards on the shoulder and said: ‘*Mein lieber Staudinger, organische Moleküle mit mehr als 50 C-Atomen gibt es nicht.*’

At about the same time, *Kurt H. Meyer* (1883–1952)³² [294] investigated polymeric compounds at the University of Geneva, in particular cellulose, chitine, and rubber. In connection with this work, he became much interested in the physical properties of these materials. As examples, we quote in *Fig. 108* his analysis, in collaboration with *C. Ferri*, of the origins of the elasticity of rubber [295]. His conclusion were that the mechanism of rubber elasticity is entropy-controlled, and not due to bond-length or bond-angle changes, as had been assumed before.

^{32Kurt H. Meyer was born in Dorpath, Esthonia, in 1883. He studied chemistry, first at the University of Marburg, then at University College London. After having obtained his Ph.D. in 1907 under the direction of *Arthur Hantzsch* at the University of Leipzig, he moved to Munich, to work with *J.F.A. von Baeyer*, and to become a ‘Privatdozent’ in 1911. After the war, when *R. Willstätter* had succeeded *von Baeyer*, *K. H. Meyer* was nominated as a.o. Professor. After a stay, from 1921 to 1932 at the *Badische Anilin und Soda Fabrik*, Ludwigshafen, he accepted a call from the University of Geneva, where he occupied the chair of Organic Chemistry until his death in 1952.}

69. Sur l'élasticité du caoutchouc

par Kurt H. Meyer et Cesare Ferri.

(25. III. 35.)

Fig. 108

La nature du mécanisme de la contraction se traduit par l'équation (2):

$$-c = \left(\frac{dS}{dl} \right)_T$$

Cette équation exprime que l'entropie varie en sens opposé à la longueur. D'autre part l'expression:

$$S = R \ln w,$$

relie l'entropie à la probabilité thermodynamique w : lors de l'étirage nous obtenons un arrangement des molécules ou de leurs parties, arrangement de probabilité plus faible. En effet dans le caoutchouc amorphe toutes les positions sont permises aux différentes parties des molécules; les directions des valences C – C sont réparties d'une manière homogène sur toutes les directions de l'espace. *La déformation, suite de l'étirage, provoque une orientation des valences principales dans la direction de l'étirage, donc un arrangement qui comporte un nombre plus faible de réalisations. Lorsque la force extérieure cesse d'agir, les mouvements thermiques provoquent le retour à l'état initial chaotique, où toutes les positions sont réalisées. Cela entraîne nécessairement une contraction dans la direction d'étirage, si la texture empêche le glissement.*

Together with *A. van der Wyk*, he proposed a model for the structure of soap micelles [296], shown in *Fig. 109*. This particular publication is remarkable, because of the clear postulation of what was later called the 'hydrophobic' bond, *i.e.* that it is the high surface tension of the solvent water that keeps the micelles together.

163. Propriétés de polymères en solution VIII¹).

Formation de micelles dans les solutions de substances à molécules caténiformes

par Kurt H. Meyer et A. van der Wyk.

(6. IX. 37.)

Fig. 109

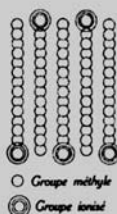
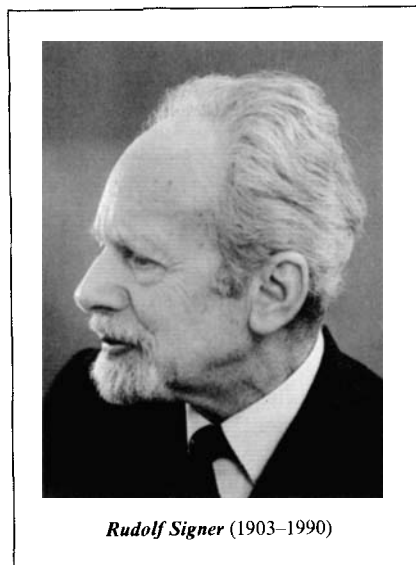


Fig. 1.



An outstanding figure in Swiss Polymer Chemistry was **Rudolf Signer** (1903–1990)³³⁾ [293] [297]. Although he occupied the chair of Organic Chemistry at the University of Berne, most of his work qualifies as physical chemistry, or organic-physical chemistry. It was strongly influenced by *Staudinger*, who held *Signer*'s many original contributions to polymer chemistry in high esteem, and who was also instrumental in directing him towards an academic position³⁴⁾.

Signer began his physico-chemical studies of polymers about 1930 with the investigation of their flow birefringence, an extension of earlier work by *Vorländer* on stearic and palmitic acid. In 1933, during his stay at *T. Svedberg*'s institute in Uppsala, he and his collaborator *H. Gross* carried out ultracentrifuge investigations, which resulted in three important publications. In the first one [298], he obtained the molecular masses of polystyrenes by measuring their sedimentation velocities, and in the second one, [299], by determining their sedimentation equilibria. The aim of this work was to prove the superiority of *Staudinger*'s empirical formula (δ) over those derived from theoretical

³³⁾ *Rudolf Signer* was born in Herisau in 1903 and went to school in St. Gallen. He studied chemistry at the ETH-Zurich, where he obtained his diploma in 1925. In 1928, he passed his doctorate examinations, after having worked under the direction of *H. Staudinger*, whom he followed to the University of Freiburg im Breisgau, where he became 'Privatdozent' in 1930. He spent some time with *W. L. Bragg* at the University of Manchester, and the year 1933 with *T. Svedberg* at the University of Uppsala. Both these stays had a strong influence on his further research, which turned mainly towards physical chemistry. In 1935, he accepted to become the successor of *Fritz Ephraim* at the University of Berne first as a.o. Professor, and then, in 1939, as Ordinarius and as director of the Institute of Organic Chemistry. He held this post for 37 years to retire in 1972. He died in Berne in 1990.

³⁴⁾ When, in 1935, *Signer* was offered simultaneously an industrial position at *Ciba* in Basle and a professorship at the University of Berne, he asked *Staudinger*'s advice, who told him: '*Wenn Sie Auto fahren wollen, sollten Sie nach Basel gehen, wenn es Ihnen aber nichts ausmacht, zu Fuss herumzulaufen, dann wählen Sie Bern*'. *Signer* chose to walk [293].

models, in particular that of *Werner Kuhn* (see below). *Fig. 110*, taken from [299], shows the comparison of η_{sp}/c derived from different formulae. Although *Signer* believed that his results supported *Staudinger's* views about a rod-like structure of macromolecules, it turned out later that they provided convincing evidence for *W. Kuhn's* proposal of a statistical coil.

35. Ultrazentrifugale Molekulargewichtsbestimmungen an synthetischen hochpolymeren Stoffen.

91. Mitteilung über hochpolymere Verbindungen¹⁾

von **R. Signer** und **H. Gross**¹⁾.

(8. II. 34.)

Fig. 110

Tabelle 4.

Beobachtete und nach verschiedenen Viskositätsformeln berechnete $\frac{\eta_{sp}}{c}$ -Werte.

Ultrazentrifugale Mol.-Gew.	Beobachtete $\frac{\eta_{sp}}{c}$ -Werte	Berechnete $\frac{\eta_{sp}}{c}$ -Werte nach			
		<i>Staudinger</i>	<i>Kuhn</i>	<i>Eisenschütz</i>	<i>Onsager</i>
30 000	2,7				
80 000	5,6	7,2	18	18	29
270 000	24	24	200	100	470
550 000	47	50	830	440	2 300
1 100 000	110	100	3300	1600	10 000

Signer's third publication, stemming from Uppsala [300], was devoted to the determination of the dispersion of molecular masses of polystyrenes, e.g. of a sample of mean molecular mass 80 000, as shown by the Table presented in *Fig. 111*.

Another of *Signer's* fields of research concerned the development of efficient methods for the purification of polymers, in particular of the counter-current distribution. These methods became of special importance, after his interest in nucleic acids had been stimulated, when *T. Casperson* and *E. Hammersten* asked him to measure the streaming birefringence of thymonucleic acid. This work resulted, in 1938, in the joint publication 'The Molecular Shape and Size of Thymonucleic Acid' [301], which *Signer* considered to be his most important publication [293]. Using his improved separation methods, he prepared in 1948, in collaboration with *H. Schwander*, highly purified nucleic acid, as shown in *Fig. 112* [302].

At a symposium, organized by *Ciba* in London, *Signer* presented the chairman, *J. A. V. Butler*, with 15 g of this material, which was then distributed to different institutions. One sample went to the University of Cambridge, England, where *F. H. C. Crick* and *J. Watson* used it for the structure determination of DNA [303].

76. Ultrazentrifugale Polydispersitätsbestimmungen an hochpolymeren Stoffen

95. Mitteilung über hochpolymere Verbindungen¹⁾

von **R. Signer** und **H. Gross**.

(4. V. 34.)

Fig. 111

Fig. 111

Tabelle 1.
Zusammensetzung des Poly-styrols vom Molgew. 80 000.

100 g enthalten:	
g	vom Molgew.
0,2	25—35 000
1,7	35—45 000
3,6	45—55 000
8,4	55—65 000
20,0	65—75 000
23,8	75—85 000
20,2	85—95 000
10,4	95—105 000
6,0	105—115 000
3,3	115—125 000
1,7	125—135 000
0,5	135—145 000
0,2	145—155 000

Fig. 112

109. Isolierung hochmolekularer Nucleinsäure aus Kalbsthymus von R. Signer und H. Schwander.

(5. XII. 48.)

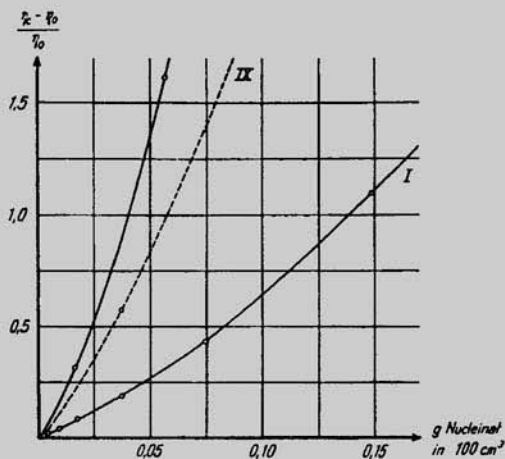


Fig. 2.

Spezifische Viskositäten von drei Natriumthymonucleinaten in Abhängigkeit der Konzentration. Kochsalzkonzentration 10 g in 100 cm³ Lösung.

Kurve I: Nucleinat von Hammarsten und Caspersson.

Kurve II: Höchstmolekulares Nucleinat von A. Knapp.

Höchstgelegene Kurve: Präparation wie in dieser Arbeit beschrieben.

Zusammenfassung.

Es wird eine Abänderung der bekannten Verfahren zur Isolierung von Desoxyribonucleinsäure angegeben. Die so hergestellten Präparate zeichnen sich durch hohes Molekulargewicht aus. Die Nucleinsäure wird gekennzeichnet durch Viskosität, Strömungsdoppelbrechung und Trübungsgrad verdünnter Lösungen und durch die Säure- und Basenbindung.

Fig. 112
(cont.)

To gain insight into the interactions between dissolved polymers, *e.g.* of polystyrene, and the solvent, the thermodynamic properties of model mixtures, such as those of ethylbenzene, toluene, and acetone, were studied in great detail [304].

Certainly, the most fundamental contributions to polymer chemistry published in *HCA* are those of **Werner Kuhn** (1899–1963)³⁵ [305] [306].

Werner Kuhn's fundamental publication, 'Über die Gestalt fadenförmiger Moleküle in Lösung' appeared in 1934 [307]. This and his ensuing theoretical and experimental investigations had a profound influence on polymer chemistry [308]. There is no doubt



Werner Kuhn (1899–1963)

³⁵) **Werner Kuhn** was born in Maur in 1899, went to school in Zurich, and began his studies of chemistry at the ETH-Zurich in 1917. After having obtained his diploma in 1921, he became assistant of *V. Henri* at the University of Zurich, and worked under his direction for his Ph. D. (1923). He then spent two years with *Niels Bohr* in Copenhagen, where he did his well known work on the sum rule of electronic transitions. After his return to Zurich, he became a 'Privatdozent' in 1927, but left the same year for Heidelberg, to work in the institute of *Karl Freudenberg*. It is there that his interest in optical activity was aroused, which led to his important theoretical contributions to the field (see *Sect. 1.1* [74] [75], *Fig. 17*, and *Chapt. 3* [279]). In 1930, he was made an a.o. Professor at the University of Karlsruhe, where he began his work on the structure of polymers. Finally, in 1939, he accepted the chair of Physical Chemistry and the directorship of the Physikalisch-chemische Anstalt at the University of Basle. He died in Basle in 1963.

that only his untimely death in 1963 prevented him from sharing the Nobel Prize with *Paul J. Flory* in 1974, the laudatio of which was: 'for fundamental achievements, both theoretical and experimental, in the physical chemistry of macromolecules'.

The assumption that macromolecules are randomly coiled systems was a radical departure from the prevailing assumptions, e.g. that of *H. Staudinger*. Together with *Franz Gr \ddot{u} n*, *Kuhn* derived the exact statistical parameters needed for the characterization of dissolved, coiled macromolecules [309], and from these, the expectation values for some of the observable properties of such solutions. His first publications in *HCA*, in collaboration with *Hans Kuhn* [310] (*Fig. 113*), deal with the change in overall shape of randomly coiled macromolecules in a flow gradient, i.e. with the dependence of viscosity and streaming birefringence on the velocity gradient of the streaming solvent. The theoretical predictions derived were fully confirmed by the experimental results published previously by *R. Signer* and *H. Gross*, as mentioned above [298].

The relevance of the model for understanding the inner viscosity and the resistance to change in shape of the coiled molecules, in particular the relaxation times for inner

Fig. 113

200. Bedeutung beschränkt freier Drehbarkeit für die Viskosität und Strömungsdoppelbrechung von Fadenmolekellösungen I

von **Werner Kuhn und Hans Kuhn.**

(20. X. 45.)

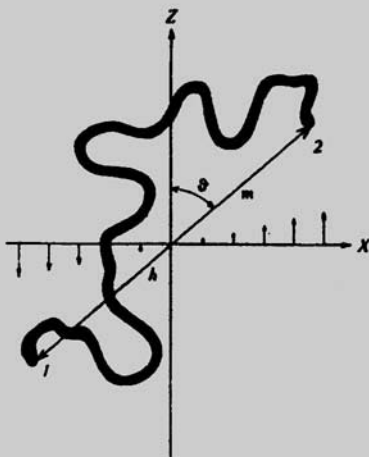


Fig. 2.

Fadenmolekel in Flüssigkeit mit Strömungsgefälle. Relativbewegung von Faden und Flüssigkeit, beobachtet von einem Koordinatensystem, dessen Ursprung im Schwerpunkt des Fadenmolekel (Mitte des Vektors h zwischen Anfangspunkt 1 und Endpunkt 2) liegt und welches die Translation des Schwerpunktes, jedoch nicht die Richtungsänderungen der Fadenachse mitmacht. Die Strömung erfolgt in der z -Richtung; das Strömungsgefälle liegt in der x -Richtung. Der Zustand der Molekel wird durch Betrag und Orientierung des Vektors m , welcher den Nullpunkt des Koordinatensystems mit dem Endpunkt 2 (Zustandspunkt) verbindet, gekennzeichnet.

motions, was discussed in detail by *W. Kuhn*, and *H. Kuhn* in two *HCA* papers [311], from one of which stems *Fig. 114*. As can be seen from the Table of rotational barriers – taken incidentally from *L. Pauling's 'Nature of the Chemical Bond'* –, *W. Kuhn* was among the first to take hindered rotation explicitly into account in his calculations concerning conformational changes.

Fig. 114

**82. Modellmässige Deutung der inneren Viskosität
(der Formzähigkeitskonstante) von Fadenmolekeln I**

von **Werner Kuhn** und **Hans Kuhn**.

(22. III. 46.)

Tabelle I.

Bindung	Molekel	q cal/Mol	θ_{μ}^* sec
C—C	CH ₃ —CH ₃	3000	$1,3 \times 10^{-9}$
C—N	Methylamin	3000	$1,3 \times 10^{-9}$
C—N	Dimethylamin	3500	$3,1 \times 10^{-9}$
C—O	CH ₃ OH	3000	$1,3 \times 10^{-9}$
C—CH ₃	CH ₃ —C≡C—CH ₃	500	$2,0 \times 10^{-11}$
C—CH ₃	CH ₃ —CO—CH ₃	1000	$4,7 \times 10^{-11}$
C—CH ₃	CH ₃ —CH=CH ₂	2100	$2,8 \times 10^{-10}$

In this connection, one of the major problems was to assess the functional relationship between the degree of coiling of the macromolecule and the viscosity of the permeating solvent. Eventually, this was solved using mechanical models, but most of the relevant papers were not published in *HCA* (for details, see [306]) except the work of *Peter Baertschi*, one of *W. Kuhn's* coworkers [312] (*cf. Fig. 115*). In these experiments, differently packed wire coils were dropped through a close fitting tube filled with a viscous liquid.

Further studies on macromolecules by *W. Kuhn*, *P. Moser*, and *H. Majer* concern the behavior of coiled macromolecules in an electric field [313]. It is shown that in such a field, these molecules assume a more extended shape. Such observations led to an investigation of the influence of 'chargeing' on the degree of coiling of a macromolecule, *e.g.* by deprotonating a polyacrylic or polymethacrylic acid. In collaboration with *O. Künzle* and with *Aharon Katchalsky* (later tragically killed by terrorists at Lod Airport, Tel Aviv), *W. Kuhn* could show that deprotonation uncoils the molecule to a completely extended

Fig. 115

**159. Durchströmungsversuche zur Untersuchung
der Struktur von Kautschuk-Gelen**

von **Peter Baertschi**.

(21. V. 51.)

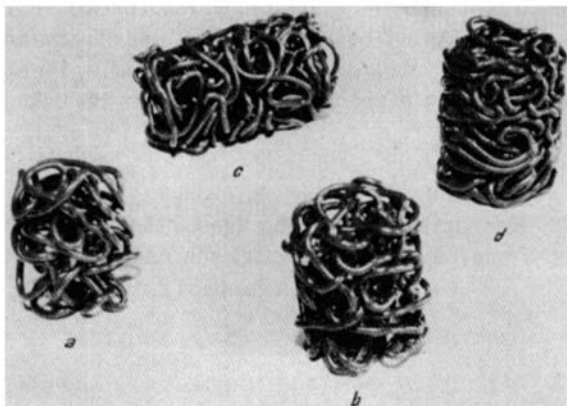
Fig. 115
(cont.)

Fig. 4.

Drahtmodelle

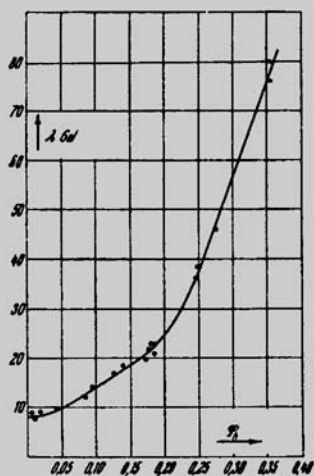
a) $\varphi_n = 0,09$; b) $\varphi_n = 0,17$; c) $\varphi_n = 0,25$; d) $\varphi_n = 0,36$.

Fig. 5.

Reibungswiderstand λ_{Gel} in Funktion der Packungsdichte φ_n für Pfropfen aus geknäueltem Draht.

structure, and that it resumes the coiled structure on reprotonation [314] (Fig. 116). This interesting behavior led later to the construction of 'synthetic muscles' [315].

Apart from an early suggestion by *K.H. Meyer* about the structure of micelles (see Fig. 109 [296]), all the work on such systems published in *HCA*, stems from the groups of

263. Verhalten polyvalenter Fadenmolekellonen in Lösung

von **W. Kuhn, O. Künzle und A. Katchalsky.**

(14. X. 48.)

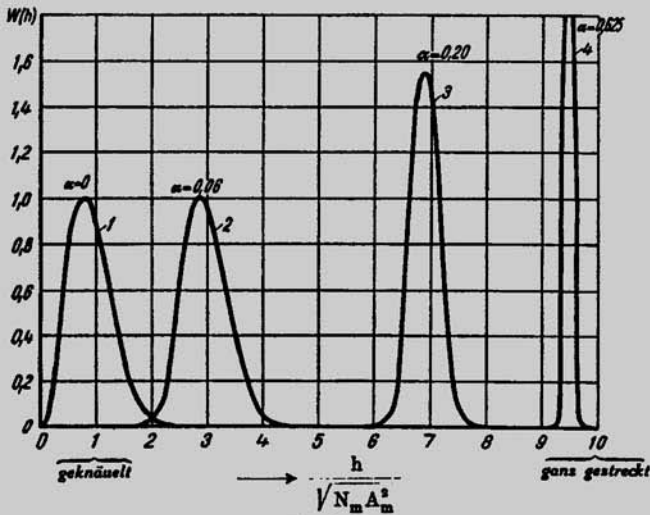


Fig. 3.

Verteilungsfunktion (berechnet) für Polymethacrylsäure vom Polymerisationsgrad $Z = 400$, $N_m = 100$, $A_m = 10^{-7}$ cm in Wasser. $W(h)$ als Ordinate gegen $h/\sqrt{N_m A_m^2}$ als Abszisse für verschiedene Ionisationsgrade α des Molekelfadens. Wiedergabe gemäss Gleichung (38). Für den völlig gestreckten Faden wäre $h = L = N_m A_m$, bzw. in unserm Beispiel $h/\sqrt{N_m A_m^2} = \sqrt{N_m} = 10$.

Kurve 1: ungeladene Molekel; $\alpha = 0$; $\nu = 0$; $\frac{U_{h-0}}{kT} = \frac{\nu^2 \epsilon^2}{D \sqrt{N_m A_m^2}} \frac{1}{kT} \sqrt{\frac{3\pi}{2}} = 0$.

Kurve 2: geladene Molekel; $\alpha = 0,063$; $\nu = 25$; $\frac{U_{h-0}}{kT} = 100$.

Kurve 3: geladene Molekel; $\alpha = 0,20$; $\nu = 80$; $\frac{U_{h-0}}{kT} = 1000$.

Kurve 4: geladene Molekel; $\alpha = 0,625$; $\nu = 250$; $\frac{U_{h-0}}{kT} = 10000$.

Man erkennt, dass die Lage des Maximums der Funktion $W(h)$ stark vom Ionisationsgrade abhängt; das Maximum ist in unserm Beispiel erreicht:

bei $\alpha = 0$	wenn $h = 8\%$	der Länge des gestreckten Fadens ist			
bei $\alpha = 0,0625$,	wenn $h = 28,5\%$	" " " " " "	"	"	"
bei $\alpha = 0,20$,	wenn $h = 69\%$	" " " " " "	"	"	"
bei $\alpha = 0,625$,	wenn $h = 95\%$	" " " " " "	"	"	"

Hans-Friedrich Eicke at the Institute of Physical Chemistry of the University of Basle. Fig. 117 is taken from an investigation by him and *J. Rehak* [316], in which it is shown that in tenside-containing liquid/liquid emulsions, a tenside molecule occupies a thermodynamically well defined surface under equilibrium conditions.

Fig. 117

306. On the Formation of Water/Oil-Microemulsions

by **Hans-Friedrich Eicke** and **Juraj Rehak**

Physikalisch-chemisches Institut der Universität Basel,
Klingelbergstrasse 80, CH-4056 Basel

(4. X. 76)

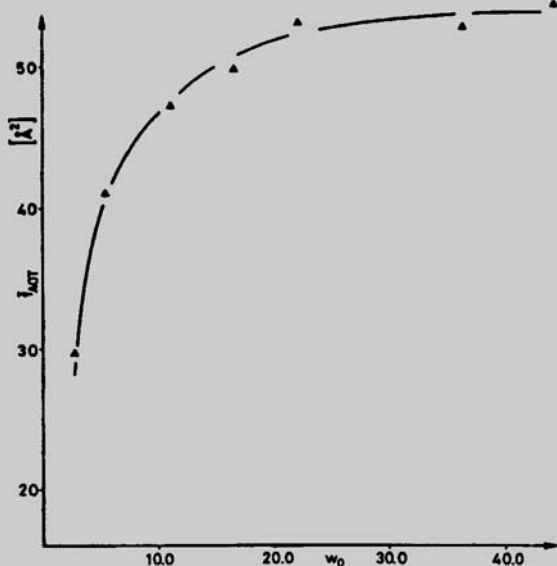


Fig. 2. Average surface fraction (\bar{i}_{AOT}) of the water/hydrocarbon interface covered by one surfactant molecule versus weighed-in amount of water $w_0 = [H_2O]/[AOT]$

We mention further the study of the percolation of nano-droplets in fluid mesophases, carried out by *H.-F. Eicke* in collaboration with *R. Hilfiker* and *M. Holz* [317], yielding important indications of the discrete nature of such droplets, which form fractal structures (Fig. 118).

More recent work by *H.-F. Eicke*, *R. Hilfiker*, and *Gu Xu* [318] is concerned with 'mesogels'.

42. Percolative Phenomena in Microemulsions of the ‘One-Component Macrofluid’ Type

by **Hans-Friedrich Eicke*** and **Rolf Hilfiker**

Institute of Physical Chemistry, University of Basel, Klingelbergstrasse 80, CH-4056 Basel

and **Manfred Holz**

Institute of Physical and Electrochemistry, University of Karlsruhe, Kaiserstrasse 12, D-7500 Karlsruhe

(13.XII.83)

Fig. 118

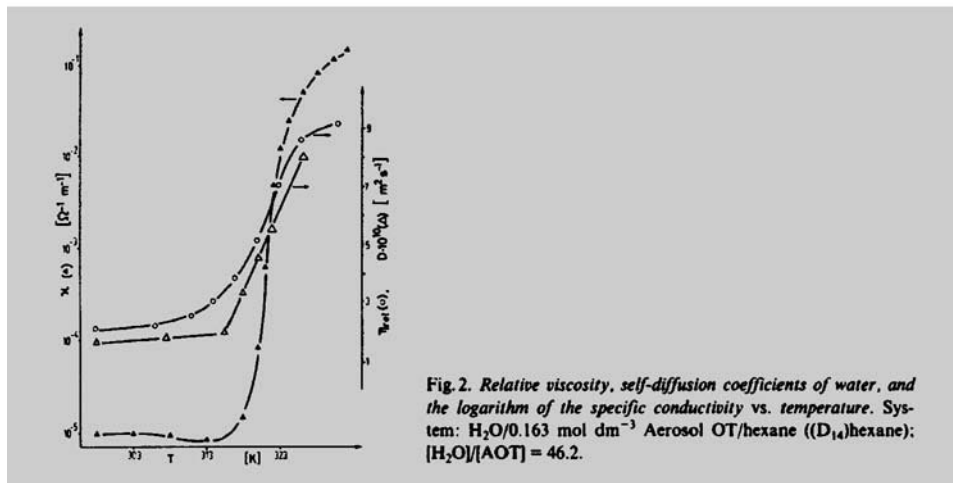


Fig. 2. Relative viscosity, self-diffusion coefficients of water, and the logarithm of the specific conductivity vs. temperature. System: $\text{H}_2\text{O}/0.163 \text{ mol dm}^{-3}$ Aerosol OT/hexane ((D_{14}) hexane); $[\text{H}_2\text{O}]/[\text{AOT}] = 46.2$.

4.2. Isotope Separation and Isotope Chemistry. The first report in *HCA* on isotope separation is due to *Hans Erlenmeyer* and *Hans Gärtner* of the Institute of Inorganic Chemistry of the University of Basle [319], who reported on the enrichment of D_2O during the electrolysis of aqueous sulfuric-acid solutions using lead electrodes (see Fig. 119). (On the other hand, examination of various biological liquids did not reveal any significant change in the $\text{H}_2\text{O}/\text{D}_2\text{O}$ ratio [320].)

Whereas the first electrolytic experiments yielded only enrichment factors of the same size as obtained a year earlier by *G. N. Lewis*, the two authors could report the preparation of 99 % pure D_2O a year later [321]. This made it possible to prepare and investigate

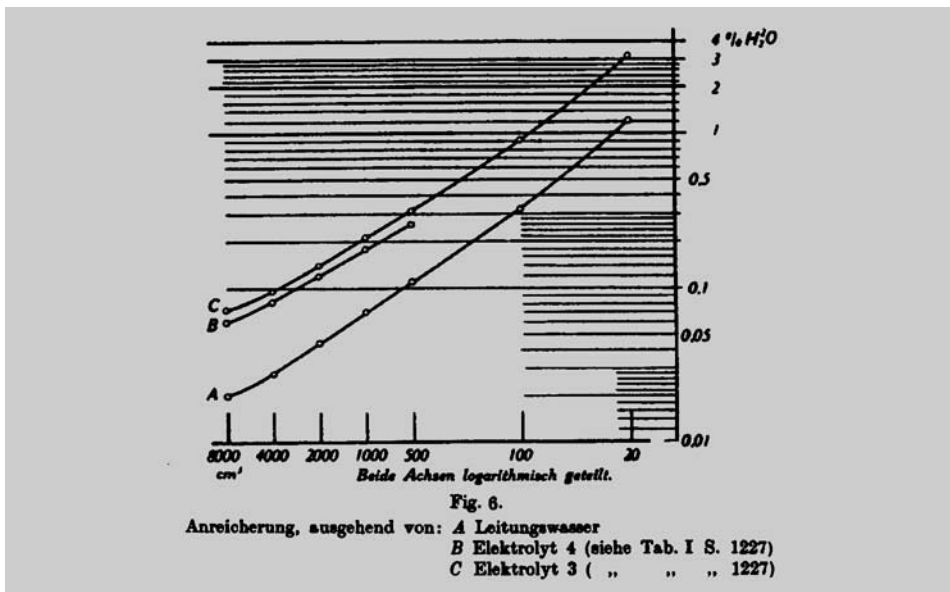
Fig. 119

137. Über eine Laboratoriumsanlage zur elektrolytischen Fraktionierung der Wasserstoffisotopen¹⁾

(II. Mitteilung²⁾)

von **H. Erlenmeyer** und **Hans Gärtner**.

(27. VIII. 34.)

Fig. 119
(cont.)

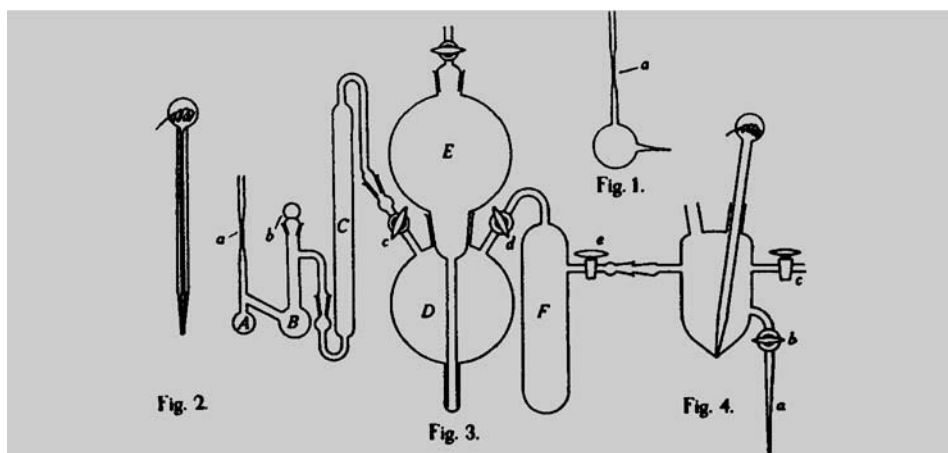
a series of deuterium-labeled molecules, in particular chiral molecules of the type CHDR'R' [322]. In collaboration with *A. Epprecht* and *G. Schwarzenbach*, *H. Erlenmeyer* investigated thermodynamic and kinetic isotope effects in deuterated compounds [323], using the experimental set-up shown in Fig. 120.

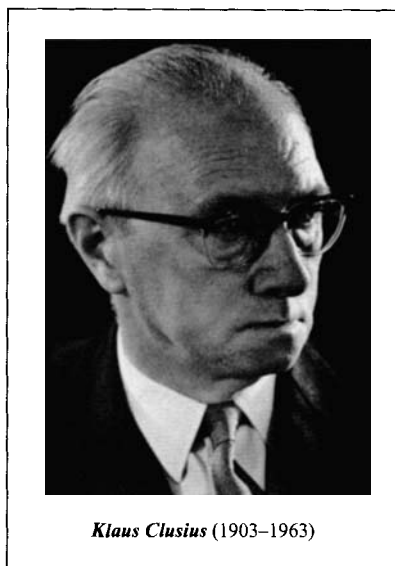
Fig. 120

**159. Über Dissoziationskonstanten in Wasser und Deuteriumoxyd.
 Messungen mit der Deuteriumelektrode**

von *G. Schwarzenbach*, *A. Epprecht* und *H. Erlenmeyer*.

(28. X. 36.)





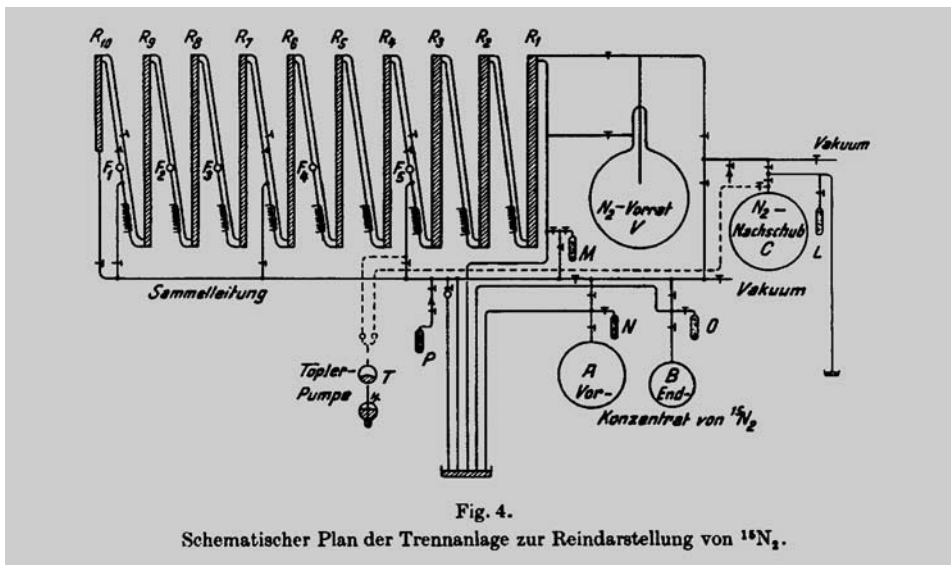
The most important work on isotope separation and isotope chemistry published in *HCA* stems from *Klaus Clusius* (1903–1963)³⁶⁾ [324] who had succeeded *H. von Halban* as Ordinarius of Physical Chemistry at the University of Zurich.

In 1938, *K. Clusius* and *G. Dickel* published their first paper on the ‘Trennröhr’, a device for the separation of isotopes and isotopomers by thermal diffusion in the gas phase [325]. *Fig. 121* shows the experimental set-up used in Zurich for the preparation of pure ¹⁵N, as described by *K. Clusius* in *HCA* in 1950 [326].

Fig. 121

268. Das Trennröhr.
IX. Reindarstellung des schweren Stickstoffs ¹⁵N¹⁾
 von **Klaus Clusius.**
 (20. X. 50.)

³⁶⁾ *Klaus Clusius* was born in 1903 in Breslau, where he studied chemistry at the Technische Hochschule. It was the influence of *Arnold Eucken* that turned him towards physical chemistry, and it was under *Eucken*’s direction that he worked for his Ph. D. He then spent some time with *C. N. Hinshelwood* at the University of Oxford, where he did work on chain reactions, and on the basis of which he became ‘Privatdozent’ for Physical Chemistry at the University of Göttingen in 1930. Shortly before moving to Göttingen, he had worked with *W. H. Keesom* at the Kammerling-Onnes Institute, to acquaint himself with low-temperature techniques, which were going to play an important role in his later research. In 1934, he was offered an a.o. professorship at the University of Würzburg, which he occupied for two years, before he accepted in 1936 an ‘Ordinariat’ in Munich. It is there that he made his most important invention, that of the ‘Trennröhr’, a device for the separation of isotopes by thermal diffusion. In 1947, he became the successor of *H. von Halban* at the University of Zurich. He died in Zurich in 1963, well before reaching retiring age.

Fig. 121
(cont.)

Beginning 1950, *K. Clusius, Ernst Schumacher* [327], and their coworkers reported the systematic application of the *Clusius-Dickel* method for the isolation of pure isotopes and isotopomers, e.g. of ^{15}N [326], ^{36}Ar , ^{38}Ar , cf. *Fig. 122*, [328], or ^{18}O [329]. In addition, the isotopically labeled compounds that became thus available were used in studies of reactions mechanisms, e.g. of ^{15}N -labeled molecules [330–332].

Clusius discussed also the isotope separation in technical processes, such as $^{12}\text{CH}_4$ / $^{13}\text{CH}_4$ [333], $^{14}\text{N}/^{15}\text{N}$ in the HNO_3 synthesis [334], or of the isotopomers of NO [335]. Finally, one should mention his investigations, together with *Ernst Schumacher*, of the influence of the hydrogen/deuterium ratio on laminar flames in air [336].

In 1942, *Werner Kuhn* and *K. Ryffel* had worked out a theory of fractional distillation [337]. Based on these results, a large precision distillation column was built in the Institute of Physical Chemistry in Basle [338] for the distillation of water, to allow the separation of

Fig. 122

124. Das Trennrohr.
XII. Reindarstellung des leichten Argonisotops ^{36}A und
Anreicherung des Argonisotops ^{38}A auf 90 % durch Hilfsgase¹⁾
von **Klaus Clusius** und **Ernst Schumacher**.

(13. V. 53.)

Tabelle 2.
Feintrennung von ^{36}A in Apparatur II.

Ver- such Nr.	Eingeführtes Argon und Arbeitsweise	Trenndauer	Hilfsgas	Menge	^{36}A -Konzentration
5	250 cm ³ mit 29% ^{36}A hier Zugabe von 97 cm ³ Argon mit 56% ^{36}A in der Mitte der Trennan- lage. (Während die- ses Versuchs wö- chentlicher Entzug von ^{40}A von der schweren Seite hor.)	nach 39 Tagen nach 51 Tagen nach 73 Tagen nach 85 Tagen	$\text{DCl} + \text{D}^{37}\text{Cl}$	30 cm ³ 23 cm ³ 57 cm ³ 32 cm ³	97,0% leichte Seite 0,8% schwere Seite 89,2% leichte Seite 96,1% leichte Seite 70,5% leichte Seite
6	Die drei Proben von Versuch 5 mit 90% ^{36}A und darüber, sowie leichtes Rest- gas mit 70% in der Anlage. (Nur sehr geringe ^{40}A -Mengen treten auf der schweren Seite wäh- rend des Versuchs auf.)	nach 30 Tagen nach 75 Tagen nach 111 Tagen	wenig D^{37}Cl mit ^{36}DCl und ^{36}HCl	18 cm ³ 50 cm ³ 50 cm ³ 6 cm ³	99,4% leichte Seite*) 99,4% leichte Seite 97,8% leichte Seite nicht gemessen

Bilanz der Versuche 5 und 6: Erhalten von 127 cm³ ^{36}A , die als Gas mit 29% bzw. 56% ^{36}A eingeführt wurden: 124 cm³ mit ~99% ^{36}A .

*) Enthielt Spuren leichter Edelgase.

the different isotopes of oxygen. In Fig. 123 is shown a scheme of this installation. It served as a prototype for commercial *Kuhn* columns built in Switzerland.

For obvious reasons, *Kuhn*'s group was much interested in the chemistry and physics of isotopically labeled compounds. Together with *Peter Baertschi*, *W. Kuhn* discussed the anomalous behavior of the vapor pressure of liquid isotopomers containing ^{13}C [339], and with *Max Thürkauf* the isotope effects in phase transitions [340]. *P. Baertschi* studied the fractionation of $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ during the assimilation process in certain plants, and

**127. Trennung und Konzentrationsverlauf
der Sauerstoffisotopen ^{16}O , ^{17}O und ^{18}O bei der Destillation von Wasser
in einer Präzisionsdestillationsanlage**

von *M. Thürkauf*, *A. Narten* und *Werner Kuhn*

(5. IV. 60)

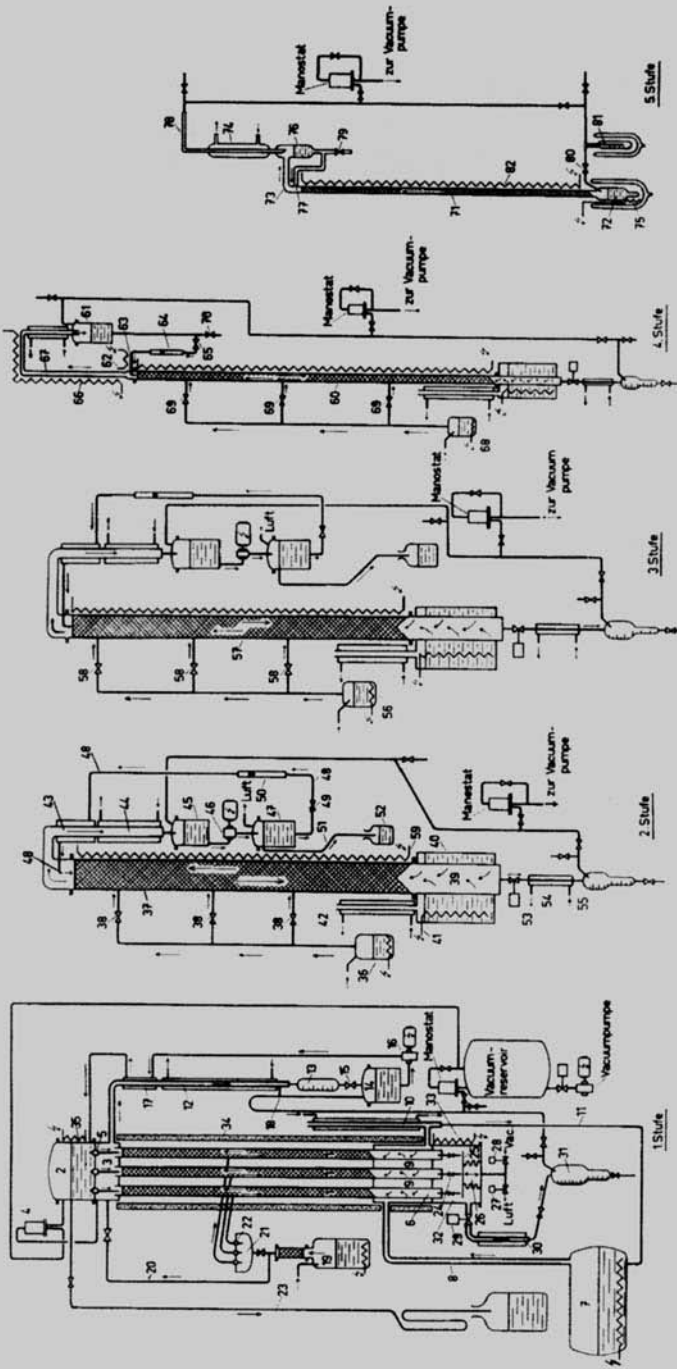
Fig. 123
(cont.)

Fig. 1. Schematische Darstellung der 5stufigen Präzisions-Destillationsanlage zur Gewinnung der Sauerstoffisotopen ^{17}O und ^{18}O durch Destillation von Wasser.

found separation factors of the order of 1.026 [341]. The same author reported mechanistic studies of exchange reactions [342], of which we show an example in *Fig. 124*.

211. Exchange Equilibrium of Oxygen Isotopes between BrO_3^- , ClO_3^- , IO_3^- and Water

by S. C. Agarwal, P. Baertschi and H. Gamsjäger¹⁾
Eidgenössisches Institut für Reaktorforschung, Würenlingen AG
(5. VII. 72)

Summary. The liquid phase fractionation factors $\alpha_{\text{H}} = (^{18}\text{O}/^{16}\text{O})_{\text{H}_2\text{O}}/(^{18}\text{O}/^{16}\text{O})_{\text{XO}_3^-}$ and $\alpha_{\text{D}} = (^{18}\text{O}/^{16}\text{O})_{\text{D}_2\text{O}}/(^{18}\text{O}/^{16}\text{O})_{\text{XO}_3^-}$ (X = Cl, Br, I) were calculated quantum mechanically between 0 and 100°. Experimental values were obtained in the case of BrO_3^- at 60° showing good agreement with the calculated results.

Fig. 124

Table 3. Calculated liquid-phase reduced partition function ratios Q_r of isotopic halogenate ions

Temp. °C	$Q_r\left(\frac{\text{Cl}^{16}\text{O}_2^{18}\text{O}^-}{\text{Cl}^{16}\text{O}_3^-}\right)$	$Q_r\left(\frac{\text{Br}^{16}\text{O}_2^{18}\text{O}^-}{\text{Br}^{16}\text{O}_3^-}\right)$	$Q_r\left(\frac{\text{I}^{16}\text{O}_2^{18}\text{O}^-}{\text{I}^{16}\text{O}_3^-}\right)$
0	1.08537	1.07440	1.07329
20	1.07563	1.06574	1.06474
40	1.06743	1.05848	1.05758
60	1.06048	1.05235	1.05153
80	1.05454	1.04711	1.04636
100	1.04941	1.04261	1.04192

An interesting application of isotopically labeled compounds for mechanistic studies is provided by *Heinrich Zollinger's* investigation of the isotope effects in coupling reactions of diazonium compounds [343], from which *Fig. 125* has been taken. An approximate theory of such isotope effects has been presented by *A. V. Willi* [344].

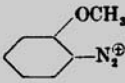
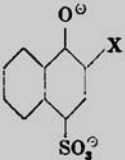
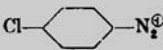
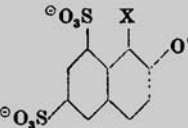
193. Kinetische Wasserstoffisotopeneffekte und allgemeine Basenkatalyse der Azokupplung¹⁾.

Zur Kenntnis der Kupplungsreaktion, 9. Mitteilung²⁾
von *Heb. Zollinger*.
(12. VIII. 55.)

Fig. 125

Fig. 125
(cont.)

Tabelle 1.
Kinetische Isotopeneffekte bei Azokupplungen.

Diazokomponente	Kupplungs-komponente	X	k_H bzw. k_D $l \cdot \text{Mol}^{-1} \cdot \text{sec}^{-1}$	k_H/k_D
		H D	8,71 9,01	0,97 ($\approx 1,0$)
		H D	0,87 0,133	6,55

Damit ist zum ersten Mal bei einer aromatischen elektrophilen Substitution ein kinetischer Isotopeneffekt gefunden worden, dessen Grösse den theoretischen Erwartungen entspricht.

A large number of mechanistic studies of isotope-exchange reactions have been published in *HCA* by the very active group of *Tino Gäumann* at the Ecole Polytechnique Fédérale in Lausanne. They concern applications to IR spectroscopy [345], problems in radiation chemistry, and mass spectrometry of isotopomeric hydrocarbons [346] (see Fig. 126), including the study of isotope effects in their physico-chemical properties [347], or gas-phase kinetic isotope effects [348].

Fig. 126

141. Strahlungschemie von Kohlenwasserstoffen

19. Mitteilung¹⁾

Die Deuteriumabspaltung in isotop-isomeren Cyclohexanen

von **M. Ballenegger, A. Ruf und T. Gäumann**

Institut für physikalische Chemie der ETH Lausanne

(17. V. 71)

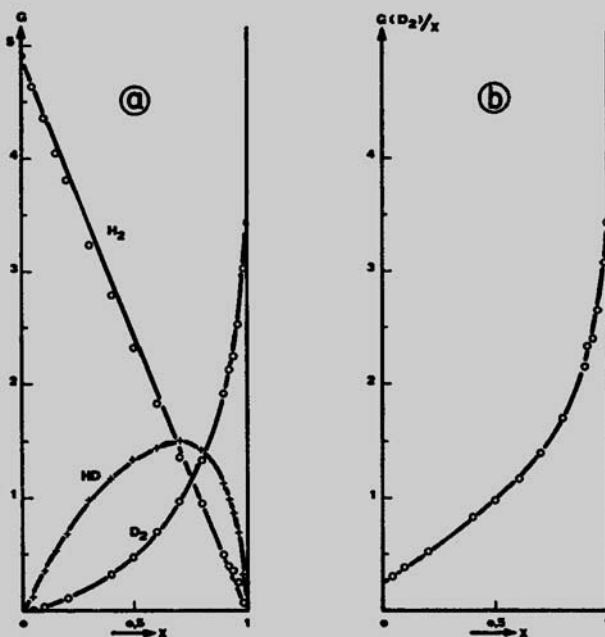


Fig. 1. Die Wasserstoffproduktion in C_6H_{12} - C_6D_{12} für 2 Mrad bei 10° als Funktion des Molenbruchs von C_6D_{12}
 a: partielle G-Werte für die Wasserstoffisotope. b: Darstellung des reduzierten G-Werts $g(D_2) \equiv G(D_2)/x$

4.3. Electrochemistry. In the following, we restrict our review to only a few examples of those papers published in *HCA*, which deal with the more physico-chemical aspects of electrochemistry. We shall not be concerned with applications.

As already mentioned in *Chapt. 2*, devoted to *Photochemistry*, *Emil Baur* and his student *A. Rebmann* reported in 1921 on investigations of the sensitized photolysis of water [203] [207], and of the electrolysis of water at high temperatures, *i.e.* of water-containing molten NaOH [202]. The aim of this work was to provide a convenient energy storage in the form of hydrogen. At about the same time, *E. Baur* began a long series of attempts at sensitized and nonsensitized photolysis of CO_2 , which met with little success, for reasons which were understood only much later. The interesting part of these writings was – as already discussed in *Chapt. 2*, – that *Baur* assumed that photochemical processes involved an intramolecular charge separation, followed by something like an electrochemical reaction [209] (see *Fig. 71*).

Electrolysis, *Faraday's* law, and ion-discharge potentials in liquid ammonia have been investigated by *M. G. del Boca* in 1933 [349]. Later, *J. Kaspar* published a generalized treatment of the electrolytic double layer, which includes ion adsorption (so-called *Stern* layer) [350]. This theory allowed to define the conditions for the occurrence of logarithmic adsorption isotherms. In connection with his extensive work on ozone, *Emile Briner* described the construction of an ozone electrode, in collaboration with *A. Valda* [351]. In

1945, *Fritz Almsy* discussed the kinetics of the formation of stationary states in *Donnan* layers, and the implications of such states for biochemistry [352].

G. Trümpler was the successor of *Emil Baur* as professor of Physical Chemistry at the ETH-Zurich. His main field of interest was polarography. In collaboration with *R. Bieber* and *P. Ruetschi*, he analyzed in detail the kinetics of the polarographic reduction of aldehydes, in particular the mechanism underlying multistep polarograms [353]. As an example, we show in *Fig. 127* an excerpt from his paper on the polarographic behavior of formaldehyde.

Fig. 127

92. Über die polarographische Reduktion der aliphatischen Aldehyde I.
Das polarographische Verhalten von Formaldehyd

von R. Bieber und G. Trümpler.

(14. II. 47)

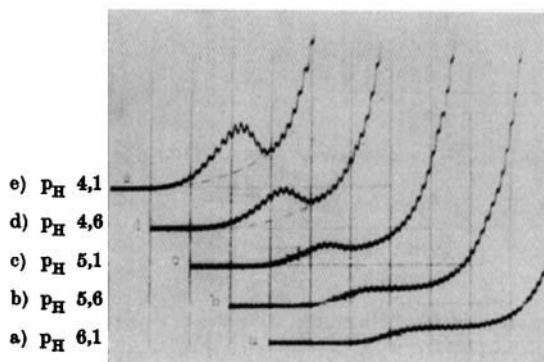


Fig. 4a.

20°C , $E = 1/20$, $V_W = 2 \text{ V}$, Kurven ab $1,3 \text{ V}$, $\pi_A = +250 \text{ mV}$, $(\text{CH}_2\text{O})_0 = 0,0218\text{-m.}^1$
Pufferlösungen nach *Britton, Thiel, Schulz und Coch*²⁾.

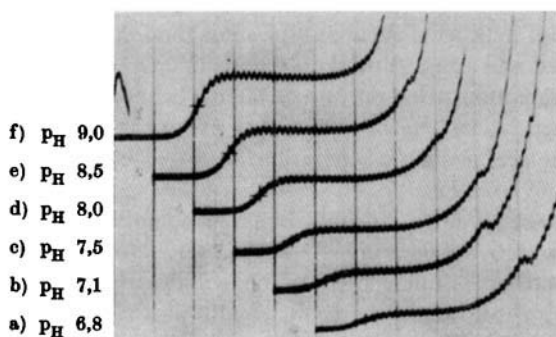


Fig. 4b.

Another series of investigations, which *G. Trümpler* carried out with *Norbert Ibl*, was devoted to the study of the diffusion processes which accompany electrolysis [354]. They worked out the theory, and they measured the convection and concentration fields near electrode surfaces using interferometric techniques, as exemplified in *Fig. 128*. These results turned out to be important for electrolytic procedures used in powder metallurgy, which was *Norbert Ibl's* field of research after he became a professor at ETH-Zurich.

**70. Zur Kenntnis der natürlichen Konvektion bei der Elektrolyse:
Interferometrische Untersuchungen der Diffusionsschicht I**

von *N. Ibl*, *Y. Barrada* und *G. Trümpler*.

(25. I. 54.)

Fig. 128



Fig. 2.
Interferenzbild vor Einschalten des
Stromes. Vergrößerung: 23×



Fig. 3.
Interferenzbild bei Stromdurchgang
(0,37 mA/cm²). Vergrößerung: 23×

At the University of Zurich, *Ernst Schumacher* and his coworkers described in a series of papers the very sensitive and versatile method of focussing ion exchange in an electric field, which they had developed [355], and from which we reproduce the example shown in *Fig. 129*.

Certainly, one of the most important contributions to analytical electrochemistry stems from the Laboratorium für Organische Chemie of the ETH-Zurich, where *Wilhelm Simon* and coworkers studied ion-specific electrodes which found numerous analytical applications, especially in biology and medicine. It is not surprising that the know-how acquired in the course of this work, and the closeness to *V. Prelog's* research group in the

Fig. 129

**210. Über fokussierenden Ionenaustausch IX¹⁾
Herstellung der kurzlebigen, trägerfreien Aktivitäten von ⁹⁰Sr, ¹⁴⁰La
und ¹⁴⁴Pr aus Spaltprodukten in hoher radiochemischer Reinheit²⁾**

von Ernst Schumacher und Walter Friedli

(18. VIII. 60)

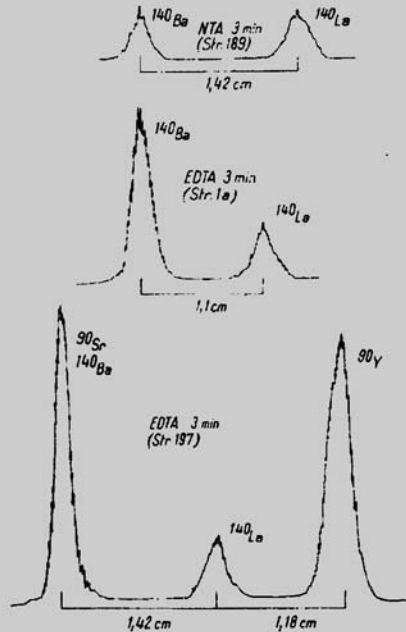


Fig. 4. Fokussierung von ¹⁴⁰Ba/¹⁴⁰La zur trägerfreien, radiochemisch > 99,95% reinen Herstellung von ¹⁴⁰La in 3 min.

Oben: mit NTA als Komplexbildner; Mitte: die gleiche Trennung mit EDTA als Komplexbildner; unten: Simultane Herstellung von trägerfreiem ⁹⁰Y und ¹⁴⁰La.

same institute, induced *W. Simon* to start a detailed investigation of the mechanism and selectivity of alkali-ion transport in membranes doped with carrier antibiotics. In *Fig. 130* we show one of the earlier titles [356] from the vast number of publications of *W. Simon*, in which he proved, in collaboration with *H.-K. Wipf* and *A. Olivier* that the ion transport is due to the carrier relay ("Träger-Stafette") mechanism. This work involved also numerous measurements of free enthalpies of formation of the alkali ion/antibiotic complexes, e.g. [357].

188. Mechanismus und Selektivität des Alkali-Ionentransportes in Modell-Membranen in Gegenwart des Antibioticums Valinomycin

von H.-K. Wipf, A. Olivier und W. Simon

Organisch-Chemisches Laboratorium, Eidgenössische Technische Hochschule, Zürich

(27. VII. 70)

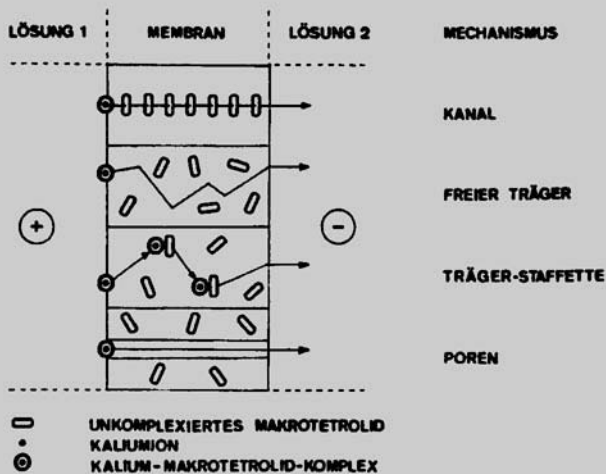


Fig. 1. Mögliche Transportmechanismen für geladene Antibiotikakomplexe in einem elektrischen Potential

A spectacular development of this work was the construction of liquid membranes, incorporating chiral ionophores, and the determination of the dependence of their membrane electrode potentials on the chirality of the ions, as shown in Fig. 131 [358].

235. Elektrochemische Untersuchungen über das enantiomerelektive Verhalten von chiralen Ionophoren in flüssigen Membranen

von André P. Thoma, Angelika Viviani-Nauer, Kurt H. Schellenberg, Davor Bedeković, Erno Pretsch, Vladimir Prelog und Wilhelm Simon

Laboratorium für Organische Chemie der Eidgenössischen Technischen Hochschule, Zürich

(20. VIII. 79)

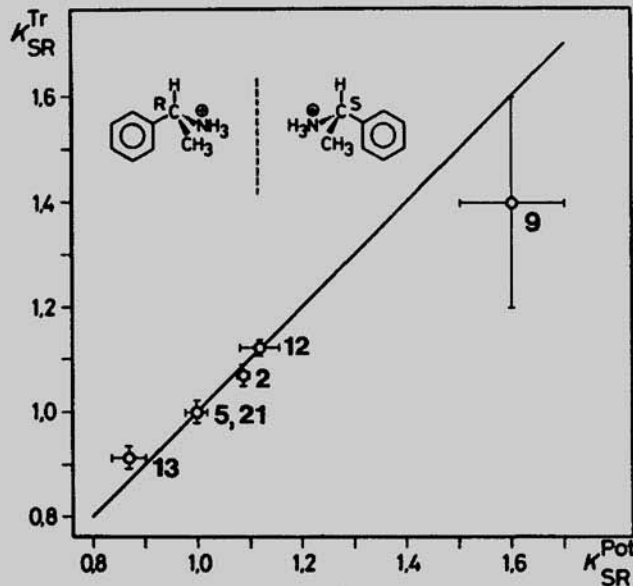
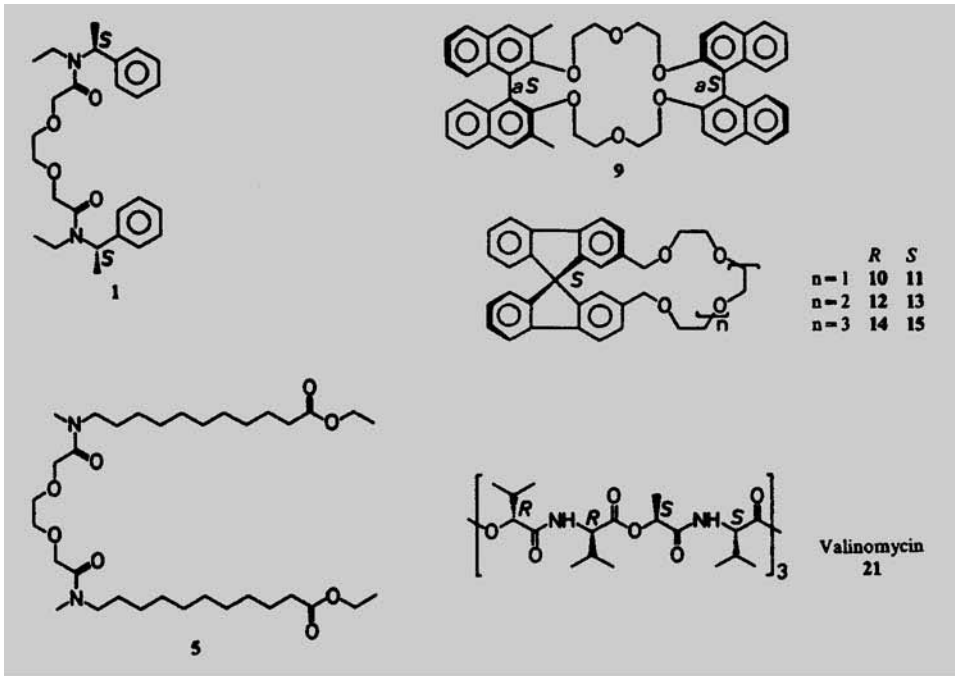
Fig. 131
(cont.)

Fig. 4. Zusammenhang der mittels Potentiometrie (K_{SR}^{Pot}) und elektrodalytischem Transport (K_{SR}^{Tr}) gefundenen Selektivität einiger Liganden für enantiomere α -Phenylethylammonium-Ionen in *o*-NPOE. Verbindung 5 ist achiral. Vgl. dazu Tabelle 1 und Tabelle 2.

The revival by *Michael Grätzel* of *Emil Baur*'s ideas about energy storage, *i.e.* the photochemical generation of hydrogen, has already been mentioned in *Chapt. 2* [223]. As a complement, we shown in *Fig. 132* an excerpt from one of his publication [359] on the sensitized photo-electrolysis of water, using zinc-porphyrin derivatives as sensitizers.

The same research group has also published on electrochemical reduction and oxidation in micro-heterogenous systems [360] and in systems containing colloidal dispersions of semiconducting TiO_2 and Fe_2O_3 [361].

Fig. 132

48. Light Induced Redox Reactions of Water Soluble Porphyrins, Sensitization of Hydrogen Generation from Water by Zincporphyrin Derivatives

by **Kuppuswamy Kalyanasundaram and Michael Grätzel**

Institut de Chimie Physique, Ecole Polytechnique Fédérale, 1015 Lausanne, Suisse

(27.XII.79)

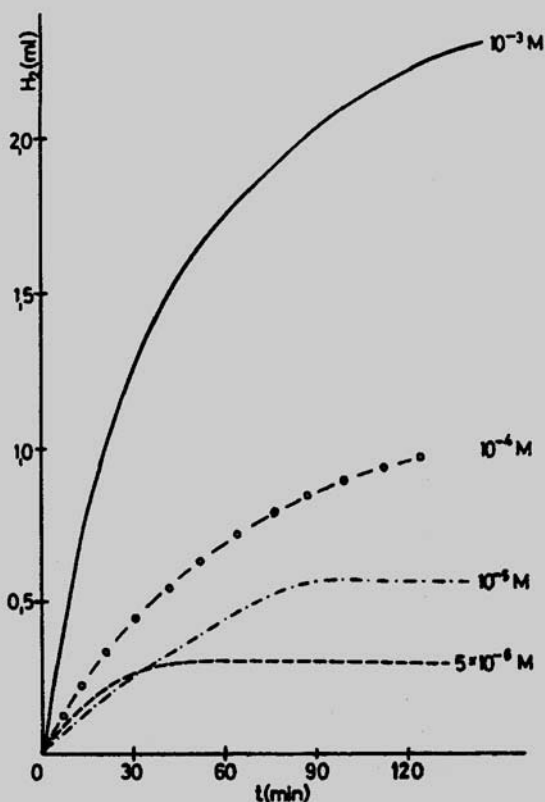


Fig. 3. H_2 -yields on photolysis ($\lambda \geq 500$ nm) of aqueous solutions (25 ml) of ZnTMPyP (10^{-4} M), EDTA (2×10^{-2} M), Pt-PVA catalyst (1 ml/25 ml), in pH 5.0 buffer solutions with different concentrations of methyl viologen (MV^{2+}) (---) 5×10^{-6} M; (-·-) 10^{-5} M; (- - -) 10^{-4} M; (—) 10^{-3} M

4.4. Dielectric and Electric Dipole Studies. The first report in *HCA* concerning measurements of dielectric properties stems from *Emile Briner's* and *Bernhard Susz's* group at the University of Geneva. They determined in 1936 the dielectric constant (permittivity) of ozonides, and found that it was noticeably higher than that of the educts, e.g. maleic acid diesters [362]. As already mentioned in *Sect. 1.1*, *H. Mohler* and *C. T.*

Fig. 133

261. Dielektrische Relaxation von Hochpolymeren II

von **Werner Kuhn**.

(20. IX. 50.)

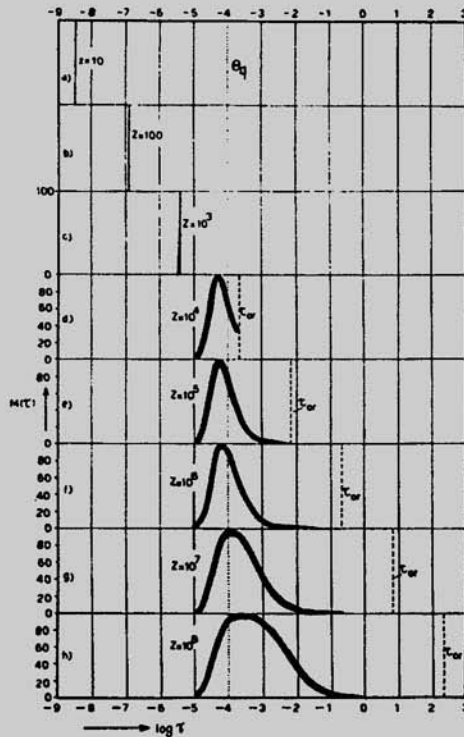


Fig. 3.

Beispiel für dielektrisches Relaxationszeitspektrum.

Intensität $M(\tau)$ (Ordinate) in Abhängigkeit von τ (Abszisse) für $Z = 10; 10^2, 10^3, 10^4, 10^5, 10^6, 10^7, 10^8$, gemäss Gl. (32). Es ist $\Theta_q = 10^{-4}$ so gesetzt [punktierte Vertikale in Fig. 3a bis h]. Es ist ferner $A_m = 13 \cdot 10^{-8}$ cm, $b = 2,88 \cdot 10^{-8}$ cm, $d_h = 5 \cdot 10^{-8}$ cm, $T = 300^\circ$ abs., $\eta_0 = 10^{-2}$ Poisen gesetzt. Der Masstab für die Ordinate $M(\tau)$ ist so gewählt, dass im Maximum [d. h. für $\tau = \tau_m$] $M(\tau) = 100$ wird.

Für kleine Werte von Z [solange $\tau_{or} < \Theta_q$ ist] tritt als Spektrum eine mit τ_{or} zusammenfallende Linie auf [Kurven a, b und c]. Für grössere Werte von Z tritt eine Bande auf, deren Maximum zunächst bei $\Theta_q/2$, bei grösseren Z -Werten etwas oberhalb $\Theta_q/2$ liegt. Die Intensität nimmt bei grossen Werten von Z wesentlich vor Erreichung der theoretischen oberen Grenze τ_{or} praktisch genommen auf Null ab. In den Kurven d bis h ist τ_{or} als gestrichelte Vertikale eingetragen.

Zahn published, in 1938, dipole moments of various compounds used in chemical warfare [51].

In connection with his work on macromolecules, discussed in *Sect. 4.1* [307–315], *Werner Kuhn* also provided a theory of the dependence of the size of the dipole moment of such molecules on their degree of coiling. This resulted in explicit predictions of their relaxation time spectra, an example of which is shown in *Fig. 133* [363].

The electric dipole moments of cyclanones were studied by *Hs. H. Günthard* and *T. Gäumann* [364], who found a significant dependence on ring size. The bulk dielectric properties of cyclanones were investigated over a wide range of temperature and frequency ranges [365]. The results, a sample of which is presented in *Fig. 134*, yielded insight into the phase transitions and dielectric relaxation of these compounds.

Fig. 134

15. Dielektrische Messungen an Cyclanonen.
I. Dielektrische Eigenschaften der Cyclanone
mit 5, 6, 7 und 10 Ringgliedern im festen und flüssigen Zustand
bei tiefen Frequenzen

von **T. Gäumann, U. Gugerli¹⁾, C. Béguin** und **Hs. H. Günthard.**

(12. XII. 55.)

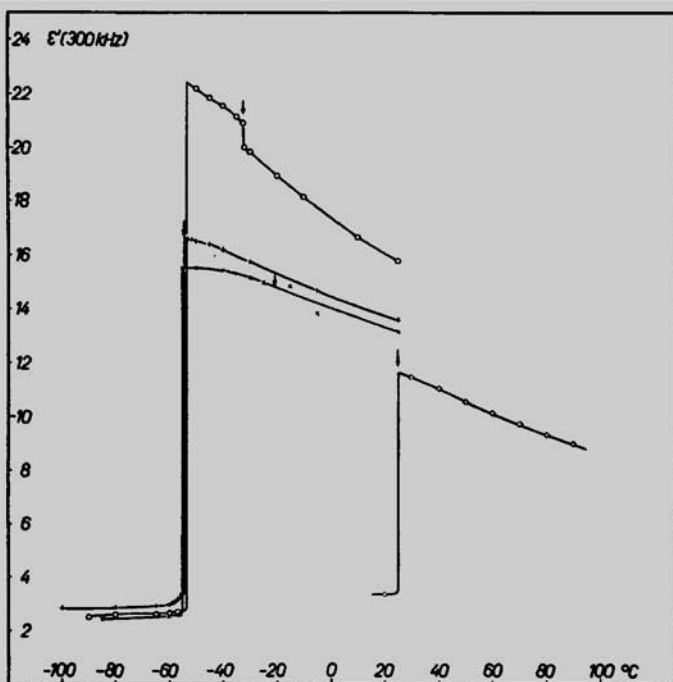


Fig. 2.

Dielektrisches Verhalten von Cyclanonen.

Cyclopentanone ○ Cyclohexanon × Cycloheptanon ◇ Cyclodekanon
 ↓ Schmelzpunkt.

The same group measured the dielectric increments of polar mixtures [366], e.g. water/dioxane, when highly polar molecules, such as amino acids, are dissolved in them, and it presented a model for the solvation of spherical ions, based on electrostatics and thermodynamics [367]. Systematic attempts to derive dipole moments and relaxation times from dielectric measurements involving polar solutions were published by *A. Beguin* and *T. Gäumann* [368]. Finally, *T. Gäumann* and his coworkers used electric dipole moment measurements to shed light on the structure of larger organic molecules [369].

Unusual temperature dependences of (apparent) dipole moments of polar molecules in apolar solvents were observed (see *Fig. 135*) and discussed by *H.-F. Eicke* and his group [370].

Fig. 135

11. Lösungsmittelbedingte Temperaturabhängigkeit des Dipolmoments polarer Molekeln in apolaren Medien

von *H. Christen*, *H.-F. Eicke*¹⁾ und *M. Jungen*
 Physikalisch-Chemisches Institut der Universität Basel,
 Klingelbergstrasse 80, 4056 Basel

(3. VII. 72)

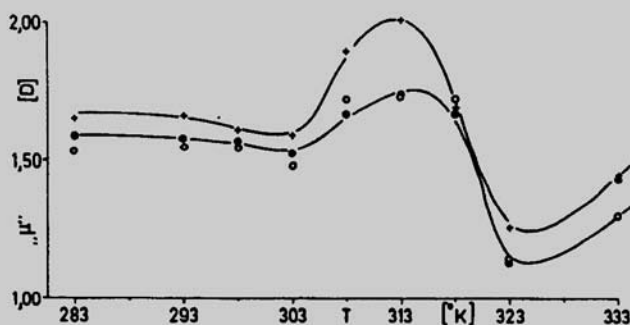


Fig. 1. Scheinbares Dipolmoment μ [D] als Funktion der abs. Temperatur

a) Monochlorbenzol in Cyclohexan

+ : 4,8 g/799 g LM } w_2 (min)
 ● : 7,2 g/799 g LM }
 ○ : 9,3 g/799 g LM }

This behavior could be explained in terms of specific solute/solvent interactions. In addition, *H. F. Eicke* and *J. C. W. Shepherd* discussed the complex problem of the dielectric behavior of apolar micelles in solutions at frequencies below 10 MHz [371].

4.5. Electronic Instrumentation for Physico-Chemical Measurements. The first mention in *HCA* of the use of an electron tube, in this instance for potentiometric and conductometric measurements, can be found in 1925 in a publication by *William D. Treadwell* [372] shown in *Fig. 136*. It is worth mentioning that the first use, by *K. H. Goode*

Über die Verwendung der Radioempfangerröhre zu elektrometrischen Titrationen

von **W. D. Treadwell**
 nach Versuchen von **C. Paoloni**.
 (8. I. 25.)

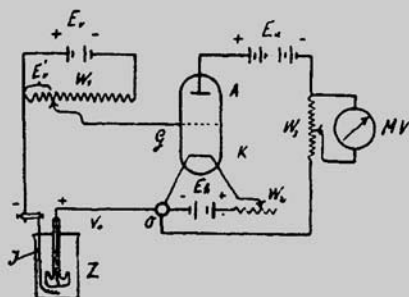


Fig. 2.

- | | |
|---------------------------------------|---|
| V_c = Vergleichselektrode | W_2 = 1 Ohm |
| I = Indikatorelektrode | A = Anode |
| E_p = Vorspannung = 4 Volt | G = Gitter |
| E_g = angew. Vorspannung = 1,6 Volt | K = Kathode |
| W_1 = 845 Ohm | E_a = Anodenspannung = 26,3 Volt |
| E_h = Heizspannung = 3,5 Volt | MV = Millivoltmeter mit 870 Ohm innerm
Widerstand. |
| O = Potentialnullpunkt | W_3 = 230 Ohm |

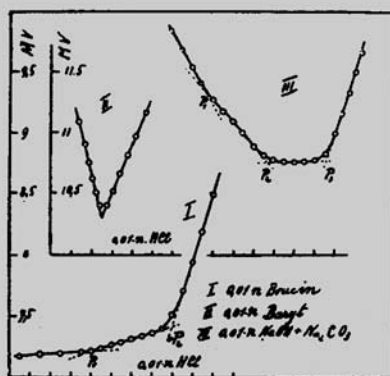


Fig. 5.

[373], of an electron tube for measuring the potential of a hydrogen electrode dates from 1922.

Five years later, a considerable improvement in sensitivity was reported by *Gerold Schwarzenbach* [374], who used a differential amplifier – *Wheatstone* bridge combination.

218. Kernquadrupolresonanz von ^{35}Cl in Chloracetylenen

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Physikalisch-Chemisches Institut der Universität Zürich und
Physikalisch-Chemisches Institut der Universität Basel

(23. VII. 71)

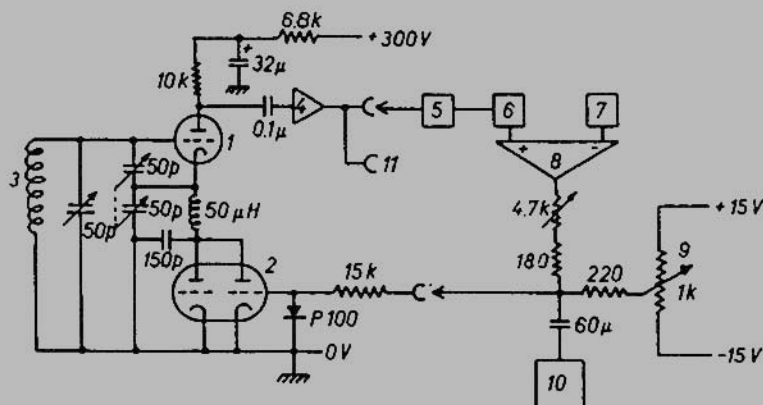


Fig. 1. Schema des verwendeten kohärenzstabilisierten Superregenerativ-Oszillators

- | | |
|---------------------------------|--|
| 1 Oszillatortröhre 6C4 | 7 Referenzspannungsgeber |
| 2 Löschröhre ECC88 | 8 Differenzverstärker |
| 3 Probenspule | 9 Spannungsteiler |
| 4 Signalvorverstärker | 10 Lösoszillator |
| 5 Filter: 115 ± 10 Hz | 11 Ausgang zu phasenempfindlichem Detektor |
| 6 Gleichrichter und Siebglieder | |

We conclude by reminding again our readers that we have tried to document only the variety of topics and the style of physico-chemical contributions in *HCA*. Our choice of examples, which is – up to a point – subjective, does not necessarily reflect on the relative importance of the papers included, and certainly not on the importance of those not quoted. We, therefore, offer our apologies to readers who will not find references to publications they cherish – perhaps their own.

As mentioned at the beginning of this review, the majority of physico-chemical investigations carried out in Switzerland – especially during the last two decades – have been submitted to foreign, specialized journals, through which the authors could reach a more receptive auditorium. Apart from this valid reason, the decision to shun *HCA* was made easier by a change in the parochial attitude of our chemists, which had prompted their elders to propose in 1921 a ‘*Table Suisse des poids atomiques*’, of which we reproduce

a small part in *Fig. 139* [383]. This was coupled with the recommendation that, within Switzerland, it should be used exclusively instead of the International Table, or – God forbid! – the German one.

Fig. 139

Table suisse des poids atomiques¹⁾ 1921

Les éléments sont classés par ordre alphabétique des symboles (Colonne V); leurs noms sont donnés dans les trois langues nationales (Colonnes I, II et III), ainsi qu'en anglais (Colonne IV).

La Colonne VI donne les valeurs proposées pour la Table suisse; la Colonne VII, donne celles de la Table internationale (1921) qui en diffèrent, et la Colonne VIII, celle de la Table allemande (1916) qui en diffèrent.

I	II	III	IV	V	VI	VII	VIII
Silber	Argent	Argento	Silver	Ag	107,88		
Aluminium	Aluminium	Alluminio	Aluminium	Al	27,1		
Argon	Argon	Argo	Argon	Ar	39,88	39,9	
Arsen	Arsenic	Arsenico	Arsenic ^a	As	74,96		
Gold	Or	Oro	Gold	Au	197,2		
Bor	Bore	Boro	Boron	B	10,90	10,9	11,0
Barium	Baryum	Bario	Barium	Ba	137,4	137,37	137,37
Beryllium	Glucinium	Berillio	Glucinum	Be (Gl)	9,1		
Wismut	Bismuth	Bismuto	Bismuth	Bi	208,0		
Brom	Brome	Bromo	Bromine	Br	79,92		
Kohlenstoff	Carbone	Carbonio	Carbon	C	12,00	12,006	12,006
Calcium	Calcium	Calcio	Calcium	Ca	40,07		
Cadmium	Cadmium	Cadmio	Cadmium	Cd	112,4	112,40	112,40
Cerium	Cérium	Cerio	Cerium	Ce	140,3	140,25	140,25
Chlor	Chlore	Cloro	Chlorine	Cl	35,46		

CONCLUSIONS.

Si le comité de la Société Suisse de Chimie approuve nos suggestions, nous le prions de faire le nécessaire auprès du Conseil de la Chimie suisse pour que la Table suisse soit employée dans notre pays à l'exclusion de toutes autres, notamment pour les travaux officiels, de façon à assurer ainsi la comparabilité et l'uniformité des résultats.

Bâle	Genève	Lausanne	Zürich
<i>A.-L. Bernoulli</i>	<i>Ph.-A. Guye</i>	<i>P. Dutoit</i>	<i>W.-D. Treadwell</i>

Février 1921.

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Finally, we wish to thank Mr. *J. Meienberger*, for having allowed us to use the library of the Department of Chemistry of the ETH-Zurich sometimes at odds with its strict regulations.

REFERENCES

- [1] G. B. Kauffman, *Education in Chem.* **1987**, 168.
- [2] M. Davies, *Chemistry in Britain* **1992**, *28*, 728.
- [3] F. J. Moore, 'A History of Chemistry', 3rd. ed. revised by W. T. Hall, McGraw-Hill Book Comp., New York, 1939.
- [4] Ph. A. Guye (obituary by E. Briner), *Helv. Chim. Acta* **1922**, *5*, 411 (obituary by R. Monnier), in 'Centenaire de l'école de chimie', Université de Genève, **1979**, p. 39.
- [5] E. Heilbronner, M. V. Kısakürek, *Helv. Chim. Acta* **1992**, *75*, 1.
- [6] Ch. K. Jørgensen, in 'Centenaire de l'école de chimie', Université de Genève, **1979**, p. 27.
- [7] G. W. A. Kahlbaum (obituary by F. Fichter), *Verhandlg. Schweiz. Naturforsch. Ges.* **1905**, *88*.
- [8] A. L. Bernoulli, obituary in 'Basler Nachrichten' of February 21, 1939, and in *National Zeitung* (Basel) of February 20, 1939.
- [9] P. Pfeifer (obituary by R. Wizinger), *Helv. Chim. Acta* **1953**, *36*, 2032.
- [10] V. Henri (obituary by H. v. Halban), *Vierteljahresschrift der Naturforsch. Ges. Zürich* **1941**, *86*, 308 (obituary by J. Duchesne), *Liber Memorialis de l'Université de Liège*, **1967**, *2*, 471.
- [11] C. H. Eugster, '150 Jahre Chemie an der Universität Zürich', BAG Brunner Verlag, Zürich, 1983.
- [12] G. Kirchhoff, R. Bunsen, *Ann. Physik* **1860**, *110*, 161; Historical review: G. Scheibe, *Z. Elektrochem.* **1960**, *64*, 784.
- [13] R. Bunsen, *J. Prakt. Chem.* **1860**, *80*, 477; *ibid.* **1861**, *83*, 198.
- [14] G. Bugge, 'Das Buch der grossen Chemiker', Vol. 2, Verlag Chemie, Weinheim/Bergstrasse, 1929, reprinted 1965.
- [15] A. Werner, *Helv. Chim. Acta* **1918**, *1*, 5.
- [16] L. M. Venanzi, *Helv. Chim. Acta* **1992**, *75*, 21.
- [17] C. Djerassi, *Bull. Soc. Chim. France* **1957**, 741; G. Snatzke, in 'Optical Activity and Chiral Discrimination', F. S. Mason edit., D. Reidel, Dordrecht, 1979.
- [18] C. Djerassi, O. Halpern, V. Halpern, O. Schindler, Ch. Tamm, *Helv. Chim. Acta* **1954**, *41*, 250; G. Snatzke, Ch. Tamm, *Helv. Chim. Acta* **1984**, *67*, 690.
- [19] F. Kehrmann, M. Sandoz, *Helv. Chim. Acta* **1918**, *1*, 270.
- [20] F. Kehrmann, M. Sandoz, *Helv. Chim. Acta* **1920**, *3*, 104; F. Kehrmann, H. Goldstein, *ibid.* **1921**, *4*, 26; F. Kehrmann, M. Sandoz, *ibid.* **1921**, *4*, 31; *ibid.* **1922**, *5*, 895.
- [21] F. Kehrmann (obituary by H. Goldstein), *Helv. Chim. Acta* **1932**, *15*, 315.
- [22] H. Zollinger, *Helv. Chim. Acta* **1992**, *75*, 1727.
- [23] F. Kehrmann, P. Borgeaud, *Helv. Chim. Acta* **1926**, *9*, 881.
- [24] F. Kehrmann, H. Goldstein, A. von Salis, *Helv. Chim. Acta* **1927**, *10*, 33.
- [25] F. Kehrmann, H. Goldstein, F. Brunner, *Helv. Chim. Acta* **1926**, *9*, 222.
- [26] A. Hagenbach, R. Percy, *Helv. Chim. Acta* **1922**, *5*, 454.
- [27] H. v. Halban (obituary by M. Kofler), *Helv. Chim. Acta* **1948**, *31*, 120.
- [28] H. v. Halban, B. Sziget, *Helv. Chim. Acta* **1937**, *20*, 746.
- [29] H. v. Halban, M. Litmanowitsch, *Helv. Chim. Acta* **1941**, *24*, 38; *ibid.* **1943**, *26*, 771; *ibid.* **1948**, *31*, 1963.
- [30] H. v. Halban, M. Litmanowitsch, *Helv. Chim. Acta* **1941**, *24*, 44; H. Keller, H. v. Halban, *Helv. Chim. Acta* **194**, *27*, 702.
- [31] F. Almasy, *Helv. Phys. Acta* **1937**, *10*, 471.
- [32] H. v. Halban, K. Wieland, *Helv. Chim. Acta* **1944**, *27*, 1032.
- [33] R. Kuhn, A. Winterstein, *Helv. Chim. Acta* **1928**, *11*, 87.
- [34] C. H. Eugster, *Helv. Chim. Acta* **1922**, *75*, 941.
- [35] R. Kuhn, A. Winterstein, *Helv. Chim. Acta* **1929**, *12*, 899.
- [36] R. Kuhn, A. Winterstein, *Helv. Chim. Acta* **1928**, *11*, 116.
- [37] K. W. Hausser, R. Kuhn, *Z. phys. Chem. [B]* **1935**, *29*, 363, 371, 378, 384, 391.
- [38] Pl. A. Plattner (obituary by A. Fürst), *Helv. Chim. Acta* **1977**, *60*, 2109.
- [39] Ch. Tamm, *Helv. Chim. Acta* **1922**, *75*, 2109.
- [40] J. Kalvoda, *Helv. Chim. Acta* **1992**, *75*, 2341.
- [41] H. Heimgartner, H.-J. Hansen, *Helv. Chim. Acta* **1992**, *75*, 359.
- [42] A. St. Pfau, Pl. A. Plattner, *Helv. Chim. Acta* **1937**, *20*, 224.
- [43] B. Susz, A. St. Pfau, Pl. A. Plattner, *Helv. Chim. Acta* **1937**, *20*, 469.
- [44] Pl. A. Plattner, *Helv. Chim. Acta* **1941**, *24*, 283 E.
- [45] J. R. Platt, *J. Chem. Phys.* **1949**, *17*, 484.

- [46] Pl. A. Plattner, E. Heilbronner, *Helv. Chim. Acta* **1947**, *30*, 910.
- [47] E. Heilbronner, in 'Non-Benzenoid Aromatic Compounds', ed. D. Ginsburg, Interscience, New York, 1959; J. N. Murrell, 'The Theory of the Electronic Spectra of Organic Compounds', Methuen and Co., London, 1963.
- [48] B. Pullmann, M. Mayot, G. Berthier, *J. Chem. Phys.* **1950**, *18*, 257.
- [49] H. C. Longuet-Higgins, R. G. Sowden, *J. Chem. Soc.* **1952**, 1404; C. A. Coulson, Proc. Roy. Soc. London **1952**, *A65*, 933.
- [50] H. Mohler, *Helv. Chim. Acta* **1936**, *19*, 283, 1222, 1239; *ibid.* **1937**, *20*, 287, 1188.
- [51] H. Mohler, *Helv. Chim. Acta* **1938**, *21*, 67, 784, 787, 789; H. Mohler, C. T. Zahn, *ibid.* **1938**, *21*, 1276; C. T. Zahn, H. Mohler, *ibid.* **1938**, *21*, 1284; H. Mohler, J. Sorge, *ibid.* **1940**, *23*, 100, 104, 119, 1200; H. Mohler, W. Hämmerle, *ibid.* **1940**, *22*, 1211; H. Mohler, *ibid.* **1941**, *24*, 571; H. Mohler, J. Hartnagel, *ibid.* **1942**, *25*, 859; H. Mohler, *ibid.* **1943**, *26*, 157.
- [52] H. Mohler, *Helv. Chim. Acta* **1937**, *20*, 289, 811; H. Mohler, H. Lohr, *ibid.* **1937**, *20*, 1183; *ibid.* **1938**, *21*, 485.
- [53] H. Mohler, J. Sorge, *Helv. Chim. Acta* **1939**, *22*, 229.
- [54] H. Mohler, H. Forster, G. Schwarzenbach, *Helv. Chim. Acta* **1937**, *20*, 654.
- [55] H. Mohler, 'Das Absorptionsspektrum der chemischen Bindung', Verlag von G. Fischer, Jena, 1943.
- [56] H. Mohler, *Helv. Chim. Acta* **1937**, *20*, 282, 285.
- [57] F. Leuthart, M. Pfister, *Helv. Chim. Acta* **1933**, *16*, 228.
- [58] H. Mohler, *Helv. Chim. Acta* **1942**, *25*, 978.
- [59] E. Briner, E. Perottet, *Helv. Chim. Acta* **1940**, *23*, 1253.
- [60] K. Wieland (obituary by G. Wagnière), Jahresbericht 1990/91 der Universität Zürich, p. 150.
- [61] K. Wieland, *Helv. Chim. Acta* **1943**, *26*, 1939.
- [62] K. Wieland, A. Herczog, *Helv. Chim. Acta* **1946**, *29*, 1702.
- [63] K. Wieland, A. Herczog, *Helv. Chim. Acta* **1949**, *32*, 889.
- [64] E. Heilbronner, K. Wieland, *Helv. Chim. Acta* **1947**, *30*, 947; E. Heilbronner, Pl. A. Plattner, K. Wieland, *Experientia* **1947**, *3*, 70.
- [65] H. Labhart (obituary by G. Wagnière), *Helv. Chim. Acta* **1978**, *61*, 30.
- [66] H. Labhart, *Helv. Chim. Acta* **1961**, *44*, 447.
- [67] H. Labhart, *Helv. Chim. Acta* **1961**, *44*, 457.
- [68] W. Kuhn, H. Dührkop, H. Martin, *Z. physik. Chem.* **1940**, *B 45*, 121.
- [69] H. Labhart, *Tetrahedron* **1963**, *19 (Suppl. 2)*, 223.
- [70] H. Labhart, E. Weltin, E. Heilbronner, *Helv. Chim. Acta* **1963**, *46*, 2041.
- [71] K. Seibold, R. Zahradnik, H. Labhart, *Helv. Chim. Acta* **1970**, *53*, 805.
- [72] H. Labhart, *Helv. Chim. Acta* **1964**, *47*, 2279.
- [73] Ch. Huggenberger, H. Labhart, *Helv. Chim. Acta* **1978**, *61*, 250.
- [74] W. Kuhn, *Naturwiss.* **1931**, *19*, 854; *Ann. Rev. Phys. Chem.* **1958**, *9*, 417.
- [75] W. Kuhn, R. Rometsch, *Helv. Chim. Acta* **1944**, *27*, 1080; 1346.
- [76] M. Iseli, G. Wagnière, J. G. Brahms, S. Brahms, *Helv. Chim. Acta* **1979**, *62*, 921.
- [77] H. Yamaguchi, M. Ata, K. Toyoda, H. Mametsuka, H. Takeshita, H. Baumann, *Helv. Chim. Acta* **1981**, *64*, 2356.
- [78] M. Higashi, H. Yamaguchi, T. Machiguchi, T. Hasegawa, H. Baumann, *Helv. Chim. Acta* **1992**, *75*, 1880.
- [79] R. Stupp, H. Kuhn, *Helv. Chim. Acta* **1952**, *35*, 2469.
- [80] J. Spanget-Larsen, K. Gubernator, R. Gleiter, E. W. Thulstrup, B. Bianco, G. Gandillon, U. Burger, *Helv. Chim. Acta* **1983**, *66*, 676.
- [81] H. Christen, P. A. Straub, *Helv. Chim. Acta* **1973**, *56*, 739.
- [82] H. Christen, E. Kloster-Jensen, *Helv. Chim. Acta* **1973**, *56*, 1752.
- [83] E. Schmidt, H. Loeliger, R. Zürcher, *Helv. Chim. Acta* **1978**, *61*, 488.
- [84] J. Errera, *Helv. Chim. Acta* **1937**, *20*, 1373.
- [85] R. Signer, J. Weiler, *Helv. Chim. Acta* **1932**, *15*, 649.
- [86] H. Staudinger, *Z. angew. Chem.* **1929**, *41*, 37.
- [87] R. Signer, J. Weiler, *Helv. Chim. Acta* **1933**, *16*, 115.
- [88] E. Briner (obituary by B. P. Susz and G. Baume), *J. Chim. Physique* **1965**, 1229.
- [89] B.-P. Susz (obituary by A. Buchs), *Compte rendu des séances de la Société de Physique et d'Histoire Naturelle de Genève*, **1977**, *11*, 8.
- [90] E. Briner, B. Susz, P. Favarger, *Helv. Chim. Acta* **1935**, *18*, 375, 378.
- [91] A. St. Pfau, J. Pictet, Pl. A. Plattner, B. Susz, *Helv. Chim. Acta* **1935**, *18*, 935.

- [92] E. Briner, J. J. Kündig, M. Berenstein, *Helv. Chim. Acta* **1945**, *28*, 1612.
- [93] E. Ganz, *Helv. Chim. Acta* **1945**, *28*, 1580, 1590.
- [94] Hs. H. Günthard, L. Ruzicka, *Helv. Chim. Acta* **1948**, *31*, 642.
- [95] B. Susz, G. Papaziau, M. Berenstein, E. Briner, *Helv. Chim. Acta* **1948**, *31*, 1133.
- [96] Hs. H. Günthard, Pl. A. Plattner, *Helv. Chim. Acta* **1949**, *32*, 284.
- [97] P. Niggli, *Helv. Chim. Acta* **1949**, *32*, 770, 913, 1453.
- [98] Hs. H. Günthard, T. Gäumann, E. Heilbronner, *Helv. Chim. Acta* **1949**, *32*, 1784.
- [99] Hs. H. Günthard, B. Messikommer, M. Köhler, *Helv. Chim. Acta* **1950**, *33*, 1809.
- [100] H. Primas, Hs. H. Günthard, *Helv. Chim. Acta* **1953**, *36*, 1659, 1791; *ibid.* **1955**, *38*, 1254; *ibid.* **1956**, *39*, 1182.
- [101] Hs. H. Günthard, S. D. Heinemann, V. Prelog, *Helv. Chim. Acta* **1953**, *36*, 1147.
- [102] H. Primas, Hs. H. Günthard, *Helv. Chim. Acta* **1954**, *37*, 360, 370.
- [103] E. Dallwigk, E. Briner, *Helv. Chim. Acta* **1953**, *36*, 1757; *ibid.* **1954**, *37*, 620, 1558, 1561.
- [104] Th. Bürer, Hs. H. Günthard, *Helv. Chim. Acta* **1956**, *39*, 356; *ibid.* **1957**, *40*, 2046, 2054; H. Fuhrer, Hs. H. Günthard, *ibid.* **1965**, *48*, 236.
- [105] H. J. Hediger, Hs. H. Günthard, *Helv. Chim. Acta* **1945**, *37*, 1125; H. R. Wyss, Hs. H. Günthard, *ibid.* **1966**, *49*, 660.
- [106] K. Frei, Hs. H. Günthard, *Helv. Chim. Acta* **1958**, *41*, 1988; *ibid.* **1959**, *42*, 1194.
- [107] Th. Bürer, E. Mäder, Hs. H. Günthard, *Helv. Chim. Acta* **1957**, *40*, 1823.
- [108] S. Julia, D. Varch, Th. Bürer, Hs. H. Günthard, *Helv. Chim. Acta* **1960**, *43*, 1623.
- [109] L. P. Kuhn, *J. Am. Chem. Soc.* **1952**, *74*, 2492.
- [110] M. Avanesoff, T. Gäumann, *Helv. Chim. Acta* **1970**, *53*, 995; M. Avanesoff, Hoo Dac Thang, T. Gäumann, *ibid.* **1971**, *54*, 1013, 1020.
- [111] M. Rossi, E. Haselbach, *Helv. Chim. Acta* **1979**, *62*, 140.
- [112] W. Hug, S. Kint, G. F. Bailey, J. P. Scherrer, *J. Am. Chem. Soc.* **1975**, *97*, 5590; W. Hug, H. Surbeck, *Chem. Phys. Letters* **1979**, *60*, 186; W. Hug, *Appl. Spectrosc.* **1981**, *35*, 115.
- [113] H.-J. Hansen, H.-R. Sliwka, W. Hug, *Helv. Chim. Acta* **1979**, *62*, 1120; *ibid.* **1982**, *65*, 325.
- [114] H. Kühne, M. Forster, J. Hulliger, H. Rupprecht, A. Bauder, Hs. H. Günthard, *Helv. Chim. Acta* **1980**, *63*, 1971; J. Dommen, M. Forster, H. Rupprecht, A. Bauder, Hs. H. Günthard, *ibid.* **1982**, *65*, 504.
- [115] R.-P. Müller, S. Murata, M. Nonella, J. R. Huber, *Helv. Chim. Acta* **1984**, *67*, 953.
- [116] G. Calzaferrri, M. Gori, *Helv. Chim. Acta* **1985**, *68*, 1617.
- [117] W. D. Lupo, M. Quack, B. Vogelsanger, *Helv. Chim. Acta* **1987**, *70*, 125.
- [118] T. Gäumann, J. M. Riveros, Z. Zhu, *Helv. Chim. Acta* **1990**, *73*, 1215.
- [119] F. I. Vilesov, B. C. Kurbatov, A. N. Terenin, *Dokl. Akad. Nauk SSSR* **1961**, *138*, 1329; *Soviet Physics – Doklady* **1962**, *8*, 883.
- [120] D. W. Turner, M. I. Al-Joboury, *J. Chem. Phys.* **1962**, *37*, 3007; *J. Chem. Soc.* **1963**, 5141.
- [121] D. W. Turner, C. Baker, A. D. Baker, C. R. Brundle, 'Molecular Photoelectron Spectroscopy', Wiley Interscience, New York, Sidney, Toronto, 1970.
- [122] W. C. Price, in 'Molecular Spectroscopy IV', (P. W. Hepple, ed.), Institute of Petroleum, London, 1969; *Phil. Trans. Roy. Soc.* **1970**, *A 268*, 59.
- [123] K. Siegbahn, C. Nordling, G. Johansson, J. Hedman, P. F. Hedén, K. Hamrin, U. Gelius, T. Bergmark, L. O. Werme, R. Manne, Y. Baer, 'ESCA Applied to Free Molecules', North-Holland, Amsterdam, 1969.
- [124] T. Koopmans, *Physica* **1934**, *1*, 104.
- [125] R. B. Woodward, R. Hoffmann, *J. Am. Chem. Soc.* **1965**, *87*, 395, 2511; R. Hoffmann, R. B. Woodward, *ibid.* **1965**, *87*, 2046; R. B. Woodward, R. Hoffmann, *Angew. Chem.* **1969**, *81*, 797.
- [126] P. Bischof, J. A. Hashmall, E. Heilbronner, *Helv. Chim. Acta* **1969**, *52*, 1745.
- [127] G. Bieri, E. Heilbronner, T. Kobayashi, A. Schmelzer, M. J. Goldstein, R. S. Leight, M. S. Lipton, *Helv. Chim. Acta* **1976**, *59*, 2657.
- [128] R. Hoffmann, A. Imamura, W. J. Hehre, *J. Am. Chem. Soc.* **1968**, *90*, 1499; R. Hoffmann, *Accounts Chem. Res.* **1971**, *4*, 1.
- [129] P. Bischof, R. Gleiter, E. Heilbronner, *Helv. Chim. Acta* **1970**, *53*, 1425.
- [130] P. Bischof, R. Gleiter, E. Heilbronner, V. Hornung, G. Schröder, *Helv. Chim. Acta* **1970**, *53*, 1645.
- [131] E. Haselbach, E. Heilbronner, G. Schröder, *Helv. Chim. Acta* **1971**, *54*, 153.
- [132] G. Bieri, E. Heilbronner, E. Kloster-Jensen, A. Schmelzer, J. Wirz, *Helv. Chim. Acta* **1974**, *57*, 1265.
- [133] B. Kovač, M. Allan, E. Heilbronner, *Helv. Chim. Acta* **1981**, *64*, 430.
- [134] M. C. Böhm, R. Gleiter, Ch. D. Batich, *Helv. Chim. Acta* **1980**, *63*, 990.
- [135] H. J. Haink, E. Heilbronner, V. Hornung, E. Kloster-Jensen, *Helv. Chim. Acta* **1970**, *53*, 1073.

- [136] E. Heilbronner, K. A. Muszkat, J. Schäublin, *Helv. Chim. Acta* **1971**, *54*, 58.
- [137] J. P. Maier, L. Misev, R. H. Shiley, *Helv. Chim. Acta* **1980**, *63*, 1920; J. P. Maier, L. Misev, F. Thommen, *ibid.* **1981**, *64*, 1985.
- [138] D. Klapstein, J. P. Maier, L. Misev, M. Ochsner, *Helv. Chim. Acta* **1984**, *67*, 1222.
- [139] F. Brogli, E. Heilbronner, *Helv. Chim. Acta* **1971**, *54*, 1423.
- [140] P. A. Clark, F. Brogli, E. Heilbronner, *Helv. Chim. Acta* **1972**, *53*, 1415.
- [141] Ch. Batich, E. Heilbronner, E. Vogel, *Helv. Chim. Acta* **1974**, *57*, 2288.
- [142] H. Baumann, J.-C. Bünzli, J. F. M. Oth, *Helv. Chim. Acta* **1972**, *65*, 582.
- [143] R. Gleiter, J. Spanget-Larsen, E. W. Thulstrup, I. Murata, K. Nakasuji, Ch. Jutz, *Helv. Chim. Acta* **1976**, *59*, 1459.
- [144] R. Gleiter, R. Gyax, D. H. Reid, *Helv. Chim. Acta* **1975**, *58*, 1591.
- [145] G. Bieri, F. Burger, E. Heilbronner, J. P. Maier, *Helv. Chim. Acta* **1977**, *60*, 2213; G. Bieri, J. D. Dill, E. Heilbronner, A. Schmelzer, *ibid.* **1977**, *60*, 2234.
- [146] A. D. Walsh, *Nature* **1947**, *159*, 167, 712; *Trans Farad. Soc.* **1949**, *45*, 179.
- [147] K. B. Wiberg, *Tetrahedron* **1968**, *24*, 1038; R. Hoffmann, R. B. Davidson, *J. Am. Chem. Soc.* **1971**, *93*, 5649.
- [148] P. Bischof, Ph. E. Eaton, R. Gleiter, E. Heilbronner, T. B. Jones, H. Musso, A. Schmelzer, R. Stober, *Helv. Chim. Acta* **1978**, *61*, 547.
- [149] E. Honegger, Ph. E. Eaton, B. K. Ravi Shankar, E. Heilbronner, *Helv. Chim. Acta* **1982**, *65*, 1982.
- [150] R. Hoffmann, P. D. Mollère, E. Heilbronner, *J. Am. Chem. Soc.* **1973**, *95*, 4860.
- [151] E. Heilbronner, E. Honegger, W. Zambach, P. Schmitt, H. Günther, *Helv. Chim. Acta* **1984**, *67*, 1681.
- [152] E. Haselbach, A. Schmelzer, *Helv. Chim. Acta* **1971**, *54*, 1575; *ibid.* **1972**, *55*, 1745, 3130.
- [153] E. Haselbach, Z. Lanyiova, M. Rossi, *Helv. Chim. Acta* **1973**, *56*, 2889.
- [154] Th. Bally, E. Haselbach, Z. Lanyiova, P. Baertschi, *Helv. Chim. Acta* **1978**, *61*, 2488.
- [155] E. Haselbach, U. Klemm, U. Buser, R. Geschwind, M. Jungen, E. Kloster-Jensen, J. P. Maier, O. Marthaler, H. Christen, P. Baertschi, *Helv. Chim. Acta* **1981**, *64*, 823; E. Haselbach, U. Klemm, R. Geschwind, Th. Bally, L. Chassot, S. Nitsche, *ibid.* **1982**, *65*, 2464; Th. Bally, L. Neuhaus, S. Nitsche, E. Haselbach, J. Jansen, W. Lüttke, *ibid.* **1983**, *66*, 1288.
- [156] C. A. Grob, *Helv. Chim. Acta* **1985**, *68*, 882.
- [157] E. Heilbronner, E. Honegger, J. Lecoultre, C. A. Grob, R. Houriet, E. Rolli, *Helv. Chim. Acta* **1986**, *69*, 2114.
- [158] R. Houriet, E. Rolli, G. Bouchoux, Y. Hoppilliard, *Helv. Chim. Acta* **1985**, *68*, 2037; Ch. Guenat, R. Houriet, D. Stahl, J. Winkler, *ibid.* **1985**, *68*, 1647.
- [159] C. A. Grob, M. G. Schlageter, *Helv. Chim. Acta* **1976**, *59*, 246; C. A. Grob, B. Schaub, M. G. Schlageter, *ibid.* **1980**, *63*, 57.
- [160] H. Bock, B. Berkner, B. Hierholzer, D. Jaculi, *Helv. Chim. Acta* **1992**, *75*, 1798.
- [161] R. Bombach, J. Dannacher, J.-P. Stadelmann, R. Neier, *Helv. Chim. Acta* **1983**, *66*, 701.
- [162] J. Dannacher, E. Heilbronner, J.-P. Stadelmann, J. Vogt, *Helv. Chim. Acta* **1979**, *62*, 2186.
- [163] E. Haselbach, Th. Bally, S. Lanyiova, *Helv. Chim. Acta* **1979**, *62*, 577; E. Haselbach, Th. Bally, S. Lanyiova, P. Baertschi, *ibid.* **1979**, *62*, 583; Th. Bally, S. Nitsche, E. Haselbach, *ibid.* **1984**, *67*, 86.
- [164] E. Haselbach, *Helv. Chim. Acta* **1970**, *53*, 1326; E. Haselbach, A. Henriksson, A. Schmelzer, H. Berthoud, *ibid.* **1973**, *56*, 705.
- [165] A. Herrmann, S. Leutwyler, E. Schumacher, L. Wöste, *Helv. Chim. Acta* **1978**, *61*, 453.
- [166] M. Allan, *Helv. Chim. Acta* **1982**, *65*, 2008; M. Allan, E. Haselbach, M. v. Büren, H.-J. Hansen, *ibid.* **1982**, *65*, 2133; B. Albrecht, M. Allan, E. Haselbach, L. Neuhaus, P.-A. Carrupt, *ibid.* **1984**, *67*, 216; M. Allan, L. Neuhaus, E. Haselbach, *ibid.* **1984**, *67*, 1776.
- [167] H. Primas, K. Frei, Hs. H. Günthard, *Helv. Chim. Acta* **1958**, *41*, 35.
- [168] H. Primas, Hs. H. Günthard, *Helv. Phys. Acta* **1957**, *30*, 315, 331.
- [169] H. A. Christ, P. Diehl, H. R. Schneider, H. Dahn, *Helv. Chim. Acta* **1961**, *44*, 865.
- [170] P. Diehl, *Helv. Chim. Acta* **1961**, *44*, 829; *ibid.* **1962**, *45*, 568.
- [171] P. Diehl, *Helv. Chim. Acta* **1964**, *47*, 1; *ibid.* **1965**, *48*, 567; P. Diehl, P. Weissenhorn, *ibid.* **1967**, *50*, 143.
- [172] P. Diehl, Th. Leipert, *Helv. Chim. Acta* **1964**, *47*, 545.
- [173] P. Diehl, C. L. Khetrapal, H. P. Kellerhals, *Helv. Chim. Acta* **1968**, *51*, 529.
- [174] Th. Bally, P. Diehl, E. Haselbach, A. S. Trasey, *Helv. Chim. Acta* **1975**, *58*, 2398.
- [175] J. F. M. Oth, K. Müllen, J.-M. Gilles, G. Schroeder, *Helv. Chim. Acta* **1974**, *57*, 1415.
- [176] J. F. M. Oth, K. Müllen, H. Schmickler, H.-W. Engels, E. Vogel, *Helv. Chim. Acta* **1980**, *63*, 2411.
- [177] J. Heinzer, J. F. M. Oth, D. Seebach, *Helv. Chim. Acta* **1985**, *68*, 1848.
- [178] J. Heinzer, J. F. M. Oth, *Helv. Chim. Acta* **1981**, *64*, 258.

- [179] W. Bosch, P. S. Pregosin, *Helv. Chim. Acta* **1979**, *62*, 838.
- [180] M. Ebener, G. v. Fircks, H. Günther, *Helv. Chim. Acta* **1991**, *74*, 1296.
- [181] F. Gerson, J. D. W. van Voorst, *Helv. Chim. Acta* **1963**, *46*, 2257.
- [182] F. Gerson, E. Heilbronner, W. A. Böll, E. Vogel, *Helv. Chim. Acta* **1965**, *48*, 1494; F. Gerson, W. Huber, J. Lopez, *J. Am. Chem. Soc.* **1984**, *106*, 5808.
- [183] F. Gerson, W. Huber, K. Müllen, *Helv. Chim. Acta* **1981**, *64*, 2766.
- [184] F. Gerson, W. B. Martin jr., H. N. C. Wong, C. C. Wing, *Helv. Chim. Acta* **1987**, *70*, 79.
- [185] P. Fürderer, F. Gerson, K. Hafner, *Helv. Chim. Acta* **1978**, *61*, 2974.
- [186] F. Gerson, Th. Wellauer, A. M. Oliver, H. N. Paddon-Row, *Helv. Chim. Acta* **1990**, *73*, 1596.
- [187] F. Gerson, X.-Z. Qin, *Helv. Chim. Acta* **1988**, *71*, 1498.
- [188] H. Baumann, J. M. F. Oth, *Helv. Chim. Acta* **1980**, *63*, 618.
- [189] K. Heusler, H. Ladiger, *Helv. Chim. Acta* **1969**, *52*, 1516.
- [190] F. Graf, K. Loth, Hs. H. Günthard, *Helv. Chim. Acta* **1977**, *60*, 710.
- [191] K. Loth, F. Graf, *Helv. Chim. Acta* **1981**, *64*, 1910.
- [192] K. Wüthrich, *Helv. Chim. Acta* **1965**, *48*, 779, 1012.
- [193] W. Schneider, A. v. Zelewsky, *Helv. Chim. Acta* **1965**, *48*, 1520.
- [194] P. Clopath, A. v. Zelewsky, *Helv. Chim. Acta* **1973**, *56*, 980.
- [195] A. v. Zelewsky, M. Zobrist, *Helv. Chim. Acta* **1981**, *64*, 2154.
- [196] J. Ammeter, N. Oswald, R. Bucher, *Helv. Chim. Acta* **1975**, *58*, 671.
- [197] M. Geoffroy, A. Llinares, *Helv. Chim. Acta* **1979**, *62*, 1605.
- [198] S. Ardjomand, E. A. C. Lucken, *Helv. Chim. Acta* **1971**, *54*, 176.
- [199] P. Gerber, H. Labhart, E. Kloster-Jensen, *Helv. Chim. Acta* **1971**, *54*, 2030.
- [200] A. Bauder, F. Tank, Hs. H. Günthard, *Helv. Chim. Acta* **1963**, *46*, 1453.
- [201] E. Baur (obituary by W. D. Treadwell), *Helv. Chim. Acta* **1944**, *27*, 1302.
- [202] E. Baur, *Helv. Chim. Acta* **1921**, *4*, 325.
- [203] E. Baur, A. Rebmann, *Helv. Chim. Acta* **1921**, *4*, 256.
- [204] E. Baur, *Helv. Chim. Acta* **1918**, *1*, 186.
- [205] E. Baur, A. Rebmann, *Helv. Chim. Acta* **1922**, *5*, 828.
- [206] E. Baur, 'Erforschung der Photolyse der Kohlensäure', Orell-Füssli Verlag, Zürich, 1943.
- [207] E. Baur, A. Rebmann, *Helv. Chim. Acta* **1922**, *5*, 221.
- [208] E. Baur, A. Perret, *Helv. Chim. Acta* **1924**, *7*, 910.
- [209] E. Baur, *Helv. Chim. Acta* **1929**, *12*, 793.
- [210] H. v. Halban, H. Geigel, *Z. physikal. Chem.* **1920**, *96*, 233; H. v. Halban, K. Rast, *ibid.* **1931** (Bodenstein Festband), *107*, 303.
- [211] H. Keller, H. v. Halban, *Helv. Chim. Acta* **1944**, *27*, 1253.
- [212] H. Keller, H. v. Halban, *Helv. Chim. Acta* **1945**, *28*, 59.
- [213] H. Schmid, M. Hochweber, H. v. Halban, *Helv. Chim. Acta* **1947**, *30*, 423, 1135.
- [214] W. Schmidt, *Helv. Chim. Acta* **1971**, *54*, 862.
- [215] P. Seiler, J. Wirz, *Helv. Chim. Acta* **1972**, *55*, 2693.
- [216] M. Gisin, J. Wirz, *Helv. Chim. Acta* **1976**, *459*, 2273.
- [217] R. Haag, J. Wirz, P. J. Wagner, *Helv. Chim. Acta* **1977**, *60*, 2595.
- [218] J. Wirz, G. Persy, E. Rommel, I. Murata, K. Nakasuji, *Helv. Chim. Acta* **1984**, *67*, 305; E. Hasler, E. Gassmann, J. Wirz, *ibid.* **1985**, *68*, 777.
- [219] R. Gschwind, E. Haselbach, *Helv. Chim. Acta* **1979**, *62*, 941.
- [220] E. Vauthey, P. Suppan, E. Haselbach, *Helv. Chim. Acta* **1988**, *71*, 93; see also: P. Suppan, *Topics Curr. Chem.* **1922**, *163*, 96.
- [221] M. Kirch, J.-M. Lehn, J.-P. Sauvage, *Helv. Chim. Acta* **1979**, *62*, 1345.
- [222] R. Ziessel, J. Hawecker, J.-M. Lehn, *Helv. Chim. Acta* **1986**, *69*, 1065.
- [223] K. Kalyanasundaram, O. Micic, E. Pramauro, M. Grätzel, *Helv. Chim. Acta* **1979**, *42*, 2432.
- [224] P. Jacques, A. Braun, *Helv. Chim. Acta* **1981**, *64*, 1800.
- [225] Ø. Burrau, *Kgl. Danske Videnskab, Selskab* **1927**, *7*, 1.
- [226] W. Heitler, F. London, *Z.f. Physik* **1927**, *44*, 455.
- [227] L. Pauling, G. W. Wheland, *J. Chem. Phys.* **1933**, *1*, 362; L. Pauling, 'The Nature of the Chemical Bond', Cornell University Press, Ithaca, 1940.
- [228] E. Hückel, *Z.f. Physik*, **1930**, *60*, 423; *ibid.* **1931**, *70*, 204; *ibid.* **1931**, *72*, 310; *ibid.* **1932**, *76*, 628; *Z. Elektrochem.* **1930**, *36*, 641; *ibid.* **1937**, *43*, 752, 827; *Z. Phys. Chem.* **1937**, *B35*, 163.

- [229] M.J.S. Dewar, *J. Am. Chem. Soc.* **1952**, *74*, 3341, 3345, 3350, 3353, 3357; M.J.S. Dewar, 'The Molecular Orbital Theory of Organic Chemistry', McGraw-Hill Book Comp., New York, 1969.
- [230] J.A. Pople, D.L. Beveridge, 'Approximate Molecular Orbital Theory', McGraw-Hill Book Comp., New York, 1970; J.N. Murrell, A.J. Harget, 'Semi-Empirical Self-Consistent-Field Molecular-Orbital Theory of Molecules', Wiley-Interscience, London, 1972.
- [231] H. Kuhn, *Helv. Chim. Acta* **1948**, *31*, 1441.
- [232] A.L. Bernoulli, *Helv. Chim. Acta* **1918**, *1*, 278, 289.
- [233] A.L. Bernoulli, *Helv. Chim. Acta* **1919**, *2*, 720.
- [234] H. Decker, *Helv. Chim. Acta* **1922**, *5*, 201, 285.
- [235] F. Ebel, E. Bretscher, *Helv. Chim. Acta* **1928**, *11*, 281.
- [236] F. Ebel, E. Bretscher, *Helv. Chim. Acta* **1929**, *12*, 443, 450.
- [237] G. Schwarzenbach, *Helv. Chim. Acta* **1929**, *12*, 820.
- [238] F. Ephraim, *Helv. Chim. Acta* **1928**, *11*, 1094.
- [239] E. Wiberg, *Helv. Chim. Acta* **1929**, *12*, 225.
- [240] G. Schwarzenbach, H. Brandenberger, G.H. Ott, O. Hagger, *Helv. Chim. Acta* **1937**, *20*, 490.
- [241] G. Schwarzenbach, G.H. Ott, O. Hagger, *Helv. Chim. Acta* **1937**, *20*, 498; G. Schwarzenbach, G.H. Ott, *ibid.* **1937**, *20*, 627.
- [242] G. Schwarzenbach, H. Brandenberger, *Helv. Chim. Acta* **1937**, *20*, 1253; G. Schwarzenbach, O. Hagger, *ibid.* **1937**, *20*, 1591.
- [243] G. Schwarzenbach, H. Mohler, J. Sorge, *Helv. Chim. Acta* **1938**, *21*, 1636.
- [244] G. Schwarzenbach, *Helv. Chim. Acta* **1944**, *27*, 576.
- [245] H. Kuhn, *Helv. Chim. Acta* **1949**, *32*, 2247.
- [246] K. Ruedenberg, ONR Technical Report, Laboratory of Molecular Spectra and Structure, University of Chicago, 1955, 230; J.R. Platt, K. Ruedenberg, C.W. Scherr, N.S. Ham, H. Labhart, W. Lichten, 'Free-Electron Theory of Conjugated Molecules', John Wiley & Sons, New York, 1964.
- [247] H. Kuhn, *Helv. Chim. Acta* **1951**, *34*, 1308.
- [248] H. Kuhn, *Helv. Chim. Acta* **1951**, *34*, 2371.
- [249] H.D. Försterling, H. Kuhn, 'Moleküle und Molekülanhäufungen, eine Einführung in die physikalische Chemie', Springer Verlag, Berlin, Heidelberg, New York, 1983.
- [250] H. Kuhn, W. Huber, *Helv. Chim. Acta* **1952**, *35*, 1155.
- [251] H. Labhart, *Helv. Chim. Acta* **1956**, *39*, 1320.
- [252] H. Labhart, *Helv. Chim. Acta* **1953**, *36*, 1689.
- [253] W. Kuhn, *Helv. Chim. Acta* **1948**, *31*, 1780.
- [254] L. Pauling, *Helv. Chim. Acta* **1949**, *32*, 2241.
- [255] O. Klement, *Helv. Chim. Acta* **1949**, *32*, 1777; *ibid.* **1951**, *34*, 1368.
- [256] O. Klement, *Helv. Chim. Acta* **1951**, *34*, 2230.
- [257] O. Klement, *Helv. Chim. Acta* **1952**, *35*, 1983.
- [258] W. Heitler, *Helv. Chim. Acta* **1955**, *38*, 5.
- [259] E. Heilbronner, M. Simonetta, *Helv. Chim. Acta* **1952**, *35*, 1036.
- [260] E. Heilbronner, R. W. Schmid, *Helv. Chim. Acta* **1954**, *37*, 2018.
- [261] E. Heilbronner, *Helv. Chim. Acta* **1953**, *36*, 170.
- [262] E. Heilbronner, *Helv. Chim. Acta* **1954**, *37*, 913.
- [263] E. Heilbronner, *Helv. Chim. Acta* **1954**, *37*, 921.
- [264] Hs. H. Günthard, H. Primas, *Helv. Chim. Acta* **1956**, *39*, 1645.
- [265] Hs. H. Günthard, E. Heilbronner, B. Messikommer, *Helv. Chim. Acta* **1952**, *35*, 2149.
- [266] E. Heilbronner, Hs. H. Günthard, *Helv. Chim. Acta* **1954**, *37*, 1037, 1534.
- [267] E. Heilbronner, Hs. H. Günthard, R. Gerdil, *Helv. Chim. Acta* **1956**, *39*, 1171.
- [268] H. Rutishauser, Nat. Bur. Standards, *Appl. Math. Series*, **1958**, *49*, 47.
- [269] E. Heilbronner, H. Rutishauser, F. Gerson, *Helv. Chim. Acta* **1959**, *42*, 2285, 2304.
- [270] F. Gerson, *Helv. Chim. Acta* **1961**, *54*, 471.
- [271] R. Hoffmann, *J. Phys. Chem.* **1963**, *39*, 1397; *ibid.* **1964**, *40*, 2047, 2474, 2745.
- [272] R. Gleiter, R. Seeger, *Helv. Chim. Acta* **1971**, *54*, 1217.
- [273] R. Gleiter, W.-D. Stohrer, R. Hoffmann, *Helv. Chim. Acta* **1972**, *55*, 893.
- [274] M.J.S. Dewar, E. Haselbach, *J. Am. Chem. Soc.* **1970**, *92*, 590; N. Bodor, M.J.S. Dewar, A. Harget, E. Haselbach, *ibid.* **1970**, *92*, 3854.
- [275] E. Haselbach, *Helv. Chim. Acta* **1971**, *54*, 1981.

- [276] E. Haselbach, *Helv. Chim. Acta* **1971**, *54*, 2257; E. Haselbach, E. Heilbronner, G. Schröder, *ibid.* **1971**, *54*, 153.
- [277] E. Haselbach, A. Schmelzer, *Helv. Chim. Acta* **1971**, *54*, 1299.
- [278] E. Heilbronner, A. Schmelzer, *Helv. Chim. Acta* **1975**, *58*, 936.
- [279] W. Kuhn, R. Rometsch, *Helv. Chim. Acta* **1944**, *27*, 1346.
- [280] G. Gustav, J. Sühnel, U. P. Wild, *Helv. Chim. Acta* **1978**, *61*, 2100.
- [281] M. Iseli, R. Geiger, G. Wagnière, *Helv. Chim. Acta* **1978**, *61*, 171.
- [282] H. Baumann, J. F. M. Oth, *Helv. Chim. Acta* **1982**, *65*, 1885.
- [283] M. Gisin, J. Wirz, *Helv. Chim. Acta* **1983**, *66*, 1556.
- [284] M. Jungen, *Helv. Chim. Acta* **1978**, *61*, 864.
- [285] T.-K. Ha, U. P. Wild, R. O. Kühne, Ch. Loesch, T. Schaffhauser, J. Stachel, A. Wokaun, *Helv. Chim. Acta* **1978**, *61*, 1193.
- [286] M. Wehrli, E. Pretsch, E. Clementi, W. Simon, *Helv. Chim. Acta* **1982**, *65*, 1996.
- [287] J. Silvestre, R. Hoffmann, *Helv. Chim. Acta* **1985**, *68*, 1461.
- [288] M. Nikles, D. Bur, U. Séquin, H. Huber, *Helv. Chim. Acta* **1992**, *75*, 1651.
- [289] H. Staudinger, *Ber. Dtsch. Chem. Ges.* **1920**, *53*, 1073.
- [290] H. Staudinger, W. Heuer, *Ber. Dtsch. Chem. Ges.* **1930**, *63*, 222.
- [291] H. Staudinger, R. Nodzu, *Helv. Chim. Acta* **1930**, *13*, 1350.
- [292] H. Staudinger, *Helv. Chim. Acta* **1932**, *15*, 213.
- [293] T. Koepfel, 'Interview with R. Signer', The Beckman Center for the History of Chemistry, 1986.
- [294] Th. Posternak, in 'Centenaire de l'École de Chimie' Université de Genève, 1979, p. 49.
- [295] K. H. Meyer, C. Ferri, *Helv. Chim. Acta* **1935**, *18*, 570.
- [296] K. H. Meyer, A. van der Wyk, *Helv. Chim. Acta* **1937**, *20*, 1321.
- [297] R. Signer (obituary by S. Gál and H. Arm), *Der Bund*, 1900, 14. Dezember.
- [298] R. Signer, H. Gross, *Helv. Chim. Acta* **1934**, *17*, 59.
- [299] R. Signer, H. Gross, *Helv. Chim. Acta* **1934**, *17*, 335.
- [300] R. Signer, H. Gross, *Helv. Chim. Acta* **1934**, *17*, 726.
- [301] R. Signer, T. Caspersen, E. Hammersten, *Nature* **1938**, *141*, 122.
- [302] R. Signer, H. Schwander, *Helv. Chim. Acta* **1949**, *32*, 853.
- [303] F. H. C. Crick, J. Watson, *Proc. Roy. Soc.* **1954**, *A223*, 80.
- [304] H. Arm, F. Hügli, R. Signer, *Helv. Chim. Acta* **1957**, *40*, 1200.
- [305] W. Kuhn (obituary by H. Kuhn), *Helv. Chim. Acta* **1964**, *47*, 689.
- [306] H. Kuhn, *Chimia* **1984**, *38*, 191.
- [307] W. Kuhn, *Kolloid Z.* **1934**, *68*, 2.
- [308] P. J. Flory, 'Principles of Polymer Chemistry', Cornell University Press, Ithaca, New York, 1953; 'Statistical Mechanics of Chain Molecules', Wiley Interscience, New York, 1969.
- [309] W. Kuhn, F. Grün, *Kolloid Z.* **1942**, *101*, 248.
- [310] W. Kuhn, H. Kuhn, *Helv. Chim. Acta* **1943**, *26*, 1394; *ibid.* **1945**, *28*, 1533.
- [311] W. Kuhn, H. Kuhn, *Helv. Chim. Acta* **1946**, *29*, 71, 609, 830.
- [312] P. Baertschi, *Helv. Chim. Acta* **1951**, *34*, 1324.
- [313] W. Kuhn, P. Moser, H. Majer, *Helv. Chim. Acta* **1961**, *44*, 770; W. Kuhn, *ibid.* **1948**, *31*, 1092, 1259; *ibid.* **1950**, *33*, 2057.
- [314] W. Kuhn, O. Künzle, A. Katchalsky, *Helv. Chim. Acta* **1948**, *31*, 1994; *Bull. Soc. Chim. Belg.* **1949**, *57*, 421.
- [315] W. Kuhn, *Experientia* **1949**, *5*, 318; W. Kuhn, B. Hargitay, *ibid.* **1951**, *7*, 1; *Angew. Chem.* **1951**, *63*, 283; W. Kuhn, B. Hargitay, A. Katchalsky, H. Eisenberg, *Nature* **1950**, *165*, 514; W. Kuhn, *Z. angew. Physik* **1952**, *4*, 108.
- [316] H.-F. Eicke, J. Rehak, *Helv. Chim. Acta* **1978**, *59*, 2883.
- [317] H.-F. Eicke, R. Hilfiker, M. Holz, *Helv. Chim. Acta* **1984**, *67*, 361.
- [318] H.-F. Eicke, R. Hilfiker, Gu Xu, *Helv. Chim. Acta* **1990**, *73*, 213.
- [319] H. Erlenmeyer, H. Gärtner, *Helv. Chim. Acta* **1934**, *17*, 30, 1226.
- [320] H. Erlenmeyer, H. Gärtner, *Helv. Chim. Acta* **1934**, *17*, 334, 549, 970.
- [321] H. Erlenmeyer, H. Gärtner, *Helv. Chim. Acta* **1935**, *18*, 419.
- [322] H. Erlenmeyer, H. Gärtner, *Helv. Chim. Acta* **1936**, *19*, 145, 331.
- [323] G. Schwarzenbach, A. Epprecht, H. Erlenmeyer, *Helv. Chim. Acta* **1936**, *19*, 1292.
- [324] K. Clusius (obituary by K. Schleich), *Helv. Chim. Acta* **1964**, *47*, 234.
- [325] K. Clusius, G. Dickel, *Naturwiss.* **1938**, *26*, 546.

- [326] K. Clusius, *Helv. Chim. Acta* **1950**, *33*, 2134.
- [327] E. Schumacher, *Helv. Chim. Acta* **1953**, *36*, 949.
- [328] E. Schumacher, K. Clusius, *Helv. Chim. Acta* **1953**, *36*, 969; K. Clusius, A. Meyer, *Helv. Chim. Acta* **1953**, *36*, 2045.
- [329] K. Clusius, K. Schleich, *Helv. Chim. Acta* **1962**, *45*, 1702.
- [330] K. Clusius, M. Hoch, *Helv. Chim. Acta* **1950**, *33*, 2122.
- [331] K. Clusius, H. R. Weisser, *Helv. Chim. Acta* **1952**, *35*, 400, 1524, 1548.
- [332] K. Clusius, M. Vecchi, *Helv. Chim. Acta* **1953**, *36*, 933; *ibid.* **1956**, *39*, 1469.
- [333] K. Clusius, F. Endtinger, K. Schleich, *Helv. Chim. Acta* **1960**, *43*, 1267.
- [334] K. Clusius, U. Piesbergen, *Helv. Chim. Acta* **1960**, *43*, 562.
- [335] K. Clusius, K. Schleich, M. Vecchi, *Helv. Chim. Acta* **1961**, *44*, 343.
- [336] K. Clusius, E. Schumacher, *Helv. Chim. Acta* **1949**, *32*, 671; *ibid.* **1958**, *41*, 2253.
- [337] W. Kuhn, *Helv. Chim. Acta* **1942**, *25*, 252; W. Kuhn, K. Ryffel, *ibid.* **1943**, *26*, 1693.
- [338] P. Baertschi, M. Thürkaf, *Helv. Chim. Acta* **1960**, *43*, 80; M. Thürkaf, N. Narten, W. Kuhn, *ibid.* **1960**, *43*, 989.
- [339] P. Baertschi, W. Kuhn, *Helv. Chim. Acta* **1957**, *40*, 1084.
- [340] W. Kuhn, M. Thürkaf, *Helv. Chim. Acta* **1958**, *41*, 938.
- [341] P. Baertschi, *Helv. Chim. Acta* **1953**, *36*, 773.
- [342] H. Gamsjäger, A. Grutter, P. Baertschi, *Helv. Chim. Acta* **1972**, *55*, 781; H. Gamsjäger, P. Baertschi, *ibid.* **1972**, *55*, 2154; S. C. Agarwal, P. Baertschi, H. Gamsjäger, *ibid.* **1972**, *55*, 2178.
- [343] H. Zollinger, *Helv. Chim. Acta* **1955**, *38*, 1597, 1617, 1623.
- [344] A. V. Willi, *Helv. Chim. Acta* **1964**, *47*, 647.
- [345] M. Avanesoff, Thang HoDac, T. Gäumann, *Helv. Chim. Acta* **1971**, *54*, 995, 1013.
- [346] M. Ballenegger, A. Ruf, T. Gäumann, *Helv. Chim. Acta* **1971**, *54*, 1373; R. Liardon, T. Gäumann, *ibid.* **1971**, *54*, 1968; M. A. Falik, T. Gäumann, *ibid.* **1976**, *59*, 987.
- [347] H. Öz, T. Gäumann, *Helv. Chim. Acta* **1975**, *58*, 2267; M. Poretti, T. Gäumann, *ibid.* **1985**, *68*, 1160.
- [348] N. Fujisaki, A. Ruf, T. Gäumann, *Helv. Chim. Acta* **1985**, *68*, 1168.
- [349] M. C. del Boca, *Helv. Chim. Acta* **1933**, *16*, 565.
- [350] J. Kaspar, *Helv. Chim. Acta* **1938**, *21*, 650.
- [351] E. Briner, A. Yalda, *Helv. Chim. Acta* **1942**, *25*, 1188.
- [352] F. Almasy, *Helv. Chim. Acta* **1945**, *28*, 1242.
- [353] R. Bieber, G. Trümpler, *Helv. Chim. Acta* **1947**, *30*, 706, 1109, 1534, 2000; P. Ruetschi, G. Trümpler, *ibid.* **1952**, *35*, 1021, 1486, 1957.
- [354] N. Ibl, G. Trümpler, *Helv. Chim. Acta* **1951**, *34*, 1217; N. Ibl, Y. Barrada, G. Trümpler, *ibid.* **1954**, *37*, 583, 2251.
- [355] E. Schumacher, F. Streiff, *Helv. Chim. Acta* **1958**, *41*, 829; E. Schumacher, E. Friedli, *ibid.* **1960**, *43*, 1706.
- [356] H.-K. Wipf, A. Olivier, W. Simon, *Helv. Chim. Acta* **1970**, *53*, 1605, 1732.
- [357] W. E. Morf, W. Simon, *Helv. Chim. Acta* **1971**, *54*, 2683.
- [358] A. P. Thoma, A. Viviani-Nauer, K. H. Schellenberg, D. Bedeković, E. Pretsch, V. Prelog, W. Simon, *Helv. Chim. Acta* **1979**, *62*, 2303.
- [359] K. Kalyanasundaram, M. Grätzel, *Helv. Chim. Acta* **1980**, *63*, 478; M. Neumann-Spallart, K. Kalyanasundaram, C. Grätzel, M. Grätzel, *ibid.* **1980**, *63*, 1111.
- [360] J. E. Sutcliffe, M. Neumann-Spallart, *Helv. Chim. Acta* **1981**, *64*, 2148.
- [361] J. Moser, M. Grätzel, *Helv. Chim. Acta* **1982**, *65*, 1436.
- [362] E. Briner, E. Perrottet, H. Paillard, B. Susz, *Helv. Chim. Acta* **1936**, *19*, 1354.
- [363] W. Kuhn, *Helv. Chim. Acta* **1948**, *31*, 1092, 1259; *ibid.* **1950**, *33*, 2057.
- [364] Hs. H. Günthard, T. Gäumann, *Helv. Chim. Acta* **1951**, *34*, 39.
- [365] T. Gäumann, U. Gugerli, C. Beguin, Hs. H. Günthard, *Helv. Chim. Acta* **1956**, *39*, 132; T. Gäumann, U. Gugerli, Hs. H. Günthard, *ibid.* **1956**, *39*, 145, 702.
- [366] T. Gäumann, Hs. H. Günthard, *Helv. Chim. Acta* **1953**, *36*, 1736.
- [367] T. Gäumann, Hs. H. Günthard, *Helv. Chim. Acta* **1954**, *37*, 971; Hs. H. Günthard, T. Gäumann, *ibid.* **1955**, *38*, 1352.
- [368] A. Beguin, T. Gäumann, *Helv. Chim. Acta* **1958**, *41*, 1951, 1971.
- [369] F. Gerson, T. Gäumann, E. Heilbronner, *Helv. Chim. Acta* **1958**, *41*, 1481; D. Meuche, T. Gäumann, E. Heilbronner, *ibid.* **1958**, *41*, 2230.

- [370] H.-F. Eicke, H. Christen, *Helv. Chim. Acta* **1972**, *55*, 213; H. Christen, H.-F. Eicke, M. Jungen, *ibid.* **1973**, *56*, 216.
- [371] H.-F. Eicke, J. C. W. Shepherd, *Helv. Chim. Acta* **1974**, *57*, 1971.
- [372] W. D. Treadwell, *Helv. Chim. Acta* **1925**, *8*, 89.
- [373] K. H. Goode, *J. Am. Chem. Soc.* **1922**, *44*, 26.
- [374] G. Schwarzenbach, *Helv. Chim. Acta* **1930**, *13*, 865.
- [375] T. Gäumann, J. Hoigné, Hs. H. Günthard, *Helv. Chim. Acta* **1959**, *42*, 426.
- [376] T. Gäumann, Hs. H. Günthard, *Helv. Chim. Acta* **1953**, *36*, 1736.
- [377] Th. Bürer, M. Kohler, Hs. H. Günthard, *Helv. Chim. Acta* **1958**, *41*, 2216.
- [378] U. P. Wild, Hs. H. Günthard, *Helv. Chim. Acta* **1965**, *48*, 1061.
- [379] R. E. Bühler, *Helv. Chim. Acta* **1968**, *51*, 1558.
- [380] J. R. Huber, U. P. Wild, Hs. H. Günthard, *Helv. Chim. Acta* **1967**, *50*, 589, 841; K. H. Gschwind, U. P. Wild, *Helv. Chim. Acta* **1973**, *56*, 809.
- [381] A. Bauder, F. Tank, Hs. H. Günthard, *Helv. Chim. Acta* **1963**, *46*, 1453.
- [382] P. Gerber, H. Labhart, E. Kloster-Jensen, *Helv. Chim. Acta* **1971**, *54*, 2030.
- [383] A. L. Bernoulli, Ph.-A. Guye, P. Dutoit, W. D. Treadwell, *Helv. Chim. Acta* **1921**, *4*, 456.