m/e 512). NMR. (CDCl$_3$): 1,23 (d, J = 7 Hz, 3 H, C(17)—CH$_3$); 1,38 (s, 6 H, C(4)-Methyle); 1,68 (s, 3 H, C(10)—CH$_3$); 1,99 (3 H), 2,33 (9 H), 2,42 (3 H) (je s, COCH$_3$); 3,45 (Sextett, J = 7 Hz, M-Teil, 1 H); 4,5–4,2 (AB-Teil, J_{AB} = 12 Hz, 2 H).

LITERATURVERZEICHNIS

[1] *P. Rüedi & C. H. Eugster*, Helv. *54*, 1606 (1971).

[2] *D. Karanatsios, J. S. Scarpa & C. H. Eugster*, Helv. *49*, 1151 (1966).

[3] *S. M. Kupchan, A. Karim & C. Marcks*, J. org. Chemistry *34*, 3912 (1969).

[4] *J. B.-son Bredenberg & J. Gripenberg*, Acta chem. scand. *10*, 1511 (1956).

[5] *J. B.-son Bredenberg*, Acta chem. scand. *14*, 385 (1960).

[6] *Y.-L. Chow & H. Erdtman*, Acta chem. scand. *16*, 1305 (1962).

[7] *A. Balmain & J. D. Connolly; M. Ferrari, E. L. Ghisalberti, U. M. Pagnoni & F. Pelizzoni*, Chem. Commun. *1970*, 1244.

[8] *M. Ribi, A. Chang Sin-Ren, H. P. Küng & C. H. Eugster*, Helv. *52*, 1685 (1969).

[9] *N. J. Leonard & P. M. Mader*, J. Amer. chem. Soc. *72*, 5388 (1950); *K. Alder, H. K. Schäfer, H. Esser, H. Krieger & R. Reubke*, Liebigs Ann. Chem. *593*, 23 (1955).

[10] *J. F. Grove & B. J. Riley*, J. chem. Soc. *1961*, 1105.

[11] *J. Delobelle & M. Fétizon*, Bull. soc. chim. France *1961*, 1632.

[12] *M. Fétizon & G. Moreau*, Bull. soc. chim. France *1965*, 3479.

[13] *J. B.-son Bredenberg & J. N. Shoolery*, Acta chem. scand. *14*, 556 (1960).

[14] *Y. Kondo, T. Ikenoue & T. Takemoto*, Chem. Pharm. Bull. (Tokyo) *11*, 678 (1963).

[15] *E. Wenkert, A. Afonso, P. Beak, R. W. J. Carney, P. W. Jeffs & J.-D. McChesney*, J. org. Chemistry *30*, 713 (1965).

[16] *G. Snatzke*, Tetrahedron *21*, 413 (1965).

[17] *E. Wenkert & B. G. Jackson*, J. Amer. chem. Soc. *80*, 211 (1958).

[18] *R. C. Cambie & W. A. Denny*, Austr. J. Chem. *22*, 1989 (1969).

[19] *K. Doi & T. Shibuya*, Phytochemistry *11*, 1175 (1972); *L. Briggs*, Tetrahedron 7, 270 (1959); *K. Hata & M. Sogo*, Chem. Abstr. *53*, 22925 (1959).

166. On the Correlation between Photoelectron and Electronic Spectra. Part. II[1]): Experimental Indications about the Shape of Lone Pair Orbitals

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

Physikalisch-Chemisches Institut der Universität Basel

(26. IV. 72)

Summary. For a π-molecular system containing two symmetry-equivalent heteroatoms, a qualitative relationship between the difference in the n-ionization potentials (ΔIP) and the difference between the $n \rightarrow \pi^*$ excitation energies ($\Delta\Delta E$) is derived, using semi-localized orbitals as a basis. The comparison between ΔIP and $\Delta\Delta E$ yields information about the energies and/or the shapes of the two lone pair MO's in the model system. The results provide further insight into the 'through space' and 'through bond' interaction concept introduced by *Hoffmann*.

Introduction. – In part I of this series [1] we have indicated a simple numerical procedure to correlate the results obtained from electronic spectra and photoelectron (PE) spectra. Its application to *trans*-azomethane has lent support to the experi-

---

[1]) Part I: cf. ref. [1].

mental indication that the splitting between the two n-ionization potentials $(\varDelta IP)$ is considerably smaller than the splitting between the two $n \rightarrow \pi^*$ transition energies $(\varDelta\varDelta E)$. This result demonstrates the importance of electron-electron repulsion, given that theoretical treatments which neglect this energy term would predict $\varDelta IP = \varDelta\varDelta E$.

In this paper we try to qualitatively illuminate the relationship between the observation $\varDelta IP \neq \varDelta\varDelta E$ and the electronic structure of such π-molecular systems with heteroatoms.

Theoretical considerations

I. 'Through space' and 'through bond' contributions to $\varDelta IP$. – Consider a planar π-molecular system containing two symmetry equivalent heteroatoms. Experience shows that any quantum-chemical calculation based on the *Hartree-Fock* method yields two high lying occupied σ-orbitals in the set of SCF-MO's (φ_i-space) which show large coefficients and particular directional properties of the orbital charge distribution at the two heteroatoms, indicating some non-bonding character for the associated electron pairs. These MO's, n_s and n_a[2]) with orbital energies $\varepsilon(n_s)$ and $\varepsilon(n_a)$, are usually called 'the lone pair MO's', despite the fact that they also extend over other spatial regions of the molecule.

A conceptually more attractive description of these lone pairs may be obtained by subjecting the SCF-MO's to a – physically irrelevant – orthogonal transformation, using *e.g.* the localization criterion of *Edmiston & Ruedenberg* [2]. The resulting orthogonal localized MO's (LMO's, φ_i'-space) correspond closely to the bond-picture used by chemists to describe the groundstate electronic structure of molecules. In our case two degenerate LMO's will be found, n_1' and n_2' (orbital energies $\alpha_{n_1'} = \alpha_{n_2'}$), with spatial properties typical for the lone pairs at one or the other of the heteroatoms. The LMO's n_1', n_2' can be used to construct the symmetry-adapted semi-localized MO's (SLMO's) n_s', n_a':

$$n_s' = 1/\sqrt{2}\,(n_1' + n_2')\ (1); \qquad n_a' = 1/\sqrt{2}\,(n_1' - n_2') \tag{2}$$

The same procedure can be applied to the remaining set of the φ_i' – LMO's, leading to the SLMO's φ_{is}' and φ_{ia}', resp. A reasonable way to pick out n_s, n_a in the φ_i-space is to calculate the overlaps:

$$\langle \varphi_i | n_s' \rangle, \langle \varphi_i | n_a' \rangle;\ i = 1, \ldots \mathrm{occ.}, \tag{3}$$

which are maximal for $\varphi_i = n_s$ or n_a, resp.:

$$\langle n_s | n_s' \rangle = s_1;\ \langle n_a | n_a' \rangle = a_1. \tag{4}$$

Let us now expand the SCF-MO's n_s and n_a, using the SLMO's as a basis set:

$$n_s = s_1\, n_s' + \sum^{\mathrm{all}\ \varphi_{is}'} s_i'\, \varphi_{is}' \tag{5}$$

$$n_a = a_1\, n_a' + \sum^{\mathrm{all}\ \varphi_{ia}'} a_i'\, \varphi_{ia}'. \tag{6}$$

---

[2])   The symbols s, a are commonly used to designate the transformational properties of the MO's – symmetric or antisymmetric – with respect to a particular symmetry element of order 2 in the molecule.

Introducing the equalities

$$\chi_s' = \frac{1}{\sqrt{1-s_1^2}} \sum^{\text{all } \varphi_{is}'} s_i' \varphi_{is}', \tag{7}$$

$$\chi_a' = \frac{1}{\sqrt{1-a_1^2}} \sum^{\text{all } \varphi_{ia}'} a_i' \varphi_{ia}', \tag{8}$$

we can write (5) and (6) as

$$n_s = s_1 n_s' + s_2 \chi_s' \quad (s_1 > s_2), \tag{9}$$
$$n_a = a_1 n_a' + a_2 \chi_a' \quad (a_1 > a_2), \tag{10}$$

with the normalization condition

$$s_1^2 + s_2^2 = a_1^2 + a_2^2 = 1. \tag{11}$$

We now define the matrix elements:

$$\langle n_s' | F | n_s' \rangle = \alpha_{n_s'}, \quad \langle n_a' | F | n_a' \rangle = \alpha_{n_a'}, \tag{12}$$

$$\langle \chi_s' | F | \chi_s' \rangle = \alpha_{\chi_s'}, \quad \langle \chi_a' | F | \chi_a' \rangle = \alpha_{\chi_a'}, \tag{13}$$

$$\langle n_s' | F | \chi_s' \rangle = \beta_s, \quad \langle n_a' | F | \chi_a' \rangle = \beta_a, \tag{14}$$

F being the *Fock*-operator. Since n_s', n_a' are the highest lying SLMO's in the σ-manifold, we have to consider only mixing with lower lying σ-SLMO's χ_s', χ_a'. Hence:

$$\Delta_s = \alpha_{n_s'} - \alpha_{\chi_s'} > 0, \quad \Delta_a = \alpha_{n_a'} - \alpha_{\chi_a'} > 0. \tag{15}$$

According to second order perturbation theory, the SCF-MO energies $\varepsilon(n_s)$, $\varepsilon(n_a)$ are approximately given by

$$\varepsilon(n_s) = \alpha_{n_s'} + \frac{\beta_s^2}{\Delta_s}, \tag{16}$$

$$\varepsilon(n_a) = \alpha_{n_a'} + \frac{\beta_a^2}{\Delta_a}, \tag{17}$$

whereas the mixing coefficients from (9), (10) are given by

$$s_2 = \frac{\beta_s}{\Delta_s} \quad (18); \qquad a_2 = \frac{\beta_a}{\Delta_a}. \tag{19}$$

We now take the difference between (17) and (16), insert (18) and (19) and apply *Koopmans'* theorem [3]. This leads to

$$\Delta IP = IP(n_s) - IP(n_a) \approx (\alpha_{n_a'} - \alpha_{n_s'}) + (a_2^2 \Delta_a - s_2^2 \Delta_s), \tag{20}$$
$$\text{Term ①} \qquad \text{Term ②}$$

where ΔIP is the difference between the observed ionization potentials, corresponding to ejection of an electron from the n_s-MO ($IP(n_s)$) and the n_a-MO ($IP(n_a)$).

   Term ① in (20) contains the 'through space' [4] contribution to ΔIP, arising from the direct interaction of the LMO's n_1', n_2'. The sign of ① (sgn ①) depends on the sign of the interaction element $\langle n_1' | F | n_2' \rangle = \beta_{n_1' n_2'}$, which in most cases can be found by inspection. $Sgn \, \beta_{n_1' n_2'}$ defines the 'natural sequence' of the SLMO's n_s', n_a'. Thus,

if $sgn\ \beta_{n_1' n_2'}$ is negative, then n_a' lies above n_s'. In this case, term ① in (20) will be positive, or *vice versa*. Term ② in (20) represents the 'through bond' [4] contribution to ΔIP. We can distinguish the following cases (c.f. (20)):

A) $sgn\ \Delta IP = sgn\ ①$

The 'natural order' is maintained for the SCF-MO's n_s, n_a. This case occurs of ① is large, *i.e.* $|\beta_{n_1' n_2'}|$ is large due to the near vicinity of n_1' and n_2'. On this basis, the PE.-spectra of pyridazine [5] and azomethane [6] have been interpreted. However, the same result may be also obtained for *e.g.* $|②| > |①|$ and $sgn\ ② = sgn\ ①$, *i.e.* by a dominant 'through bond' effect. This case seems to prevail in p-benzoquinone [7] [8].

B) $sgn\ \Delta IP \neq sgn\ ①$

Here the MO's n_s, n_a do not follow the 'natural order' due to $|②| > |①|$, $sgn\ ② \neq sgn\ ①$. This clear manifestation of 'through bond' coupling can occure if $|\beta_{n_1' n_2'}|$ is small. This line of reasoning has been employed in the discussion of the PE-spectra of pyrazine [5] and diazabicyclooctane [9].

II. 'Through bond' coupling and orbital energies. – From (20) it follows that the measurement of ΔIP does not allow a decision to be made about the relative amounts of 'through space' and 'through bond' contributions. Moreover, since $sgn\ \Delta IP$ is not observable, we are even unable to distinguish between cases A) and B). (The examples cited above were based on model calculations.) Only for molecules where term ① is bound to be negligible because of widely separated lone pairs, the observation of a split $\Delta IP \neq 0$ clearly demonstrates the presence of 'through bond' interaction.

III. 'Through bond' coupling and orbital shape. – 'Through bond' mixing of SLMO's leads to a redistribution of orbital charge density, *i.e.* to a change in the shape of orbitals. In our notation this requires non-zero coefficients s_2 and a_2 (*c.f.* (9), (10)). Inspection of (20) reveals that there is no way to find out about the relative magnitude of s_2^2 and a_2^2 from the measurement of ΔIP, not even in cases where the presence of 'through bond' coupling is evident (*vide supra*). For example, it could be possible that, say, n_a' has been raised more than n_s' by 'through bond' interaction, but nevertheless $a_2^2 < s_2^2$ if $\Delta_s/\Delta_a < a_2^2/s_2^2$. This means that, relative to n_s, the energetically more affected orbital n_a has preserved more of its original lone pair character, a quite unexpected outcome. Since Δ_s, Δ_a are not accessible experimentally, the measurement of ΔIP does not yield direct information about the shape of orbitals.

We shall now show that for favourable cases the comparison between PE- and electronic spectra, *i.e.* ionization and excitation energies can reveal some qualitative features concerning the shape of orbitals. The general ideas behind this treatment as well as its limitations have been outlined in part I of this series [1].

IV. $\Delta\Delta E$ vs. ΔIP: Information about the shape of orbitals. – Consider the energy difference between the $n_s \rightarrow \pi^*$ and $n_a \rightarrow \pi^*$ transition in our π-system. Following [1] we obtain

$$\Delta E(n_s \rightarrow \pi^*) - \Delta E(n_a \rightarrow \pi^*) = IP(n_s) - IP(n_a) + J_{n_a\pi^*} - J_{n_s\pi^*}$$
$$+ 2(K_{n_s\pi^*} - K_{n_a\pi^*}). \tag{21}$$

In zero differential overlap (ZDO)-approximation the exchange terms K in (21) vanish. Hence, with appropriate substitution and rearrangement

$$\Delta\Delta E - \Delta IP = J_{n_a\pi^*} - J_{n_s\pi^*}, \tag{22}$$

$\Delta\Delta E$ being the difference in $n \to \pi^*$ transition energies. Obviously the relative magnitude of $\Delta\Delta E$ vs. ΔIP depends upon the relative magnitude of the two J-terms. In order to obtain further insight we shall expand these J-integrals in terms of the SLMO's defined in (9) and (10):

$$J_{n_s\pi^*} = s_1^2 \langle n_s' \, n_s' | G | \pi^* \, \pi^* \rangle + s_2^2 \langle \chi_s' \, \chi_s' | G | \pi^* \, \pi^* \rangle$$
$$+ 2\, s_1\, s_2 \langle n_s' \, \chi_s' | G | \pi^* \, \pi^* \rangle, \tag{23}$$

$$J_{n_a\pi^*} = a_1^2 \langle n_a' \, n_a' | G | \pi^* \, \pi^* \rangle + a_2^2 \langle \chi_a' \, \chi_a' | G | \pi^* \, \pi^* \rangle$$
$$+ 2\, a_1\, a_2 \langle n_a' \, \chi_a' | G | \pi^* \, \pi^* \rangle, \tag{24}$$

G being the e^2/r_{12}-operator. Since we shall concentrate on the lowest energy $n \to \pi^*$ transitions, we have to consider the lowest antibonding π^*-MO. As examples for our model system, we shall later discuss azomethane and p-benzoquinone. Both these molecules have their lowest antibonding π^*-MO mainly localized at the heteroatoms where n_s' and n_a' are located. We shall base our discussion on this fact after noting that it may not be a property of all conceivable examples of our model system.

Hence the first integral in (23), (24) includes the *Coulomb* repulsion of charge, which is highly localized in the same region of space, *i.e.* at the heteroatoms. Since the charge distribution in n_s' and n_a' is entirely equivalent we set

$$\langle n_s' \, n_s' | G | \pi^* \, \pi^* \rangle = \langle n_a' \, n_a' | G | \pi^* \, \pi^* \rangle = J_1 > 0. \tag{25}$$

From the definition of χ_s' and χ_a' (*c.f.* (7), (8)), the second integral in (23), (24) includes some averaged *Coulomb* repulsion, composed of integrals $\langle \varphi_{is}' \, \varphi_{js}' | G | \pi^* \, \pi^* \rangle$ or $\langle \varphi_{ia}' \, \varphi_{ja}' | G | \pi^* \, \pi^* \rangle$. Most of these will be much smaller than J_1 because they involve clouds of charge more distant from each other than those of (25). In particular most of the integrals where $i \neq j$ will be negligible since the differential overlap between two LMO's and therefore also between two SLMO's is very small everywhere in space. (This is true except for those few integrals where φ_{is}', φ_{js}' or φ_{ia}', φ_{ja}' have an atom in common around which the differential overlap can become appreciable.) Guided by some numerical experience, we believe that for our model system, the approximation

$$\langle \chi_s' \, \chi_s' | G | \pi^* \, \pi^* \rangle \approx \langle \chi_a' \, \chi_a' | G | \pi^* \, \pi^* \rangle = J_2 > 0, \tag{26}$$

with

$$J_1 - J_2 = \Delta J > 0 \tag{27}$$

is reasonable, although not rigorously justifiable.

The third integral in (23), (24) involves again one electron moving in an overlap region between SLMO's and shall also be neglected. Hence from (22) with regard to (23)–(27), we obtain the relationship

$$\Delta\Delta E - \Delta IP \approx (a_1^2 - s_1^2)\,\Delta J. \tag{28}$$

Equ. (28) provides a direct insight into the 'relative' shape of the orbitals n_s and n_a. It correlates an observable quantity with the difference between the percentages of lone pair character which have survived in n_a and n_s after 'through bond' mixing of n_a' and n_s' with χ_a' and χ_s', resp.

Discussion. – On the basis of (20) and (28) we can construct tab. 1. Evidently an unambigous decision about the relative orbital energy as well as the relative orbital shape of the MO's n_s and n_a can be achieved if the magnitude as well as the sign of ΔIP and $\Delta\Delta E$ would be known.

However, as mentioned previously, $sgn\,\Delta IP$ can not be determined from the PE-spectrum. On the other hand it is reasonable to assume that $\Delta\Delta E$ can be measured with its sign. The identification of the two $n \to \pi^*$ transitions in the electronic spectrum requires polarization and intensity studies, which will reveal the proper energetic sequence of the two excited states and therefore $sgn\,\Delta\Delta E$ as defined in (21). On this basis, only one positive decision can be made from tab. 1: for $|\Delta IP| > |\Delta\Delta E|$, the higher lying n-MO has less lone-pair character, *i.e.* is more diffuse. (Obviously, this follows also if $sgn\,\Delta\Delta E$ is unknown.)

The applicability of tab. 1 could be extended if one could estimate an upper limit for the term to the right in (28). Consider an extreme case in which, say, n_a is pure n_a' ($a_1^2 = 1$), whereas n_s contains only 50% of n_s'-character ($s_1^2 = 0.5$), the other 50% being distributed among the admixing φ_{is}' – SLMO's. Furthermore, from (27) ΔJ will be at most equal to J_1 (if $J_2 = 0$), which lies in the order of 12 eV. This leads to:

$$|\Delta\Delta E - \Delta IP| \leq 6 \text{ eV.} \tag{29}$$

Consequently, if $|\Delta\Delta E| + |\Delta IP| > 6$ eV is observed, then we may safely conclude $sgn\,\Delta\Delta E = sgn\,\Delta IP$. In this case tab. 1 reduces to four possibilities which can be unambiguously distinguished on the basis of the observations $|\Delta\Delta E|$, $sgn\,\Delta\Delta E$ and $|\Delta IP|$. Even if $sgn\,\Delta\Delta E$ would not be known, one still could distinguish between two cases for the higher lying n-MO: (i) for $|\Delta IP| < |\Delta\Delta E|$ it is more diffuse, and (ii) for $|\Delta IP| > |\Delta\Delta E|$ it is less diffuse than its lower lying counterpart (*c.f.* tab. 1 for cases where $sgn\,\Delta IP = sgn\,\Delta\Delta E$).

Examples. – *Trans*-azomethane, which has been treated numerically in [1], provides an example of the latter case, discussed above. From the experimental evidence $|\Delta\Delta E| \approx 7$ eV [10] and $|\Delta IP| = 3.3$ eV [11], we can deduce that the higher lying n-MO is less diffuse than the lower lying one. Polarization studies for *t*-azobenzene [12] have established that the lowest energy absorption band corresponds to the forbidden $n_s \to \pi^*$ transition. Assuming the same to be true for *t*-azomethane, it follows from (21) that $sgn\,\Delta\Delta E$ is negative. From (29) we conclude that $sgn\,\Delta IP$ is also negative. Hence, the higher lying SCF-MO is the n_s-component (tab. 1). The 'natural sequence' of the SLMO's n_s' and n_a' in *t*-azomethane is found by inspection to be: n_s' above n_a' (*c.f.* [4] and [11]). Consequently, the orbital energies $\varepsilon(n_s)$ and $\varepsilon(n_a)$ follow the 'natural sequence'! These conclusions are also borne out by explicit calculation of the n-orbitals (*c.f.* [1] and [11]).

For *p*-benzoquinone (PBQ), $|\Delta IP| = 0.9$ eV has been found [8]. Recent measurements of the polarized single crystal spectra of PBQ and its methyl derivatives at 4.2° K [13][3] have unambiguously located the two $n \to \pi^*$ transitions at 20060 cm^{-1} ($n_a \to \pi^*$) and at 20315 cm^{-1} ($n_s \to \pi^*$), leading to $\Delta\Delta E \approx 0$ eV. Hence, $|\Delta IP| > |\Delta\Delta E|$ and we deduce from tab. 1 that the higher lying n-orbital has less lone pair character, *i.e.* is more diffuse, in agreement with the results of CNDO/2-calculations [7]. (No

---

[3]   We thank Dr. *Trommsdorff* for informing us of his results prior to publication.

Table 1. *Relation between the observables ΔIP, $\Delta\Delta E$ and the relative energy and shape of lone pair orbitals* [a]

$sgn\,\Delta IP$		$sgn\,\Delta\Delta E$ positive		$sgn\,\Delta\Delta E$ negative	
		higher lying MO	MO with more lone-pair character	higher lying MO	MO with more lone-pair character
$\|\Delta IP\| < \|\Delta\Delta E\|$	positive	n_a	n_a	n_a	n_s
	negative	n_s	n_a	n_s	n_s
$\|\Delta IP\| > \|\Delta\Delta E\|$	positive	n_a	n_s	n_a	n_s
	negative	n_s	n_a	n_s	n_a

[a]   The table applies only to molecules which contain two symmetry equivalent heteroatoms and where (i) σ–π separation is applicable and (ii) the lowest antibonding π^*–MO is mainly localized at the heteroatoms.

more information can be obtained since here it is meaningless to consider $sgn\,\Delta\Delta E$.) As with azomethane [1] we examined the basis of our qualitative rules by explicit CNDO/2-calculation of the J-terms appearing in (21) (tab. 2). $\Delta\Delta E = 0.06$ eV is found, in excellent agreement with the experimental value, which in turn supports the interpretation of the photoelectron spectrum, made in [8]. More rigorous treatments with inclusion of configuration interaction yield values for $\Delta\Delta E$ of 0.13 eV [14], 0.31 eV and 0.73 eV [15], the latter being less in line with experiment (*c.f.* tab. 2).

Table 2. *Calculated and observed values for* p-*benzoquinone*
(for explanation of symbols see equ. (21) and text)

x	$IP(x)$ (eV) [a]	$J_{x\pi^*}$ (eV)	$\Delta\Delta E$ (eV) this work	$\Delta\Delta E$ (eV) other references
$n_a(b_{3g})$	10.03	7.42		0.03 [b]
			0.06	0.13 [c]
$n_s(b_{2u})$	10.93	8.26		0.31, 0.73 [d]

[a]   From photoelectron spectra [8].
[b]   From crystal phase spectra [13].
[c]   CNDO-CI calculations [14], cited in [13].
[d]   CNDO-CI calculations, using two different parametrizations [15].

Conclusions. – The present study, although performed for rather special molecular systems, leads to the following general conclusions:

1) Splitting patterns observed in electronic spectra cannot be transformed directly into orbital language. This must be emphasized since there are many examples in the literature where such attempts have been undertaken.

2) Conclusion 1) has its origin in electron-repulsion terms. The magnitude of these terms does not depend upon the orbital energy but rather upon the orbital shape. Hence a comparison between ionization potentials and excitation energies can, in principle, yield qualitative information about the shape of orbitals without recourse to theoretical calculations. It also gives some insight into the conceptually very attractive 'through bond' interaction mechanism.

Since this latter concept was brought up on theoretical grounds [4], there have been a number of attempts in order to demonstrate its operation experimentally. In the area of PE-spectroscopy these have included the study of vibrational fine structure [16] or the correlation of PE-data, obtained from a set of molecules carrying 'key'-groups [17]. Recently the criterion of allowedness or forbidness of $n \rightarrow \pi^*$ transitions in higher diazines was employed for this purpose [18]. The approach indicated in this paper provides a further possibility along these lines.

BIBLIOGRAPHY

[1] *E. Haselbach & A. Schmelzer*, Helv. *54*, 1575 (1971).
[2] *E. Edminston & K. Ruedenberg*, Rev. mod. Physics *35*, 457 (1963).
[3] *T. Koopmans*, Physica *1*, 104 (1934); *W. G. Richards*, Intern. J. Mass. Spectrom. Ion Physics *2*, 419 (1969).
[4] *R. Hoffmann, A. Imamura & W. J. Hehre*, J. Amer. chem. Soc. *90*, 1499 (1968); *R. Hoffmann*, Acc. chem. Res. *4*, 1 (1971).
[5] *R. Gleiter, E. Heilbronner & V. Hornung*, Helv. *55*, 255 (1972).
[6] *E. Haselbach & E. Heilbronner*, Helv. *53*, 684 (1970).
[7] *J. R. Swenson & R. Hoffmann*, Helv. *53*, 2331 (1970).
[8] *D. O. Cowan, R. Gleiter, J. A. Hashmall, E. Heilbronner & V. Hornung*, Angew. Chem. *83*, 405 (1971).
[9] *P. Bischof, J. A. Hashmall, E. Heilbronner & V. Hornung*, Tetrahedron Letters *1969*, 4025.
[10] *M. B. Robin, R. R. Hart & N. A. Kuebler*, J. Amer. chem. Soc. *89*, 1564 (1967).
[11] *E. Haselbach & E. Heilbronner*, Helv. *53*, 684 (1970).
[12] *R. M. Hochstrasser & S. K. Lower*, J. Chem. Phys. *35*, 3505 (1962).
[13] *H. P. Trommsdorff*, J. Chem. Phys. (in press).
[14] *M. F. Merienne-Lafore*, cited in [13].
[15] *W. Hug, J. Kuhn, K. Seibold, H. Labhart & G. Wagnière*, Helv. *54*, 1451 (1971).
[16] *E. Heilbronner & K. A. Muszkat*, J. Amer. chem. Soc. *92*, 3818 (1970).
[17] *E. Heilbronner*, Int. Union of Pure and Applied Chemistry *7*, 9 (1971).
[18] *A. D. Jordan, I. G. Ross, R. Hoffmann, J. R. Swenson & R. Gleiter*, Chem. Phys. Letters *10*, 572 (1971).

---

167. Über die Ausdrucksweisen der Konzentration des Wasserdampfes bei Wasserdampf-Sorptionsmessungen

von **S. Gál**

Institut für Organische Chemie der Universität Bern, 3000 Bern 9

Summary. The definitions of the partial pressure of water vapor, the activity of water, the relative humidity and the partial relative density of water vapor are reproduced and their functional relationships are given. The numerical values of these variables between $-10\,°C$ and $+100\,°C$ and at total pressures between the pressure of the own vapor and $10,133$ mbar have been computed and tabulated (tables available in form of microfilm or xerox-copies from Buchhandlung *Herbert Lang & Cie*, Münzgraben 2, CH-3000 Bern). The limits of indistinct use of these variables are discussed.