

may be cast in the form

$$\log_{10} \frac{K_A}{D^{1/2}} = 4.905 + \log_{10} \left[\frac{\bar{a}_e^{7/2}}{(s-1)^{1/2}} \right] + 243 \left(\frac{s-1}{s \bar{a}_e} \right) \cdot \frac{1}{D}$$

$$= 4.905 + \log_{10} \beta + 243 \gamma \frac{1}{D}, \quad (15)$$

where β and γ are specific constants which may be obtained from the intercept and gradient, respectively, of the isothermal plot of $\log_{10}(K_A/D^{1/2})$ against $1/D$. This treatment allows an evaluation of s and a_e . The former may be obtained from the equation

$$s = \beta^2 \gamma^7 \left(1 - \frac{1}{s} \right)^6. \quad (16)$$

The method is sensitive to uncertainties in β or γ , and yields values of s ranging from 5 for silver nitrate to 50 for tetra-*iso*-amylammonium nitrate. These values of s are reasonable in themselves and when compared with repulsive integers found in the study of crystals and gases.

Two items concerning this treatment call for comment.

(1) No appeal has been made to the concept of ionic radius. The term a_e is the average distance apart of the charges in the ion pair when in its state of lowest potential energy. The root-mean-square displacement about the average separation is given by the equation

$$\frac{\bar{x}}{a_e} = \left[\frac{D a_e k T}{(s-1) \varepsilon^2} \right]^{1/2}. \quad (17)$$

(2) If $\log_{10} K_A$, rather than $\log_{10}(K_A/D^{1/2})$ is plotted against $1/D$, a constant gradient is not obtained since

$$\frac{d \log_{10} K_A}{d(1/D)} = \frac{1}{2.303} \left[\frac{\varepsilon^2}{a_e k T} \left(\frac{s-1}{s} \right) - \frac{D}{2} \right], \quad (18)$$

which increases as $1/D$ increases. It is in this direction that deviations from linearity have recently been observed by BODENSEH and RAMSEY⁸.

I am indebted to Professor C. W. DAVIES for some fruitful discussions and to Professor J. B. RAMSEY for valuable criticisms and the courtesy of letting me have some of his publications in advance.

⁸ H. K. BODENSEH and J. B. RAMSEY, in the press.

The Zero Point Energies of Isotopic Homologues and Isomers*

By JACOB BIGELEISEN

Chemistry Department, Brookhaven National Laboratory, Upton, L. I., New York, and
Eidg. Techn. Hochschule, Zürich 6, Switzerland

and PAUL GOLDSTEIN

Chemistry Department, Brookhaven National Laboratory, Upton, L. I., New York
(Z. Naturforschg. **18 a**, 205—209 [1963]; eingegangen am 26. November 1962)

KLAUS CLUSIUS zum 60. Geburtstag gewidmet

An explicit formula is derived for the zero point energy of a system of coupled harmonic oscillators. It is shown that for the case of isotopic homologues this leads to an approximate linear relation in the number of equivalent isotopic substituents. It is shown that the zero point energy differences of successive members of an isotopic homologous series increases with further substitution of the heavy isotope. Through a study of the parabolic deviations from the linear rule, it is shown that intermediate members of an isotopic homologous series form a better basis for interpolation and extrapolation than the end members. The appropriate intermediate members are given by the second order sum rule.

It is a well-established empirical fact that the zero point energies of a set of homologous isotopic molecules are approximately a linear function of the number of equivalent isotopic substituents¹. In this

approximation, the zero point energies of equivalent isotopic isomers are the same. In fact, the zero point energies seem to obey the linear sum rule in $\lambda_i = 4\pi^2 \nu_i^2$ of DECIUS and WILSON² and SVERDLOW³.

* Research carried out under the auspices of both the U.S. Atomic Energy Commission and National Science Foundation.

¹ H. J. BERNSTEIN and A. D. E. PULLIN, J. Chem. Phys. **21**, 2188 [1953].

² J. C. DECIUS and E. B. WILSON, JR., J. Chem. Phys. **19**, 1409 [1951].

³ L. M. SVERDLOW, Dokl. Akad. Nauk, SSSR **78**, 1115 [1951].



BERNSTEIN and PULLIN¹ have further shown that similar rules are obeyed for

$$\sum v_i^x (A Y_{n-z} Y'_z) - \sum v^x (A Y_{n-z+1} Y'_{z-1}),$$

where $x=3/2$ and 3. For non-isotopic homologues they have found empirical rules in $x=1, 2, -1, -2$. The rules hold separately for common symmetry classes.

The basis of the BERNSTEIN rules is as follows. A property of a molecule can be represented as an additive property, if it can be expressed in terms of the properties of the atoms plus interaction between atomic pairs. Such a constitutive property will have a parabolic dependence on the number of substituents. For instance, in the case of the substituted methanes

$$P_{CX_4-n}Y_n = PCX_4 + \frac{n}{4}(PCY_4 - PCX_4 + 8\Delta_{XY}) - \frac{n^2\Delta_{XY}}{2} \quad (1)$$

where P is a constitutive property and

$$\Delta_{XY} = 2p_{XY} - p_{XX} - p_{YY}. \quad (2)$$

The quantities p_{XY} , p_{XX} , and p_{YY} are the contributions to P from the interaction between X and Y, two X's and two Y's respectively. It is precisely this quantity Δ_{XY} which is zero for $\sum \lambda_i$, the sums of the squares of the frequencies, for isotopic homologues and isomers. The quantity Δ_{XY} has been shown not to be zero in general for $\sum \lambda_i^2$ for a homologous series of isotopic molecules^{4,5}. The special reason why Δ_{XY} is zero for $\sum \lambda_i$ for isotopic molecules is the fact that $\sum \lambda_i$ depends on the properties of the atoms taken one at a time in the force field of the other atoms of the molecule. If the force field is independent of the substituent, as it is for isotopic molecules, then and only then does one obtain $\Delta_{XY}=0$ and a linear rule. The relationship $\Delta_{XY}=0$ does not hold in general for $\sum \lambda_K^2$ for isotopic homologues since

$$\sum_{i,j}^{3n-6} \lambda_K^2 = \sum_i^{3n} \sum_j^{3n} a_{ij}^2 \mu_i \mu_j,$$

where μ_i and μ_j are the reciprocal masses of the

i 'th and j 'th atoms respectively. Although a_{ij}^2 is isotope invariant, the product $a_{ij}^2 \mu_i \mu_j$ is not and $\sum \lambda^2$ will have a parabolic dependence on the number of substituents. Specific members of the isotopic homologous series obey a linear rule in $\sum \lambda_K^2$. Higher order rules both in $\sum \lambda_K^n$ and $\sum \pi \lambda_i \lambda_j \lambda_k \dots \lambda_l$ have been obtained⁶ and the number of members of a homologous series that obey linear rules in $\sum \lambda^n$ or $\sum \pi \lambda_i \lambda_j \dots \lambda_l$ decreases rapidly as the power n or the number of eigenvalues in the product increases. The ultimate rule, the product rule of TELLER⁷ and REDLICH⁸, relates any pair of isotopic molecules. For the product of the $3n-6$ internal vibrations one obtains a linear rule for a set of isotopic homologues only in the approximation that the ratio of the molecular weights and moments of inertia of successive pairs is a constant.

To date, the zero point energy rules rest only on a well established empirical basis plus the argument of BERNSTEIN^{7,9} concerning the requirements for a constitutive property. Further examples, with calculated harmonic frequencies, are given in the following paper¹⁰. In the present paper we shall give a mathematical formulation of the rule, which will then show us the nature of the approximations involved plus the range of the validity of the rule¹¹. The zero point energy of a molecule or a system of coupled oscillators is a quantity of fundamental interest and any method of obtaining the zero point energy without a complete solution of the secular equation is useful¹²⁻¹⁴.

Zero Point Energy and the Eigenvalues of the Classical Secular Equations of Motion

In this section we obtain a relationship between the zero point energy of a system of coupled oscillators and the eigenvalues of order n of the secular equations

$$\mathbf{H}^n \mathbf{A}_K = \lambda_K^n \mathbf{A}_K. \quad (3)$$

In Cartesian coordinates, the elements of \mathbf{H} are $H_{ij} = \mu_i a_{ij}$, where μ_i is the reciprocal of the mass of the i 'th atom and a_{ij} is a Cartesian force con-

⁴ J. BIGELEISEN, J. Chem. Phys. **28**, 694 [1958].

⁵ L. M. SVERDLOV, Optika i Spektroskopija **8**, 36 [1960].

⁶ L. M. SVERDLOV, Dokl. Akad. Nauk, SSSR **86**, 513 [1952].

⁷ W. R. ANGUS et al., J. Chem. Soc. **1936**, 971.

⁸ O. REDLICH, Z. phys. Chem. B **28**, 371 [1935].

⁹ H. J. BERNSTEIN, J. Chem. Phys. **20**, 263 [1952].

¹⁰ J. BIGELEISEN, R. E. WESTON, JR., and M. WOLFSBURG, Z. Naturforsch. **18a**, 210 [1963].

¹¹ For another approach to this problem see M. WOLFSBERG, Z. Naturforsch. **18a**, 216 [1963].

¹² C. DOMB and L. SALTER, Phil. Mag. **43**, 1083 [1952].

¹³ E. MONTROLL and R. B. POTTS, Phys. Rev. **100**, 525 [1955].

¹⁴ J. BIGELEISEN, J. Chem. Phys. **34**, 1485 [1961].

stant⁴. The vector \mathbf{A}_k is a vector whose components give the transformation from Cartesian coordinates to the k 'th normal coordinate. We define a characteristic length, ω_0 , for a set of homologous isotopic

molecules¹⁵. This permits us to express each frequency in reduced units

$$x_k^{1/2} \equiv \omega_k/\omega_0 \equiv (\lambda_k/\lambda_0)^{1/2}. \quad (4)$$

We now expand ω_k/ω_0 about the point $x_k - 1$ and obtain the series

$$x_k^{1/2} \equiv \omega_k/\omega_0 \equiv (\lambda_k/\lambda_0)^{1/2} = \frac{1}{2} + \frac{x_k}{2} + \sum_{p=2}^{\infty} \frac{(-1)^{p+1} (2p-2)!}{2^{2p-1} (p-1)! p!} (x_k - 1)^p, \quad [|x_k - 1| \leq 1]. \quad (5)$$

Since the series in $(x - 1)^p$ is absolutely convergent, we can add each term to the corresponding term of an absolutely convergent series to obtain the total zero point energy, ε_0 , in reduced units

$$2\varepsilon_0 = \sum_k^{3n-6} x_k^{1/2} = \frac{3n-6}{2} + \frac{\sum_k x_k}{2} + \sum_k^{3n-6} \sum_{p=2}^{\infty} \frac{(-1)^{p+1} (2p-2)!}{2^{2p-1} (p-1)! p!} (x_k - 1)^p, \quad [|x_k - 1| \leq 1]. \quad (6)$$

The zero point energy difference between two molecules, ε_0' and ε_0 , is similarly obtained by term by term subtraction of two absolutely convergent series

$$\begin{aligned} 2(\varepsilon_0' - \varepsilon_0) &= \sum_k^{3n-6} x_k'^{1/2} - x_k^{1/2} = \sum_k^{3n-6} (\omega_k' - \omega_k)/\omega_0 \\ &= \frac{1}{2} \sum_k^{3n-6} (x_k' - x_k) + \sum_k^{3n-6} \sum_{p=2}^{\infty} \frac{(-1)^{p+1} (2p-2)!}{2^{2p-1} (p-1)! p!} \{ (x_k' - 1)^p - (x_k - 1)^p \} \quad [|x_k' - 1| \leq 1, \quad |x_k - 1| \leq 1] \end{aligned} \quad (7)$$

which can be written

$$\begin{aligned} (1/\omega_0) \sum_k^{3n-6} (\omega_k' - \omega_k) &= \frac{1}{2} \sum_k^{3n-6} \delta \lambda_k/\lambda_0 + \sum_k^{3n-6} \sum_{p=2}^{\infty} \frac{(-1)^{p+1} (2p-2)!}{2^{2p-1} (p-1)!} \sum_{j=0}^{p-1} \frac{(-1)^j}{j!(p-j)!} \frac{\delta \lambda_k^{p-j}}{\lambda_0^{p-j}} \\ &\quad \left[\frac{\lambda_k'}{\lambda_0} - 1 \leq 1; \quad \frac{\lambda_k}{\lambda_0} - 1 \leq 1 \right] \end{aligned} \quad (8)$$

where $\delta \lambda_k^{p-j} \equiv \lambda_k'^{p-j} - \lambda_k^{p-j}$. We note that series (8) cannot be rearranged into a sum over p in $\delta \lambda_i^{p-j}/\lambda_0^{p-j}$, since such a series is *per se* not convergent.

The first term in the series in equation (8) has the properties of the first order sum rule in $\sum \lambda_k$. That is, the difference between successive members of an isotopic homologous series is constant and independent of the isotopic composition of other atoms in the molecule. Equivalent isomers are the same. This term leads to a linear dependence of the zero point energy for a homologous series. The second term $p=2$ has the properties of both the first and second order sum rules, $\sum \lambda_k$ and $\sum \lambda_k^2$. The term in $\sum \lambda_k^2$ is the first deviation to be expected from a linear law and it is of the form $a_{ij}^2 \mu_i \mu_j$, the mutual motion of two atoms from their equilibrium position. Higher terms similarly add (or subtract) terms in $\sum \lambda_k^3$, $\sum \lambda_k^2$, $\sum \lambda_k$ for $p=3$

$\sum \lambda_k^4$, $\sum \lambda_k^3$, $\sum \lambda_k^2$, $\sum \lambda_k$ for $p=4$, etc. It is immediately apparent that the present series expansion in $\sum (\lambda_k/\lambda_0)^p$ makes use of all of the isotope sum rules discussed in the Introduction.

In the following paper, the convergence properties of the various series are investigated in some detail. Convergence is shown to be fairly good, with proper choice of ω_0 , for zero point energies and isotope effects on them when one uses the series expansion with only terms up to $p=2$. It therefore appears worthwhile to investigate the truncated expansion

$$\sum \omega_k' - \omega_k = \frac{3}{4\omega_0} \sum_k [\delta \lambda_k - \frac{1}{6} \delta \lambda_k^2/\lambda_0 + \dots]. \quad (9)$$

The properties of the individual terms, $\sum \delta \lambda_k$ and $\sum \delta \lambda_k^2$, have been discussed previously^{2-4, 16}.

¹⁵ The advantages of using one characteristic length for a given sequence of isotopic homologues was pointed out to us by Professor JOSEPH B. KELLER.

¹⁶ J. BIGELEISEN, "Proceedings of the International Symposium on Isotope Separation", edited by J. KISTEMAKER, J. BIGELEISEN and A. O. C. NIER, North-Holland Publ. Co., Amsterdam 1958, pp. 149-152.

From equation (9) we shall now derive a theorem relating the zero point energy differences of successive members of a homologous isotopic sequence: "In any isotopic homologous series the zero point energy difference between successive pairs increases with the number of heavy isotopic substituents." The term in $\sum \delta \lambda_k$ is a constant, equal to $(\mu'_i - \mu_i) a_{ii}$, between successive members of the series. The i 'th type atom undergoes successive isotopic substitution. The term $\sum \delta \lambda_k^2$ is equal to

$$\sum \lambda_k'^2 - \lambda_k^2 = (\mu_i'^2 - \mu_i^2) \sum_{q_i}^3 \sum_{q_i}^3 a_{q_i q_i}^2 + 2(\mu_i' - \mu_i) \sum_{j \neq i}^3 \sum_{q_i}^3 \mu_j a_{q_i q_j}^2 \quad (10)$$

The term $(\mu_i'^2 - \mu_i^2) a_{ii}^2$ again is constant between successive members of the series. However, the term $2(\mu_i' - \mu_i) \sum \sum \mu_j a_{q_i q_j}^2$ will be different for successive pairs in the series. This sum over all atoms in the molecule will differ between successive pairs by the number of isotopic substitutions of the type i that have taken place. The term will be smaller as one goes to higher substitution of the heavy isotope. It makes a negative contribution to the zero point energy difference [cf. equation (9)]. This completes the proof of the theorem, which is illustrated in the following paper¹⁰.

We are now in a position to understand why the zero point energy is practically a linear function of the number of isotopic substituents for benzene, shows slight deviations for the ethylenes and still larger ones for the isotopic hydrogens as shown in the following paper¹⁰. The deviations from linearity come from the $(\mu_i' - \mu_i) \sum \mu_j a_{ij}^2$ terms. In all cases the mass factor $(\mu_i' - \mu_i)$ is 1/2 in atomic units. For the case of hydrogen $\mu_j a_{ij}^2$ is proportional to the square of the stretching vibrational frequency of the hydrogen molecule multiplied by the stretching force constant. For the ethylene molecules, the difference between successive pairs comes from mutual motion of hydrogen atoms, which is therefore a bending vibration. These vibrations have force constants some 5 times smaller than stretching force constants and so the zero point energy rule shows deviations 25 times smaller. Further, the out-of-plane motions each involve mutual motion of hydrogen atoms in the bending modes. They should show the largest percentage deviation from linearity and the calculations¹⁰ show just this behavior.

Finally, for the case of the benzene molecules, the difference between successive pairs involves the motion of hydrogen atoms which are separated by at least two carbon atoms. The force constant for this motion is very small and the benzenes, therefore, obey a linear zero point energy rule to a very high approximation.

The Second Order Corrections and the Application of the Second Order Sum Rules

In equations (9) and (10) we have found the general parabolic terms for the zero point energy of a sequence of isotopic homologues. This explicit expression can now be used to improve the interpolation of zero point energies either by exact calculation, using expression (10), or by the linear interpolation and extrapolation procedure to be discussed presently. We shall use the specific example of the deuterio methanes inasmuch as BERNSTEIN⁹ has developed parabolic formulae for the case of substituted methanes. For simplicity we write

$$\begin{aligned} \sum \omega_k' &= E_0, & \sum (\omega_k)_n &= E_n, & \sum \lambda_k' &= S_0, \\ \sum (\lambda_k)_n &= S_n, & \sum \lambda_k'^2 &= L_0^2, & \sum (\lambda_k)_n^2 &= L_n^2 \end{aligned}$$

and equation (9) reads

$$E_n = E_0 - \frac{3}{4 \omega_0} \left[(S_0 - S_n) - \frac{L_0^2 - L_n^2}{6 \lambda_0} \right]. \quad (9')$$

$$\text{But} \quad S_0 - S_n = n(S_0 - S_1), \quad (11)$$

$$\frac{L_0^2 - L_n^2}{6 \lambda_0} \quad (10')$$

$$= \frac{1}{6 \lambda_0} \sum^n \{ (\mu'^2 - \mu^2) a_{qq}^2 + 2(\mu' - \mu) \sum \mu_j a_{ij}^2 \}.$$

In equation (10') \sum^n is the summation over the successive isotopic substitutions to arrive at $\text{CH}_{4-n}\text{D}_n$ from CH_4 . In this context n is the number of deuterium atoms in the last molecule. The sum over the $(\mu'^2 - \mu^2)$ terms is n times the term itself. The sum over this term, after multiplication by $(1/6 \lambda_0)$, can be written as $n b$. The pair interaction summation is most conveniently carried out by first summing the interaction $2(\mu' - \mu) \sum \mu_j a_{ij}^2$ in going from $\text{CH}_{4-i}\text{D}_i$ to $\text{CH}_{3-i}\text{D}_{i+1}$ and then summing i from zero to $n-1$. The pair interaction to go from $\text{CH}_{4-i}\text{D}_i$ to $\text{CH}_{3-i}\text{D}_{i+1}$ is

$$\frac{2(\mu' - \mu)}{6 \lambda_0} \sum \mu_j a_{ij}^2 = 4(n_{\text{IH}} \alpha_{\text{H}} + n_{\text{ID}} \alpha_{\text{D}}) \quad (12)$$

$$\text{where } \alpha_H = \frac{1}{12 \lambda_0} (\mu_H - \mu_D) \mu_H a_{HH}^2, \quad (13)$$

$$\alpha_D = \frac{1}{12 \lambda_0} (\mu_H - \mu_D) \mu_D a_{HH}^2. \quad (13 a)$$

In equation (12) n_{iH} is the number of equivalent protons in $\text{CH}_{3-i}\text{D}_{i+1}$ and n_{iD} is the number of equivalent deuterons in $\text{CH}_{4-i}\text{D}_i$. The summation over i to give the molecule $\text{CH}_{4-n}\text{D}_n$ gives

$$\sum n_{iH} \alpha_H + n_{iD} \alpha_D = 6 \alpha_H - \frac{(n_H)(n_H-1)}{2} \alpha_H + \frac{(n_D)(n_D-1)}{2} \alpha_D. \quad (14)$$

$$\text{Since } n_H = 4 - n_D = 4 - n \quad (15)$$

$$\text{and } \alpha_H = 2 \alpha_D = \alpha \quad (16)$$

we obtain

$$\frac{L_0^2 - L_n^2}{6 \lambda_0} = n b + \alpha n (13 - n). \quad (17)$$

Equations (11) and (17) combine with (9') to give

$$E_n = E_0 + \frac{n}{4} \left(E_4 - E_0 + \frac{12 \alpha}{\omega_0} \right) - \frac{3 n^2 \alpha}{4 \omega_0}. \quad (18)$$

If we compare equation (18) with equation (1), we see that

$$\Delta_{XY} = \frac{3}{2} \frac{\alpha}{\omega_0}. \quad (19)$$

It is obvious from equation (18) as well as the theorem that the difference in zero point energies of successive pairs increases with the number of heavy isotopic substituents, that E_n calculated by a linear interpolation between E_0 and E_4 will be lower than the true value. The deviations in units of α/ω_0 are shown in Fig. 1. Equation (18) is a parabola with its axis at $n=2$ parallel to the axis $E_n - E_0$. As such the deviations at $n=1$ and $n=3$ are equal. A line drawn through these points is parallel to the horizontal axis. This can also be deduced directly from the first and second order sum rules since in the case of the methanes⁴

$$2(S_1 - S_3) = (S_0 - S_4) \quad (20)$$

$$\text{and } 2(L_1^2 - L_3^2) = (L_0^2 - L_4^2). \quad (21)$$

The set CH_3D and CHD_3 thus form a better basis for the interpolation and extrapolation of the zero point energies than CH_4 and CD_4 . In terms of the mono- and tri-deutero compounds, the zero point energy of any member of the sequence is

$$E_n = E_1 - \frac{9 \alpha}{4 \omega_0} + \frac{(n-1)}{2} (E_3 - E_1) + \frac{3 n \alpha}{\omega_0} - \frac{3 n^2 \alpha}{4 \omega_0}. \quad (22)$$

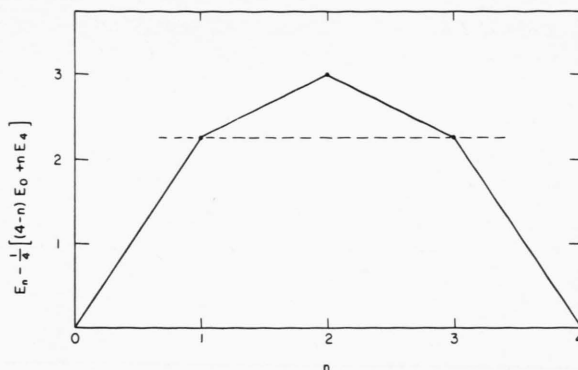


Fig. 1. Deviations from the linear zero point energy rule in the deuteromethanes (in units of α/ω_0).

The relative deviations calculated on the $\text{CH}_3\text{D} - \text{CHD}_3$ basis *vs.* the $\text{CH}_4 - \text{CD}_4$ basis are shown in Table 1. The root mean square deviation on the $\text{CH}_3\text{D} - \text{CHD}_3$ is 0.75 that on the $\text{CH}_4 - \text{CD}_4$ basis.

n	($\text{CH}_3\text{D} - \text{CHD}_3$) basis δ	($\text{CH}_4 - \text{CD}_4$) basis δ
0	-9/4	0
1	0	9/4
2	3/4	3
3	0	9/4
4	-9/4	0
$\sum \delta^2$	171/16	306/16

Table 1. Parabolic Deviations in the Zero Point Energies of the Deuteromethanes (in units of α/ω_0).

The disadvantage in the use of the intermediate molecules with their lower symmetry is that their spectra are not as easily established as the more symmetrical molecules. When this problem does not present itself, then the intermediate molecules should be used as a basis for the interpolation and extrapolation of the zero point energies of the homologous sequence. For isotopic homologues the appropriate choice is readily determined from the second order sum rule.

Acknowledgement

It is a pleasure to acknowledge a fruitful discussion with Professor JOSEPH B. KELLER, which led to the particular expansion method developed. One of us (J.B.) wishes to thank Professor Hs. H. GÜNTARD for the hospitality of the Laboratorium für physikalische Chemie at the E. T. H.