80. Studies of Molecular Ions. IX. Detection of Low-lying 'Non-*Koopmans*' States in Polyacetylene Molecular Cations[1])

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Dedicated to Professor *Edgar Heilbronner*, on the occasion of his 60th birthday, with respect and gratitude

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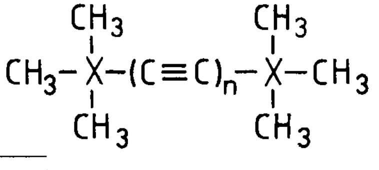
Summary

Comparison of the photoelectron spectra of the title compounds with the electronic absorption spectra of the corresponding radical cations led to the detection of low lying 'Non-*Koopmans*'-states in the ionic species.

Introduction. - Charge transfer is a key step in a variety of chemical processes. If the reactants are closed shell neutrals (M), radical cations M^+ are produced. Their identification is commonly performed by means of their electronic spectra where a prediction for those transitions leading to *Koopmans*-states ψ_K can be obtained from the photoelectron spectrum (PE.) of the neutral precursor M as outlined in [2]. Transitions to so called 'Non-*Koopmans*'-states ψ_{NK} do not find, however, a prediction from PE.-spectroscopy. This is particularly troublesome as such states have recently been found to lie at rather low energies [3]. Hence, from



$$CH_3-\underset{CH_3}{\overset{CH_3}{X}}-(C\equiv C)_n-\underset{CH_3}{\overset{CH_3}{X}}-CH_3$$

X	n = 1	2	3	4	5
C	**1**	**2**	**3**	**4**	**5**
Si		$\mathbf{2}_{Si}$	$\mathbf{3}_{Si}$		

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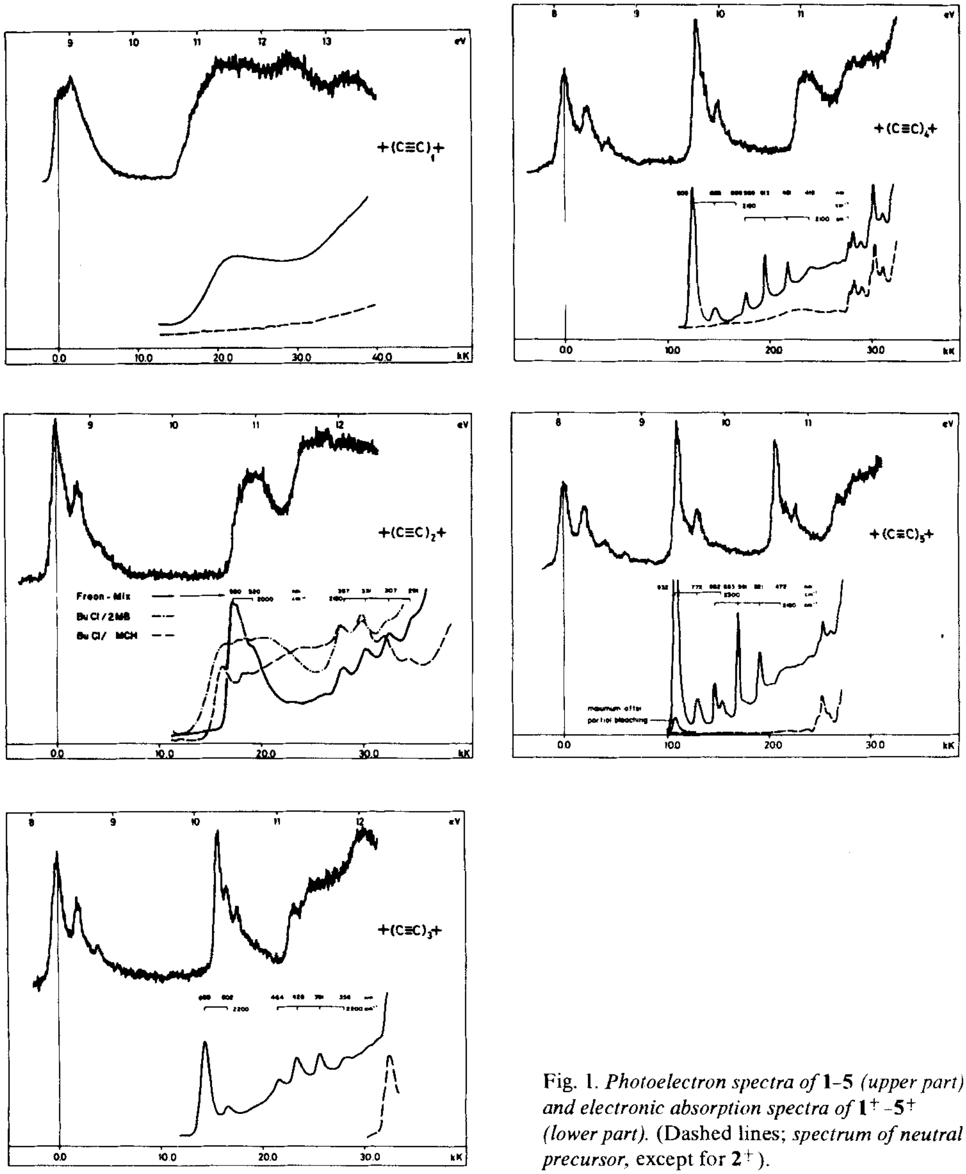


Fig. 1. *Photoelectron spectra of* **1-5** *(upper part) and electronic absorption spectra of* **1**$^+$-**5**$^+$ *(lower part).* (Dashed lines; *spectrum of neutral precursor,* except for **2**$^+$).

a purely practical standpoint, but also aiming at a knowledge of all low-lying excited states of molecular cations M^+, we started a program in this direction and will here report about the ψ_{NK}-states of some title cations.

Results and Discussion. - *Figure 1* shows the PE.-spectra of **1-5** [4] (upper figure) and the electronic spectra of the parent radical cations **1**$^+$-**5**$^+$, produced by γ-irradiation of the corresponding neutral precursors in the indicated electron scavenging matrix (lower figure). For a detailed account of the irradiation procedure we refer to [5]. The origin of the electronic spectra matches the *O, O*-transition energy of the first ionisation event in the corresponding PE.-spectrum (*cf.* [2]). The states are classified with respect to an idealized $D_{\infty h}$ symmetry as outlined in [4].

Band System I. - Molecular cations 3^+-5^+. All three ions show an intense band system with dominant *O, O*-component where the PE.-spectrum shows the band assigned to the ejection of an electron from the second highest occupied π-MO of the corresponding parent neutral. The electronic transitions are therefore of '*Koopmans*'-type and are labeled $\tilde{A}(^2\Pi_u) \leftarrow \tilde{X}(^2\Pi_g)$ for 4^+ and $\tilde{A}(^2\Pi_g) \leftarrow \tilde{X}(^2\Pi_u)$ for 3^+ and 5^+, respectively. The vibrational fine structure in both spectral types is very similar and corresponds to excitation of C≡C-stretching motions in the Ã-state of the ion.

We note a general red shift of the main peak in the matrix environment with respect to the gas phase PE.-spectrum. This medium effect is not unexpected since excited states are generally more polarisable than the ground states [2]. Interestingly, the red shift increases from 5^+ (500 cm^{-1}) to 4^+ (1000 cm^{-1}) to 3^+ (1500 cm^{-1}). We attribute this observation to the fact that the charge dispersion decreases in this order, thus, 3^+ exhibiting the strongest specific interaction with the medium. Another assessment of the red shift of 3^+ is found in *Figure 2* where its matrix absorption and the corresponding gas phase emission band ($\tilde{A}(^2\Pi_g) \rightarrow \tilde{X}(^2\Pi_u)$) are compared.

Molecular cation 2^+. For 2^+ a reasonable spectrum could only be obtained by using the freon mixture as described in [5] as the electron scavenging medium.

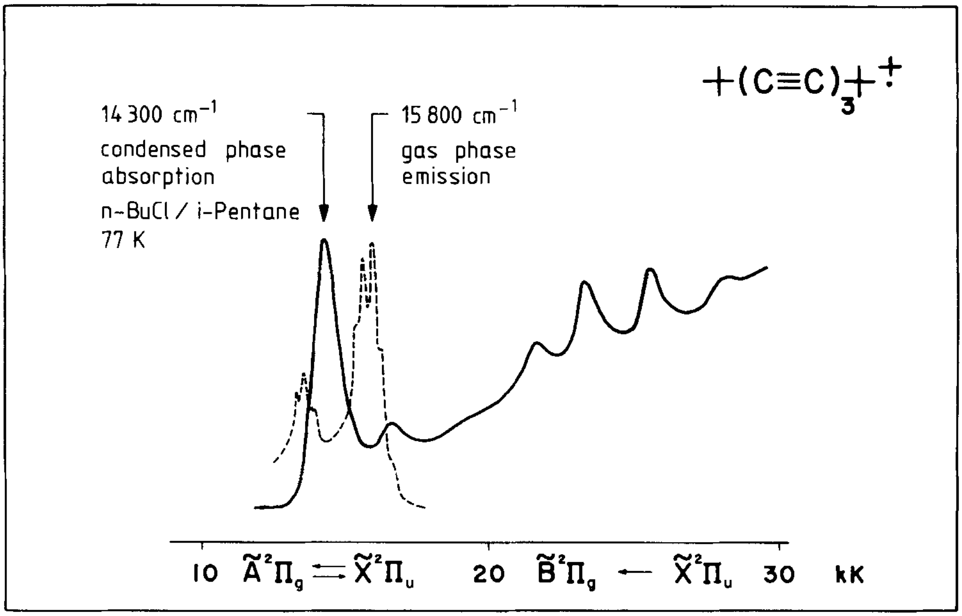


Fig. 2. *Assessment of the medium effect on the Ã-state of* 3^+ *from its electronic absorption spectrum (in condensed phase) and its emission spectrum (gas phase)*

Reasons for the failure of the other two matrices are presently unknown. The band peaks at 580 nm and shows vibrational fine structure ($\tilde{\nu} \approx 2000$ cm^{-1}). A similar frequency shows up in the corresponding PE.- and electronic-spectral bands of the higher homologues as discussed above. This and the energetic match of the band with the PE.-band around 11 eV suggests the assignment $\tilde{A}(^2\Pi_u) \leftarrow \tilde{X}(^2\Pi_g)$ for the ion transition.

The above PE.-band has been assigned to two or more states of the ion arising from ejection of the electron from the π_u-MO of the diacetylene π-system, and from pseudo-π- and/or -σ-MO's confined to the *t*-butylgroups [4]. An assessment of the energetic sequence of these states, *i.e.* the true nature of the $\tilde{A}$-state of **3**$^+$, however, is not possible from the PE.-spectrum alone. That this state most probably is not associated with the hole residing in the diacetylenic π_u-MO was subsequently deduced from the absence of emission from that state [6]. One should add, however, that emission from a state $\tilde{A}(^2\Pi_u)$ with the hole residing in the *t*-butyl pseudo-π-MO's would be allowed, but associated with a low probability due to the small transition moment (*vide infra* for **1**$^+$). Hence, also in this case non-radiative decay processes could be favoured over radiative ones.

The electronic spectrum of **2**$^+$ sheds some light on this question. Linear extrapolation of the red shift between gas- and condensed phase-spectra as discussed for **3**$^+$-**5**$^+$ predicts for **2**$^+$ a red shift of ~2000 cm^{-1}. *Figure 3* shows its first

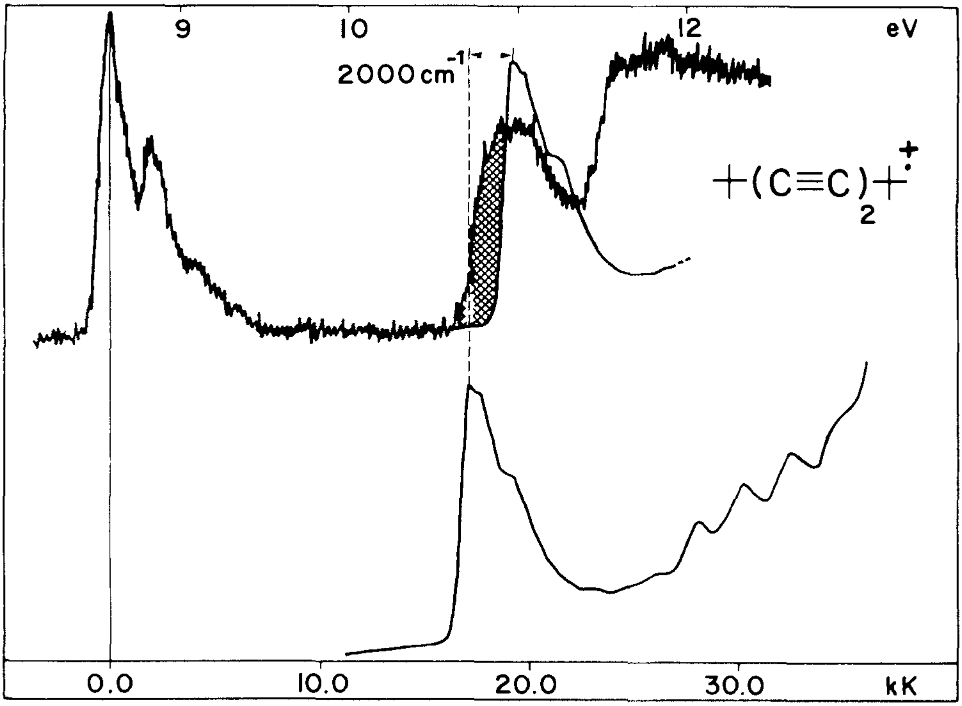


Fig. 3. *Assessment of the nature of the* $\tilde{A}$*-state of* **2**$^+$

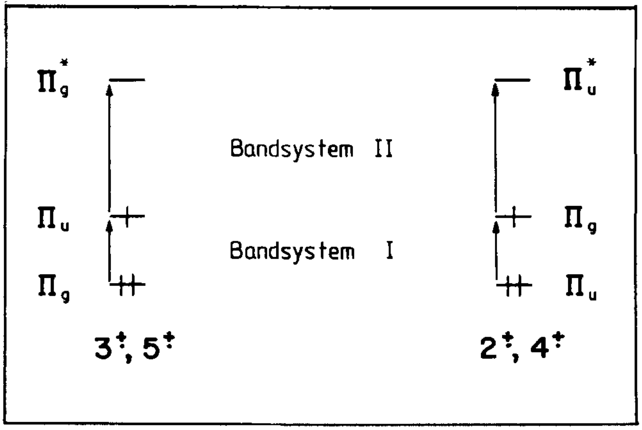
electronic spectral band displaced by this amount of energy to the blue and drawn on top of the PE.-band. The residual intensity at lower ionisation energies supports the previous contention that the Ã-state of $\mathbf{2}^+$ is not associated with the diacetylenic π-system. The present example also shows nicely the useful complementary nature of the two spectral techniques resulting from the different selection rules governing the two types of transition $M \rightarrow M^{+*} + e^-$, and $M^+ \rightarrow M^{+*}$.

Molecular cation $\mathbf{1}^+$. This system shows its first electronic transition around 20 kK where the PE.-spectrum indicates states of the ion to be present. The upper state is thus most probably of *'Koopmans'* nature, a conclusion which will find support later in this paper. The *Franck-Condon* (*F.-C.*) envelope of both spectral bands indicates considerable vibrational activity in the upper state. **1** possesses only one (degenerate) π-MO in the bonding manifold, which is confined to the triple bond, *i.e.* the π_u-HOMO. Hence, electron promotion must occur from a pseudo-π_g-MO lying next below and centered at the *t*-butyl groups in order to make the transition allowed. The accompanying charge migration results in excitation of low frequency motions, in agreement with the observed *FC*-envelope. Unfortunately, we do not know the extinction coefficient of this transition. That it is smaller than the one of the first bands of $\mathbf{2}^+$-$\mathbf{5}^+$ follows from the fact that higher concentrations of the neutral precursor **1** had to be used to render a sufficient optical density. On the basis of experience with measurements of this kind we think that ε of this transition is of order 100, hence, not negligible.

Band System II. In the spectra of $\mathbf{2}^+$ to $\mathbf{5}^+$, a second band system at higher energies is clearly discernible. It exhibits typically four members of a vibrational progression ($\tilde{\nu}$ = 2100-2200 cm^{-1}), the second peak being always the most intense one. In $\mathbf{5}^+$, the progressions of the first and second band system in fact overlap. Note that all three matrices used for $\mathbf{2}^+$ show this band system, though with different absolute intensities due to different background absorptions.

The uniform appearance of this second band system throughout the series suggests some common origin. A first hint stems from the fact that for $\mathbf{4}^+$ and $\mathbf{5}^+$ the band appears at energies where the PE.-spectrum is 'empty'. This points towards

Scheme



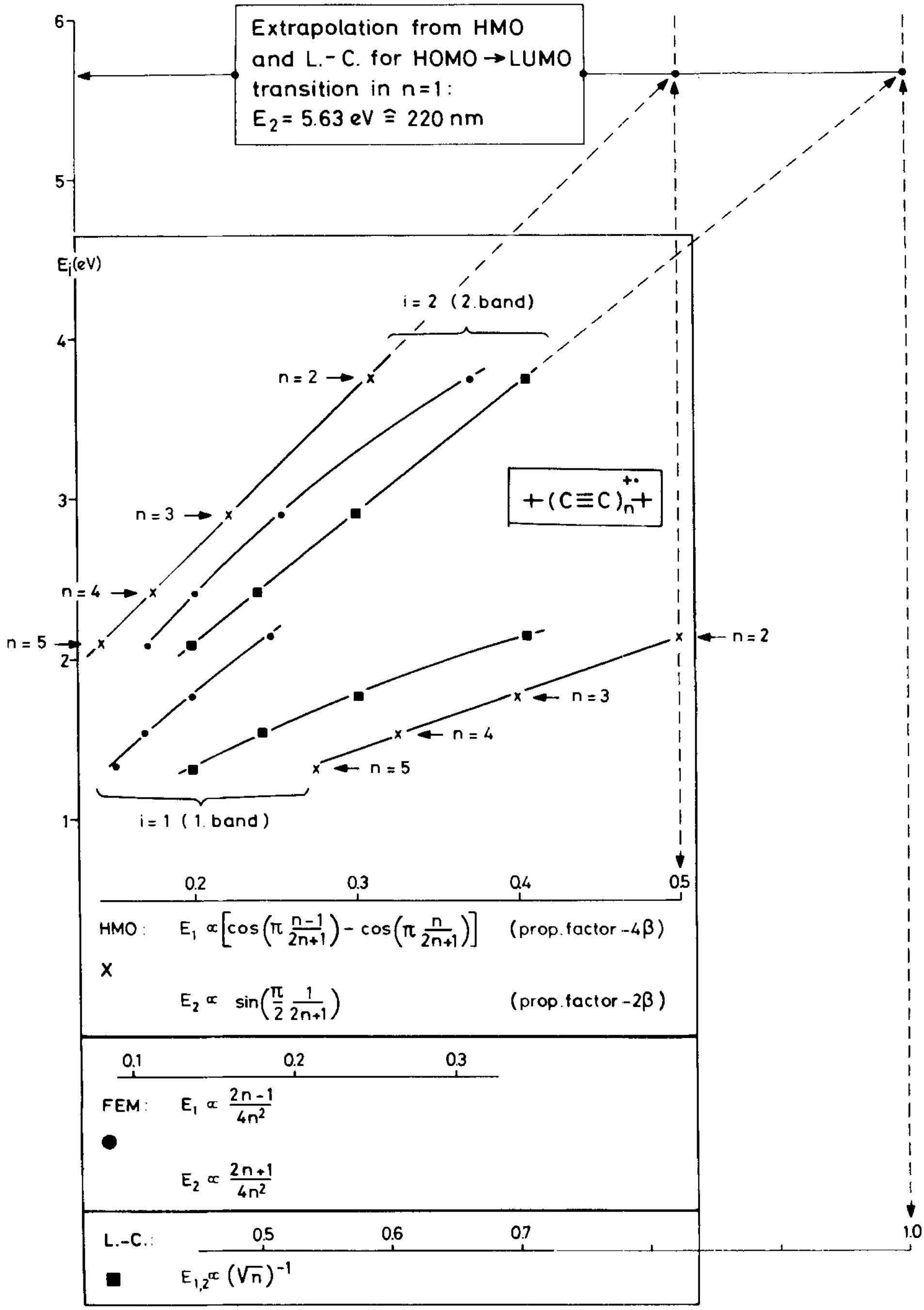


Fig. 4. *Correlation of the transition energies of* $\mathbf{2}^+$–$\mathbf{5}^+$ *with theoretical model quantities; prediction of the lowest lying 'Non-*Koopmans*'-state of* $\mathbf{1}^+$

an electron promotion to a virtual MO, *i.e.* the population of a 'Non-*Koopmans*' state ψ_{NK} in the ion. Based on the assumption of a $\pi \rightarrow \pi^*$ excitation ($\pi_g \rightarrow \pi_u^*$ for 2^+, 4^+; $\pi_u \rightarrow \pi_g^*$ for 3^+, 5^+), we performed theoretical calculations using three models: the HMO-, the 'free electron'(FEM)- and the *Lewis-Calvin* (*L.-C.*) method [7]. The results are displayed in *Figure 4*. For HMO- and *(L.-C.)*-models a linear correlation emerges which interestingly extrapolates to the same value for the corresponding transition in $\mathbf{1}^+$, $\lambda = 220$ nm. The strong matrix absorption in this region unfortunately precludes a verification of this prediction; work is in progress with respect to this question using rare gas matrices. With the FEM-model at least a monotonic correlation results. We note that similar good correlations evolve for band system I discussed above. These results strongly support the assumed electron excitation *Scheme* shown below.

Further support for this *Scheme* stems from the consideration of the very different (*F.-C.*)-structure of the two band systems. In *Figure 5* are shown the partial bond orders in the three relevant π-MO's.

It follows that the change in these quantities upon $\pi_{u,g} \rightarrow \pi_{g,u}$ and $\pi_{g,u} \rightarrow \pi_{u,g}^*$ promotion, respectively, is vastly different. In fact, for the latter, every strong bond becomes weaker and *vice versa*, the ground state polyacetylene ions turning into some sort of cumulene ions. This explains the strong excitation of the corresponding stretching motion. Note, that the lowest energy excitation of the neutral is bound to be of ($\pi \rightarrow \pi^*$)-type; here, long progressions are also observed [8].

Spectroscopic designation of the $\pi \rightarrow \pi^*$ *transition.* While $\pi_{g,u} \rightarrow \pi_{u,g}$ promotion (band system I) only gives rise to one state, ($\pi_{u,g} \rightarrow \pi_{g,u}^*$)-promotion (band system II),

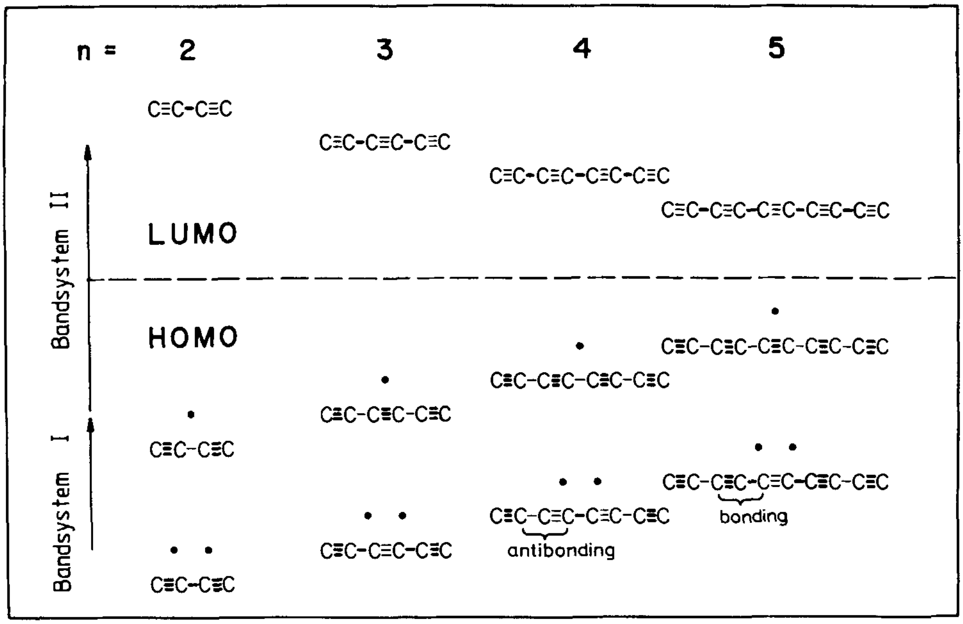


Fig. 5. *Pictorial representation of the partial π-bond orders of the MO's involved in the transitions of band system I and II, respectively.* (Bonding interaction: thick bonds; antibonding interaction: thin bonds)

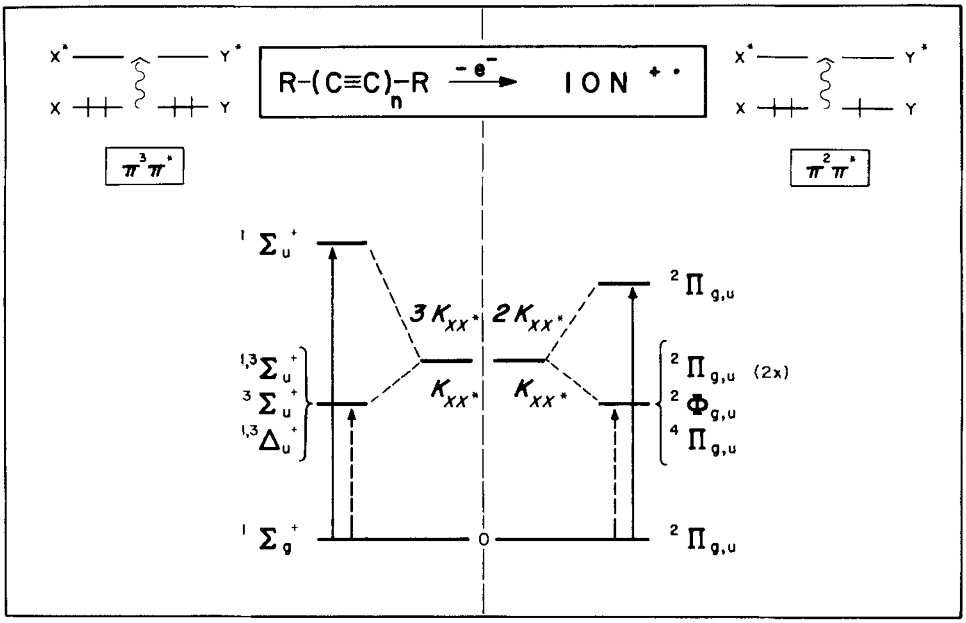


Fig. 6. *Spectroscopic designation of the states of* 1^+-5^+ *arising from HOMO → LUMO electron promotion; comparison with the corresponding states of the neutrals* **1-5**

i.e. the excited configuration ($\pi^2\pi^{*1}$) leads to five states as shown in *Figure 6* (right). This parallels the situation in neutral acetylenics where the excited configuration ($\pi^3\pi^{*1}$) generates six states which are also displayed in *Figure 6* (left). Assuming the ZDO-approximation to hold, these states are split as indicated in passing from a theoretical model without electron repulsing to one including it. Furthermore, within the frozen orbital approximation, the five lower lying states of M are energetically degenerate with the four of M^+ whereas the single upper one of M is disfavored with respect to the one of M^+ by an amount of energy equivalent to the exchange integral $K_{\pi_x\pi_x^*} \equiv K_{\pi_y\pi_y^*}$. Transitions to all states of the lower energy type are electric-dipole-forbidden both for M and M^+, but - as is well known - may gain intensity through vibrational borrowing. In addition, for the present systems, $D_{\infty h}$ symmetry is strongly idealized; the actual instantaneous symmetry may well lead to finite transition moments and the appearance of transition which are strictly forbidden within $D_{\infty h}$. We shall, therefore, not place to much emphasise

Table

	Ion 'HOMO → LUMO' transition (eV)	Neutral $^3\Sigma_u^+$	$^1\Sigma_u^-$	$^1\Sigma_u^+$
n=2	3.75	~3.4	4.9	?
n=3	2.90	~2.8	4.0	5.8
n=4	2.42	~2.3	3.5	5.2

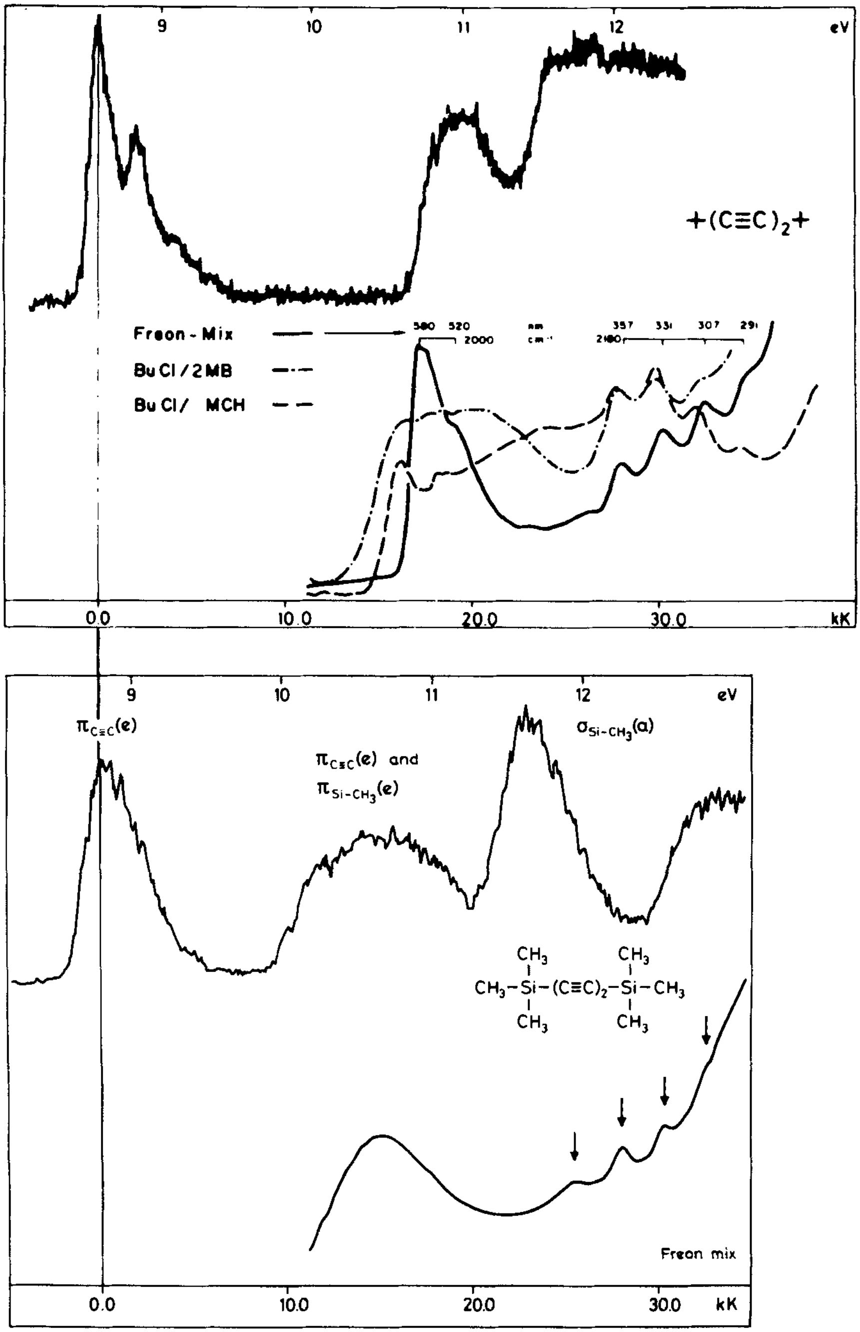


Fig. 7. *Comparison of the spectra of* **2**/**2**$^+$ *and of its trimethylsilyl analogue* $\mathbf{2}_{Si}/\mathbf{2}_{Si}^{+}$

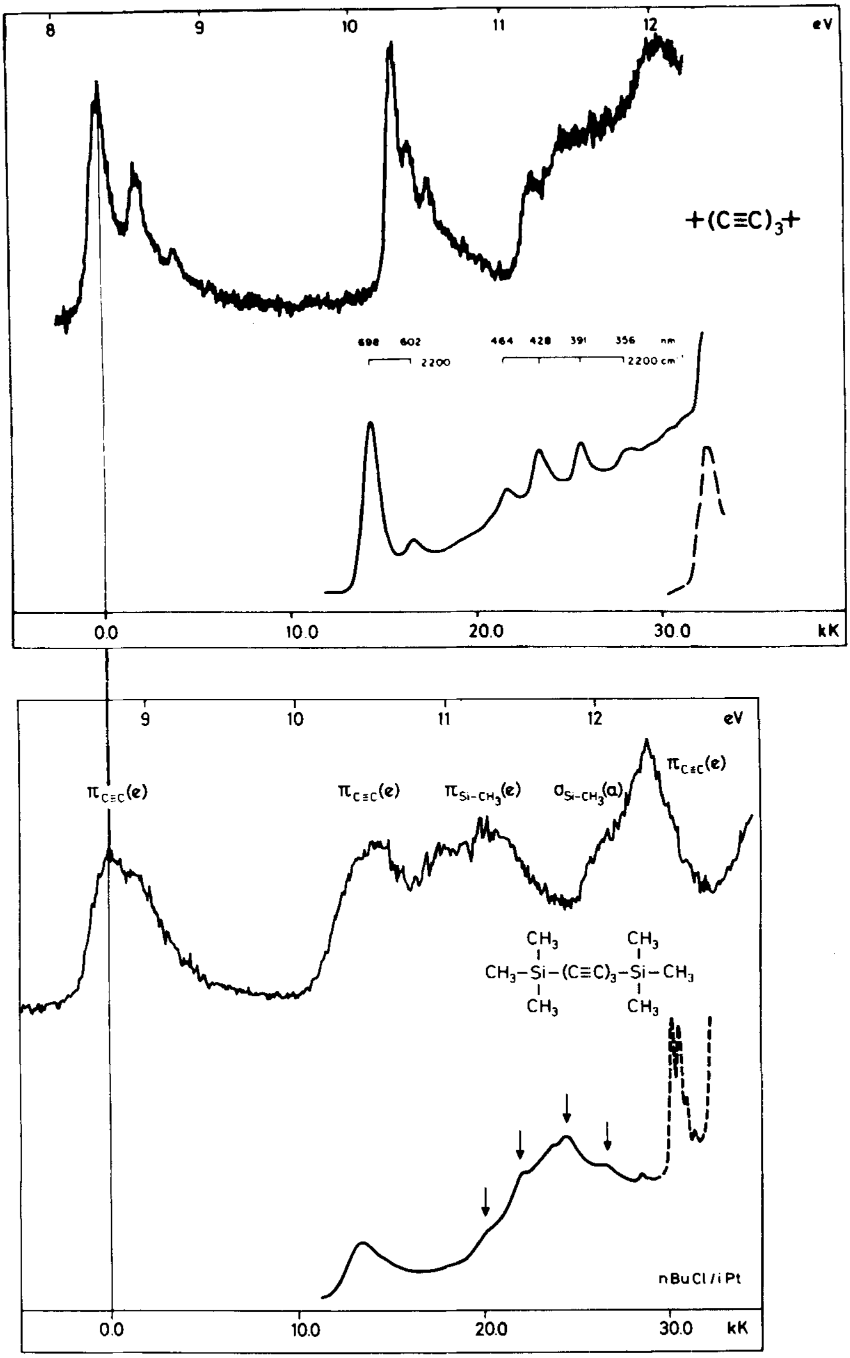


Fig. 8. *Comparison of the spectra of* 3/3^+ *and of its trimethylsilyl analogue* $3_{Si}/3_{Si}^{+}$. (Dashed lines: spectrum of neutral precursor)

in the subsequent discussion on intensities, but rather on the energies of the transitions.

The *Table* below shows a comparison between the energies of the ($\pi_{g,u} \rightarrow \pi^*_{u,g}$)-transition ('HOMO → LUMO') in M^+ discussed in this paper, and some assigned transitions in the corresponding neutrals *M*.

There is a close relationship between the ion transitions and ${}^3\Sigma_u^+ \leftarrow {}^1\Sigma_g^+$ of *M*. The energy of the ${}^1\Sigma_u^-$-state of *M* is clearly further up, showing the limits of the assumptions which led to *Figure 6*. However, the ${}^1\Sigma_u^+$-state is even much more distant. We conclude that the 'Non-*Koopmans*'-state discussed for $\mathbf{1}^+$-$\mathbf{5}^+$ in this paper is a member of the lower class of four states of M^+. The selection rules applied to these suggest specifically that we deal with one of two ${}^2\Pi_{g,u}$-states shown in *Figure 6*.

Trimethylsilyl-analogues. Figures 7 and *8* show the spectra of the trimethylsilyl-analogues of $\mathbf{2}/\mathbf{2}^+$ and $\mathbf{3}/\mathbf{3}^+$, *i.e.* $\mathbf{2}_{Si}/\mathbf{2}^+_{Si}$ and $\mathbf{3}_{Si}/\mathbf{3}^+_{Si}$. Both ions show a band system of type I which agrees with the assignment of the PE.-band with respect to energy and selection rules. Similar to **2**, the PE.-band of $\mathbf{2}_{Si}$ embraces two ionization events. From the electronic spectrum of $\mathbf{2}^+_{Si}$, accounting also for a red shift due to the medium effect, it appears that the Ã-state of the ion carries the hole in the π_{Si-CH_3}-MO. Though symmetry arguments allow a transition to this state, the associated transition moment apparently is very small as the two orbitals involved are centered at different regions in space. This is supported by the findings for $\mathbf{3}^+_{Si}$, where the state of the above type is the B̃-state of this ion. Indeed, no absorption occurs in this energy region. On the other hand, a transition to the Ã-state is observed for which electron promotion occurs between two orbitals both confined to the triple bond skeleton.

A final manifestation of the apparent rigor of the selection rules is provided by the finding that the PE.-spectrum of $\mathbf{2}_{Si}$ exhibits a ${}^2\Sigma$-state ~3 eV above its ground state. The electronic spectrum of the corresponding ion, however, is essentially empty in this region.

At higher energies both ions exhibit a further band system displaying vibrational progression (arrows). Admittedly, its resolution is rather poor and matrix absorption intervenes strongly. Nevertheless, the general appearance of the fine structure pattern resembles that of band system II discussed for the carbon analogues earlier. It is also noteworthy that these band systems of the hydrocarbons and the corresponding silyl derivatives are situated at roughly the same energy.

The congruency in vibrational fine structure discussed above allows us to conclude that we have established the position of the $\pi_{u,g} \rightarrow \pi^*_{g,u}$ 'Non-*Koopmans*'-states also for the ions of the silyl derivates. Their energetic match with those of the corresponding hydrocarbon ions supports this conclusion, as such an outcome is expected from first order perturbation theory.

Conclusions. - In [2] we have summarized the virtues of simultaneous considerations of the electronic spectrum of a molecular cation M^+ and the PE.-spectrum of the parent neutral *M*. The present paper concentrates on the establishment of 'Non-*Koopmans*'-states in the radical cations of some di-*t*-butyl-polyacetalenes with n triple bonds (n = 1-5) and some corresponding di-trimethylsilyl analogues (n = 2,3). For all systems (except n = 1) a low lying 'Non-*Koopmans*'-state could be established beyond reasonable doubt. For n = 1 this state is expected at 5.6 eV from an extrapolation procedure. This prediction could be tested if matrix material were used which does not absorb itself in this region. Experiments in this direction are presently under way using rare gas matrices.

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