245. 'Non-*Koopmans*' States in Stilbene Cations and a Remarkable Example to the 'SDT-Equation': Indeno[2,1-*a*]indene[1]

by **Edwin Haselbach**[2], **Urs Klemm**[3] and **Rudolf Gschwind**
Physikalisch-chemisches Institut der Universität, Klingelbergstrasse 80, CH-4056 Basel

and **Thomas Bally**, **Laurant Chassot**[4] and **Stephan Nitsche**
Institut de chimie physique de l'Université, Pérolles, CH-1700 Fribourg

(15.IX.82)

Summary

The radical cations of indeno[2,1-*a*]indene (**1**), stilbene (**2**) and 3,5,3',5'-tetramethylstilbene (**3**) were prepared by γ-irradiation of the neutral precursors in an electron-scavenging matrix at 77 K. Their electronic spectra were recorded and compared to the photoelectron spectra (PE.) of the neutral precursors. The results show that either the fourth or the fifth excited doublet state of the cations is of 'Non-*Koopmans*'-type, with specific doublet energy (D) $D(^2B_g) = 2.74$ eV ($\mathbf{1}^+$), $= 2.59$ eV ($\mathbf{2}^+$), $= 2.49$ eV ($\mathbf{3}^+$). Remarkably, $\mathbf{1}^+$ possesses *two* electronic states in the 2.7–2.8 eV energy range: ^2A_u ('*Koopmans*'-type) and ^2B_g ('Non-*Koopmans*'-type). The 'SDT'-equation $D = \sqrt{S \cdot T}$ approximately connecting excited singlet (S) and triplet (T) states of a neutral alternant system with the excited doublet (D) states of its radical cation – provided e^--promotion occurs for all three excited states between the same (paired) orbitals – is satisfyingly exemplified by **1**: $S_1 = 3.92$ eV and $T_1 = 2.06$ eV for **1**, $D_{4 \text{or} 5} = 2.74$ eV for $\mathbf{1}^+$.

Introduction. – We have recently reported [2] an equation (henceforth called 'SDT'-equation') which interconnects the energies of excited singlet (S) and triplet (T) states of an alternant system **M** to those of the excited doublet (D) states of the corresponding radical cation $\mathbf{M}^+$, provided *a)* the electron promotions leading to the above three excited states involve the same two MO's which furthermore are 'paired' ones; *b)* the frozen orbital approximation holds; *c)* the ZDO-approximation holds.

Neglecting configuration interaction (CI.) then leads to *Equation 1* for the corresponding energies [2]:

$$D = \frac{1}{2}(S + T) \text{ (arithmetic mean).} \tag{1}$$

---

[1] 'Studies on Radical Ions', Part XII. For Part XI see [1].

[2] Present address: Institut de chimie physique de l'Université, Pérolles, CH-1700 Fribourg.

[3] Present address: Kant. Chemisches Laboratorium, Kunsthausweg 24, CH-5000 Aarau.

[4] Present address: Institut de chimie inorganique de l'Université, Pérolles, CH-1700 Fribourg.

0018-019X/82/8/2464-08$01.00/0

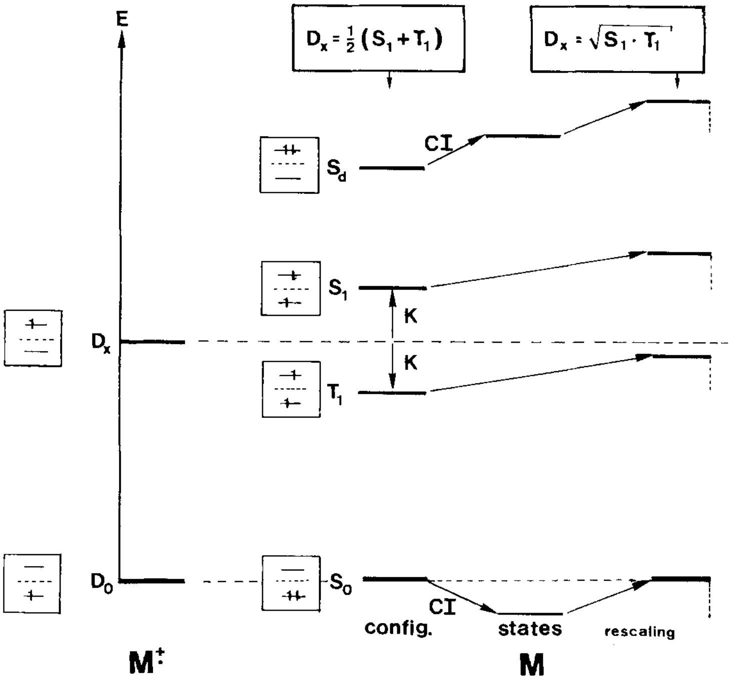


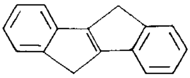
Fig. 1. *Energy disposition of the states connected in the 'SDT-equation'* (see the text)(K: HOMO/LUMO-exchange integral)

More appropriately, allowing 2×2(CI.) between the ground (S_0) and the doubly excited (S_d) singlet configurations results in *Equation 2* [2]:

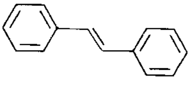
$$D = \sqrt{S \cdot T} \quad \text{(geometric mean).} \qquad (2)$$

For clarity these relationships are schematically presented in *Figure 1*. There, the label '1' is added to the symbols related to neutral **M** as the lowest excited singlet (S_1) and triplet (T_1) state for most representatives arise from the HOMO → LUMO electron promotion. Hence, condition *a* is fulfilled and the system can be used as an example. Note, however, that the label of the D-state of M^+ is not specified as the one associated with S_1 and T_1 of **M** is commonly *not* the first excited one of M^+. The lowest excited states of M^+ are generally associated with electron promotions within the bonding orbital manifold. Such so-called *'Koopmans'* states are accessible in the photoelectron-spectroscopy (PE.) experiment. States of M^+ shown in *Figure 1*, however, are of so-called 'Non-*Koopmans*'-or 'shake-up'-type; they can only be assessed through the strategy outlined in [3]. We recently found such a state to be the lowest excited one (*i.e.* D_1) in a well-chosen molecular cation [2]. This, however, is an exception to the rule. For other low-lying states of this nature *cf.* [4].

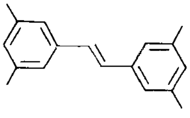
In the following we shall verify the theoretical prediction *(Eqn. 2)* for indeno[2,1-*a*]indene (**1**) and its radical cation $\mathbf{1}^{+}$. In order to support some spectral assignments, analogous measurements were made for **2** and **3**.



1



2



3

PE. spectrum of 1. – *Figure 2* (upper part) displays the PE. spectrum of **1**. The given assignment is straightforward; extensive use was made of previous work dealing with various stilbene-type systems [5]. In addition there is almost perfect correspondence between the measured band positions and the corresponding HMO-bonding orbital energies displayed in *Figure 3*. Note also the increased intensity of the band around 8.9 eV, indicating two energetically close-lying ionization events. This agrees with the HMO-prediction that π_5 and π_6 are accidentally degenerate.

Electronic absorption (EA.) spectrum of $\mathit{1}^{+}$: $\mathrm{D_x}$-energy. – Radical cation $\mathbf{1}^{+}$ was prepared by γ-irradiation of **1** in an electron-scavenging matrix at 77 K (for details see [6]). Two band systems are discernible in its spectrum, shown in *Figure 2* (middle part).

Band system $\boxed{1}$ This broad low-intensity band peaks at ~15 kK. It obviously corresponds to the allowed transition $^2\mathrm{B_g}(\pi_4) \leftarrow {}^2\mathrm{A_u}(\pi_7)$[5]), especially if allowance is made for a slight red-shift of the condensed-phase absorption of $\mathbf{1}^{+}$ with respect to the corresponding gas-phase PE. band of **1** (see also [3]). From the shape of the orbitals involved in the transition *(Fig. 3)*, a significant transition moment can already be deduced qualitatively.

It is important to note that the transition $^2\mathrm{B_g}(\pi_5) \leftarrow {}^2\mathrm{A_u}(\pi_7)$ is also symmetry-allowed. Nevertheless, there is no absorption discernible in the expected energy range. *Figure 3* provides a clue to this result: the orbitals π_7 and π_5 are localized in rather different spatial parts of the molecule, resulting in a very small transition moment.

Band system $\boxed{2}$ This system consists of an intense sharp band with prominent 0,0-feature at 2.74 eV and several members of a vibrational progression. Its peak coincides with that of the PE. band attributed to the $^2\mathrm{A_u}(\pi_3)$-state. However, the '*Koopmans*'-transition $^2\mathrm{A_u}(\pi_3) \leftarrow {}^2\mathrm{A_u}(\pi_7)$ is forbidden by symmetry. The foregoing discussion has shown that even symmetry-allowed transitions do not show up in the electronic spectrum if their transition moment is small. We therefore are reluctant to attribute the 2.74-eV band to $^2\mathrm{A_u}(\pi_3)$ of $\mathbf{1}^{+}$.

A way out of this problem is indicated in *Figure 3:* the energy gaps $\varepsilon(\pi_7)$-$\varepsilon(\pi_3)$ and $\varepsilon(\pi_8^*)$-$\varepsilon(\pi_7)$ are almost equal. The latter quantity corresponds to the 'Non-*Koopmans*' transition $^2\mathrm{B_g}(\pi_8^*) \leftarrow {}^2\mathrm{A_u}(\pi_7)$ in $\mathbf{1}^{+}$ which is symmetry-allowed and

---

5) The unpaired electron occupies the orbital indicated in parentheses after the state designation.

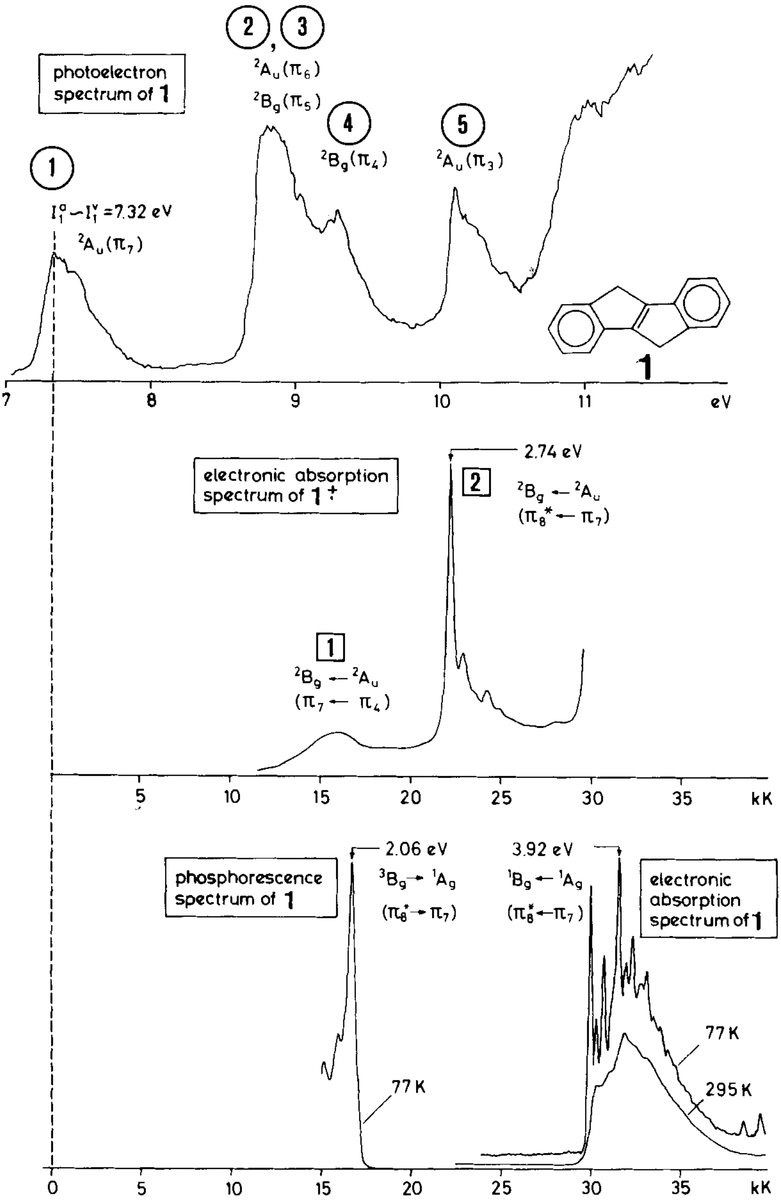


Fig. 2. *PE. spectrum of* **1** (top), *EA. spectrum of* **1**$^+$ (middle) and *EA. and phosphorescence emission spectra of* **1** (below) (The origin of the electronic spectra is set at I_1^a of **1** from PE. spectrum; see [3] for details)

possesses a large transition moment. On this basis we attribute the upper state involved in the 2.74-eV transition to the $^2B_g(\pi_8^*)$ 'Non-*Koopmans*' or 'shake-up' state of **1**$^+$. Two conclusions emerge: *1)* both the PE. spectrum of **1** and the electronic spectrum of **1**$^+$ reveal an excited state of the ion at 2.7–2.8 eV. The analysis,

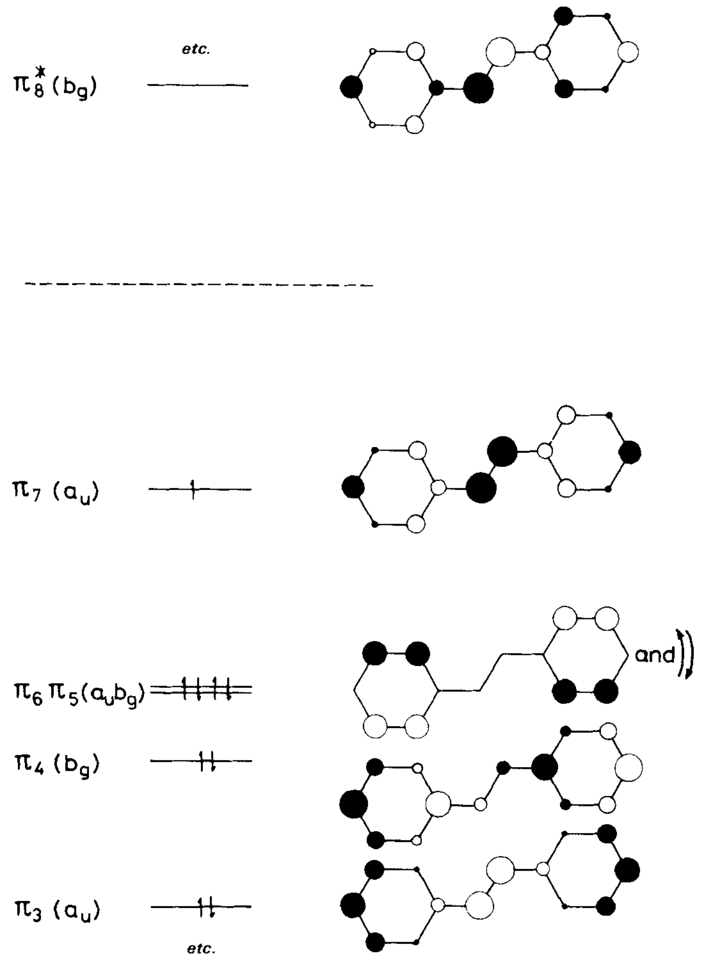


Fig. 3. *Pictorial representation of the relevant HMO-orbitals of stilbene*

however, yields the remarkable result that there is not one but *two* states of $\mathbf{1}^+$ of different symmetry at this energy: the '*Koopmans*' state $^2A_u(\pi_3)$ (from the PE. spectrum of **1**) and the 'Non-*Koopmans*' state $^2B_g(\pi_8^*)$ (from the electronic spectrum of $\mathbf{1}^+$). Support to this conclusion stems also from an analogous study of the stilbene systems **2** and **3** which differ from **1** in the alkyl-substitution pattern. This feature induces a differential change of orbital energies with respect to **1**. *Figures 4* and *5* display the collected spectra, the peak positions being summarized in the *Table*. The results can be analyzed in a manner analogous to that presented above for **1**. Most importantly, the accidental degeneracy of $^2A_u(\pi_3)$ and $^2B_g(\pi_8^*)$ found for $\mathbf{1}^+$ is now removed in both $\mathbf{2}^+$ and $\mathbf{3}^+$.

It should, however, be noted that the comparison of EA. spectrum of $\mathbf{2}^+$ and $\mathbf{3}^+$ with PE. spectrum of **2** and **3**, respectively, is not as straightforward as in the case of $\mathbf{1}^+/\mathbf{1}$. While **2** is non-planar in the gas-phase [7] $\mathbf{2}^+$ most probably assumes a planar conformation due to formation of a partial double

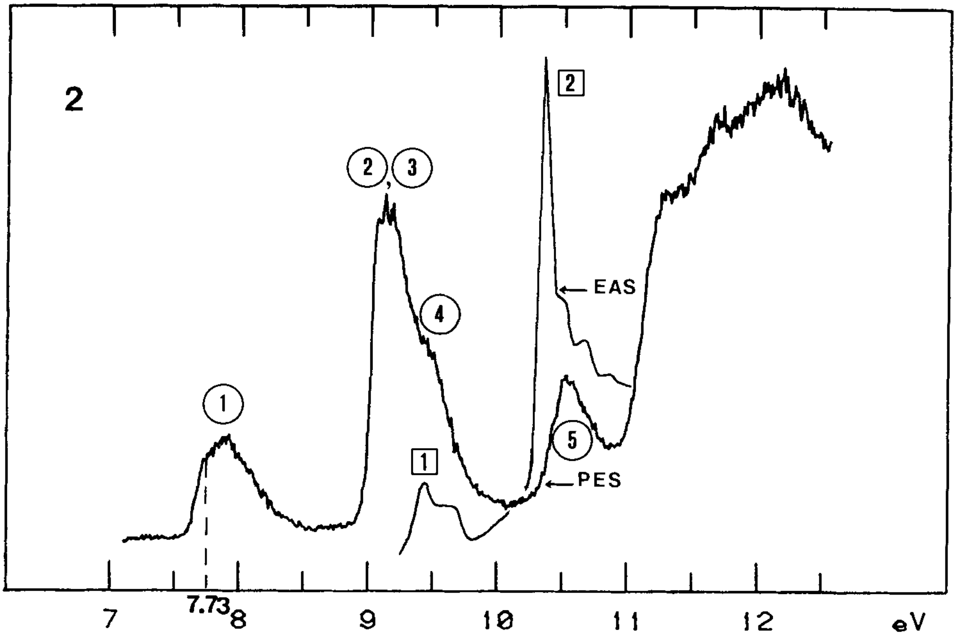


Fig. 4. *PE. spectrum of* **2** *and EA. spectrum of* $\mathbf{2}^+$

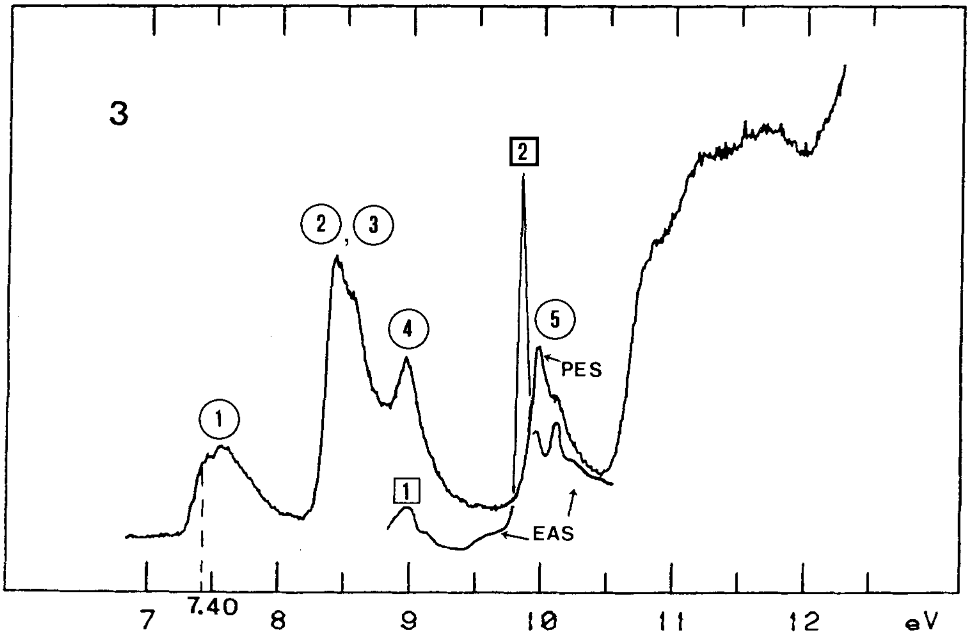


Fig. 5. *PE. spectrum of* **3** *and EA. spectrum of* $\mathbf{3}^+$

Table. *Spectral parameters* (in eV) *for* **1**, **2** *and* **3** *(PE. spectrum) and their radical cations (EA. spectrum)* ((a): adiabatic values)

		1	**2**	**3**
PE. (gas phase)				
①	$^2A_u(\pi_7)$	7.32 (a)	7.73 (a)	7.40 (a)
		7.32	7.93	7.57
②, ③	$^2A_u(\pi_6)$, $^2B_g(\pi_5)$	8.83	9.13	8.44/8.55
④	$^2B_g(\pi_4)$	9.28	9.42	8.95
⑤	$^2A_u(\pi_3)$	10.10	10.54	9.98
EA. (condensed phase)				
$\boxed{1}$	$^2B_g(\pi_4) \leftarrow {}^2A_u(\pi_7)$	1.95	1.64	1.59
$\boxed{2}$	$^2B_g(\pi_8^*) \leftarrow {}^2A_u(\pi_7)$	2.74	2.59	2.49

bond upon ionization of **2** between each of the phenyl rings and the central C,C-unit (see *e.g.* the related case of biphenyl and its cation [8]). The same feature will prevail in **3**/**3**$^+$. From first-order perturbation theory and inspection of *Figure 3* it follows that planarization of this kind leads to a narrowing of the HOMO-LUMO gap (*i.e.* $\varepsilon(\pi_8^*) - \varepsilon(\pi_7)$). Concomitantly, $\varepsilon(\pi_7) - \varepsilon(\pi_3)$ increases by about the same amount given the relevant partial bond orders for the C_d,C_{Ph}-bonds: +0.095 (π_8^*), −0.095 (π_7), +0.083 (π_3). On this basis, however, a *hypsochromic* displacement of the vertical '*Koopmans*' transition in **2**$^+$ and **3**$^+$ relative to the corresponding vertical value from the PE. spectrum (*i.e.* $I_4^v - I_1^a$) would be expected (perhaps balanced to some extent by solvation effects). The fact that we observe in both cases a *bathochromic* shift thus further supports to our conclusion that the prominent EA. band for **2**$^+$ and **3**$^+$ corresponds to the first 'Non-*Koopmans*' excited state of these ions.

2) The $^2B_g(\pi_8^*)$-state fulfills condition *a* of the *Introduction*. We therefore set $D_x = 2.74$ eV to be used in *Equation 2*. With respect to the label x it follows from the analysis that x = 4 or 5, depending on the true sequence of the states $^2A_u(\pi_3)$ and $^2B_g(\pi_8^*)$ which we are unable to establish for **1**$^+$.

The above conclusions are in full accord with open-shell PPP-calculations performed for stilbene radical cation (**2**$^+$) *(Fig. 6)*. As all the involved states turned

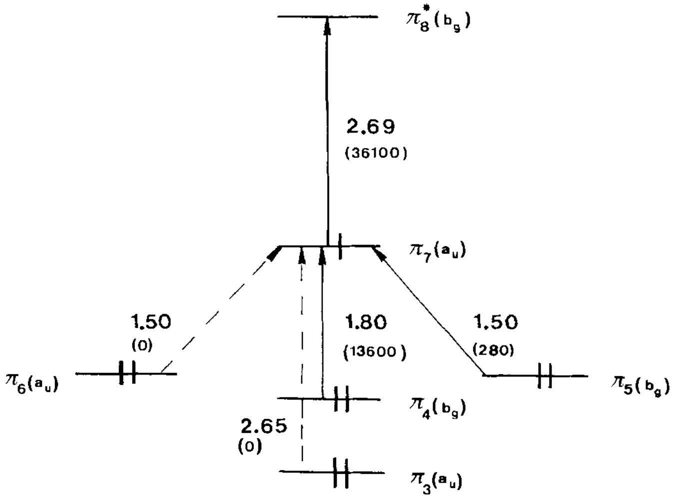


Fig. 6. *Results of open-shell PPP-calculations for stilbene radical cation* (**2**$^+$) (Energies in eV, ε-values in parentheses)

out to be strongly dominated by a single configuration, the theoretical results can be presented using an orbital diagram equivalent to that in *Figure 3*. Specifically, the calculations yield the excited $^2B_g(\pi_8^*)$-state at 2.69 eV, in excellent agreement with the experiment ($D_x = 2.74$ eV). This state contains the HOMO→LUMO ($\pi_7 \rightarrow \pi_8^*$) excited configuration with a weight of 75% (the pure configuration lies at 2.9 eV).

EA. and phosphorescence spectrum of *1*: S_1 and T_1. – Both these spectra have been given in [9] and are redrawn in *Figure 2* (below). To assess the vertical $S_0 \rightarrow S_1$ transition energy (which properly ought to be used in *Eqn. 2*) the absorption spectrum of **1** was measured also at room temperature, yielding $S_1 = 3.92$ eV. From the phosphorescence spectrum $T_1 = 2.06$ eV is obtained. Both these states are, according to PPP-calculations, strongly dominated by the HOMO→LUMO ($\pi_7 \rightarrow \pi_8^*$) excited configuration.

Application of *Equation 2*. – Using the data for S_1 and T_1 discussed above in *Equation 2* yields the prediction $D_x = \sqrt{3.92 \cdot 2.06} = 2.84$ eV, which is in remarkable agreement with the experimental value of 2.74 eV. Application of *Equation 1* yields $D_x = 2.99$ which is slightly more off. Apparently, the depression of the ground configuration S_0 of **1** through CI. with S_d plays some role, though a minor one.

Conclusions. – The present paper demonstrates: *1)* once more the important complementary nature of the two experimental approaches (PE. spectroscopy of **M**, EA. spectroscopy of $\mathbf{M}^+$) in the elucidation of the excited states of molecular ions $\mathbf{M}^+$, in particular those of 'Non-*Koopmans*' nature; *2)* the applicability of *Equation 2* within the boundary conditions stated. *Equation 2* thus provides a bridge between the electronic states of neutrals (**M**) and their parent cations ($\mathbf{M}^+$). It may become useful in cases where two of the three interconnected data are known, as then the third can be estimated. Work is presently in progress to test the range of applicability of *Equation 2*, in particular when relaxing the requirement of an 'alternant' system. In this respect we note that **1** already is not of that type proper due to the bridging methylene groups.

This work is supported by the *Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung*. We thank Profs. *J. Saltiel* (Florida) and *E. Giovannini* (Fribourg) for samples of **1** and **3**, respectively.

REFERENCES

[1] *E. Haselbach, M. Allan, M. v. Büren & H.-J. Hansen,* Helv. Chim. Acta *65,* 2133 (1982).
[2] *P. Forster, R. Gschwind, E. Haselbach, U. Klemm & J. Wirz,* Nouv. J. Chim. *4,* 365 (1980).
[3] *E. Haselbach, T. Bally, R. Gschwind, U. Klemm & Z. Lanyiova,* Chimia *33,* 405 (1979).
[4] *E. Haselbach, U. Klemm, U. Buser, R. Gschwind, M. Jungen, E. Kloster-Jensen, J.P. Maier, O. Marthaler, H. Christen & P. Baertschi,* Helv. Chim. Acta *64,* 823 (1981).
[5] *E.J. McAlduff & T. Chan,* Can. J. Chem. *56,* 2714 (1978), and references cited therein.
[6] *T. Shida,* J. Phys. Chem. *82,* 695, 991 (1978) and references cited therein.
[7] *M. Traetteberg, E.B. Frantzen, F.C. Mijlhoff & A. Hockstra,* J. Mol. Struct. *26,* 57 (1975).
[8] *E. Haselbach, T. Bally, S. Nitsche & P. Jolliet,* in preparation.
[9] *J. Saltiel, G.-E. Khalil & K. Schanze,* Chem. Phys. Lett. *70,* 233 (1980).