

Breakdown of the One-Electron Picture of Ionization for Hydrocarbon π Systems

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The photoelectron spectra of a number of characteristic hydrocarbon π systems are analyzed in terms of Koopmans' and non-Koopmans' contributions within a limited configuration interaction (CI) framework. The results for several compounds, including quinodimethanes, fulvenes, annulenes, and related systems, suggest frequent invalidity of the one-electron picture of ionization even in the outer valence region. A similar situation may apply for the corresponding anion spectra, as indicated by the electron transmission spectrum of *p*-benzoquinone. This and several recent investigations demonstrate a general need for the introduction of a more realistic excited state concept than the one implied by Koopmans' approximation.

1. INTRODUCTION

Soon after its introduction in the early 1960's¹⁻⁴, uv-photoelectron spectroscopy gained considerable popularity among organic chemists and this technique is now an indispensable tool in physical organic chemistry^{3,5}. This remarkable development is not the result of a pronounced chemical interest in the radical cations generated in the spectrometer. Rather, photoelectron spectroscopy is generally appreciated as a source of information on the ground state orbital structure of the neutral molecule. The ionization energies of a molecule, corresponding to the measured photoelectron bands, can frequently to a good approximation be set equal to the negative of the energies of the occupied canonical molecular orbitals (Koopmans' approximation⁶, see Section 2). Hence, photoelectron spectroscopy comes close to an experimental probe of the orbital energies of a molecule. The popularity of organic photoelectron spectroscopy can thus be seen as a reflection of the increasing »orbital consciousness« of organic chemists⁵, a development which coincides with the breakthrough of the Woodward-Hoffmann rules^{7,8}.

The advent of photoelectron spectroscopy was welcomed with enthusiasm:

»Chemists can see the orbital structure of even fairly large molecules and no longer have to rely on the predictions of theoreticians«⁹

»Photoelectron spectroscopy has demonstrated experimentally to chemists, physicists and other sceptics that molecular orbitals really exist«¹⁰

Unfortunately, statements like these tend to be directly misleading to the uninitiated reader. First of all, the »molecular orbital« is a model concept, a one-electron function which serves as a convenient theoretical building block in the description of molecular many-electron states, but it has no physical existence and is not observable. Secondly, numerous cases are known where Koopmans' approximation breaks down, thereby destroying the approximate correlation between ionization energies and orbital energies (for recent reviews, see, *e. g.*, Refs. 11—14).

The aim of this communication is to contribute to the understanding of some of the limitations of Koopmans' approximation. In particular, we shall consider the possible breakdown of the one-electron picture of ionization for some characteristic hydrocarbon π systems. Planar unsaturated hydrocarbons are particularly suitable for photoelectron spectroscopic investigations, because their spectra tend to be relatively simple and because of the applicability of π electron theory⁵. In hundreds of investigations, the validity of the one-electron (or at least the quasi-particle) picture of ionization has been taken for granted. However, in recent years a number of studies¹²⁻²¹ have indicated that even for this class of apparently well-behaved compounds severe breakdown of Koopmans' approximation may be observed in the outer valence region, leading in some cases to complete inapplicability of the orbital approach. The most famous case is undoubtedly that of *p*-quinodimethane, which was first investigated by Koenig *et al.*^{15,16}, and which is the subject of dispute in the literature^{19,22}. In an increasing number of examples, as reviewed by Haselbach and coworkers¹²⁻¹⁴, the investigation of polyene ions by optical or photodissociation spectroscopy has identified so-called non-Koopmans' states in the low energy region. It is thus becoming increasingly clear that the general applicability of Koopmans' approximation to apparently normal polyenes is an absolutely non-trivial matter.

In the following Section we discuss in simple conceptual terms, the assumptions which are involved in the one-electron picture of ionization and the significance of configuration interaction. In the remaining part of the paper the discussion is exemplified by a consideration of some selected polyenes which offer favorable conditions for a breakdown of the one-electron approach. Calculational data are presented by using a recently developed »Linear Combination of Orthogonalized Atomic Orbitals« (LCOAO) model^{23,24} and open-shell configuration interaction (CI) in the canonical ensemble average approximation²⁵; the calculational strategy is outlined in the Appendix.

2. KOOPMANS' APPROXIMATION AND BEYOND

The bands in the experimental photoelectron spectrum indicate differences in energy between the ground state of the neutral species M and the various states *J* of the cation M⁺, corresponding to the different ionization energies *I_J*. Practically all theoretical predictions of molecular photoelectron spectra are based on canonical molecular orbital theory. Let us adopt the Born-Oppenheimer approximation (»fixed nuclei« assumption) and approximate the electronic ground state wave function of the closed-shell molecule M by a single Slater determinant corresponding to the ground electronic configuration of M. Formal removal of an electron from one of the occupied orbitals, neglecting electronic rearrangement on ionization (»frozen orbital« assumption), generates

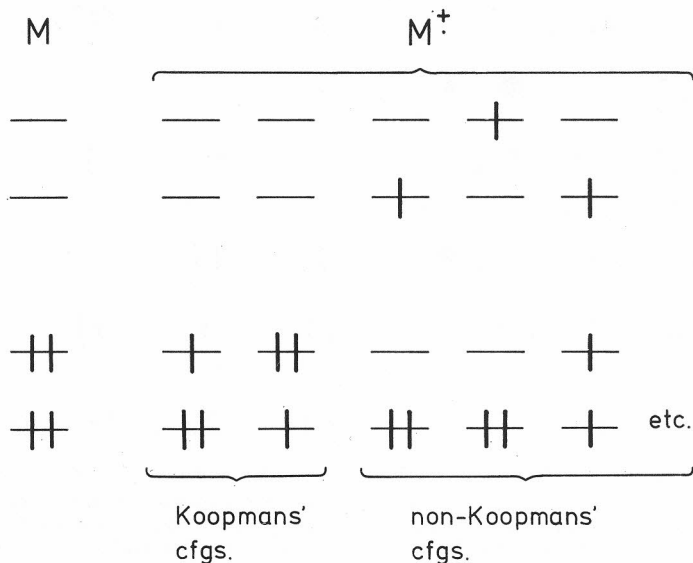


Figure 1. Schematic representation of the ground electronic configuration for a closed-shell molecule M and of Koopmans' and non-Koopmans' configurations for the radical cation M⁺.

a so-called Koopmans' configuration, which in the absence of configuration interaction defines a particular state of the radical cation M⁺ (Figure 1). Within this strictly one-electron picture of ionization, only transitions terminating on a Koopmans' configuration are electric dipole allowed, and we have a one-to-one correspondence between the number of individual photoelectron bands and the number of occupied orbitals. Moreover, the energy required to remove an electron from the *J*'th orbital is equal to minus the orbital energy, $-\varepsilon_J$. The *J*'th vertical ionization energy, I_J , can thus be predicted from the energy of the *J*'th orbital:

$$I_J = -\varepsilon_J \quad (1)$$

This result was first obtained by Koopmans and is usually referred to as »Koopmans' theorem«⁶. Koopmans showed that the variationally best set of orbitals for description of ionization processes is identical to the canonical Hartree-Fock-Slater set, thereby attaching a certain uniqueness and physical significance to this set²⁶.

Let us consider a simple example, namely the π system of C_{2h} butadiene. Figure 2 indicates the shape of the four π orbitals. Two of those, b_g and a_u , are occupied in the ¹A_g ground configuration, and we can thus generate two Koopmans' configurations for the radical cation, corresponding to ²B_g and ²A_u terms. Figure 2 also indicates the lowest non-Koopmans' configuration which can be arrived at from the ²B_g ground configuration of the cation by promotion of an electron from the highest occupied to the lowest unoccupied orbital, *i. e.* $b_g \rightarrow a_u^*$, leading to an ²A_u* term (the asterisk in the term symbol is used here to indicate the non-Koopmans' character).

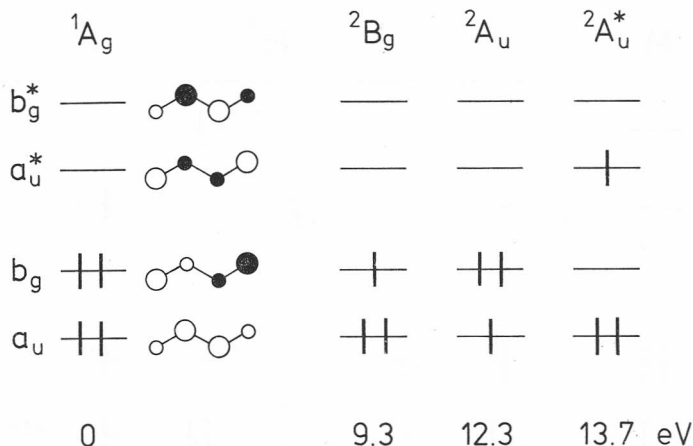


Figure 2. Indication of the ground electronic configuration for the π system of C_{2h} butadiene and of the three lowest electronic configurations for the π system of the radical cation. The relative configuration energies were calculated by the restricted open-shell LCAO-CI procedure (see Appendix).

Transitions from 1A_g to the two Koopmans' configurations 2B_g and 2A_u are one-photon allowed; they can be assigned the spectral intensity »unity« (the wave function of the emitted electron can always be chosen such as to permit ionization). In contrast, transition from 1A_g to ${}^2A_u^*$ or any other non-Koopmans' configuration is one-photon forbidden since the latter is more than singly excited with respect to 1A_g (Slater's rules)²⁶. Hence, at this level of approximation, we predict two and only two π bands in the photoelectron spectrum of butadiene.

The idealized one-electron picture of ionization outlined above is usually referred to as Koopmans' approximation, but it effectively involves a series of individual assumptions which can be summarized as follows:

- a) The Born-Oppenheimer »fixed nuclei« approximation
- b) The Hartree-Fock-Slater canonical orbital model
- c) The »frozen orbital« approximation
- d) Neglect of configuration interaction

In the following, we shall discuss a somewhat extended scheme which essentially incorporates the assumptions a), b), and c), but which considers explicitly configuration interaction in the radical cation, in particular between Koopmans' and non-Koopmans' configurations. As we shall see, this extension generally leads to an increase in the number of predicted photoelectron bands.

In our simple case of butadiene, for example, we thus consider the interaction between the Koopmans' configuration 2A_u and the non-Koopmans' configuration ${}^2A_u^*$ of the same symmetry (Figure 2). The interaction energy is given by the matrix element^{27,28}

where the two-electron integral on the right-hand side can be considered as the Coulomb interaction between the two overlap densities $a_u b_g$ and $b_g a_u^*$. Interactions between overlap densities tend to be small because of cancellation of contributions of opposite sign; they may be relatively large, however, if the densities are highly localized in the same region of space. Using standard semi-empirical π electron theory or the LCOAO theory outlined in the Appendix, the integral in Eq. (2) is estimated to be close to 1.0 eV. We further need the energies of the interacting configurations. Adopting the energies predicted by the restricted open-shell LCOAO theory (relative to the 1A_g ground state of butadiene), we obtain the 2×2 CI matrix

$$\begin{matrix} {}^2A_u & \left[\begin{array}{cc} 12.3 & 1.0 \\ 1.0 & 13.7 \end{array} \right] \\ {}^2A_u^* & \end{matrix}$$

with the eigenvalues and eigenvectors

$$\begin{aligned} E_1 &= 11.8 \text{ eV}, & \psi_1 &= 0.9 {}^2A_u + 0.4 {}^2A_u^* \\ E_2 &= 14.2 \text{ eV}, & \psi_2 &= 0.4 {}^2A_u - 0.9 {}^2A_u^* \end{aligned}$$

The resulting two states represent a mixture of Koopmans' and non-Koopmans' contributions. The Koopmans' character of ψ_1 amounts to $0.9^2 \times 100\% \approx 80\%$, that of ψ_2 to $0.4^2 \times 100\% \approx 20\%$. Hence, the intensity of the original Koopmans' transition ${}^1A_g \rightarrow {}^2A_u$ is distributed over two transitions, in proportions of 80% and 20%. Or, in other words, the single 2A_u line in the »Koopmans' spectrum« is split into two, one relatively strong and one relatively weak. In the usual terminology, the first peak is referred to as the »main«, »parent«, or »primary« peak, whereas the second one is referred to as a »satellite« or a »shake-up« peak. The satellite peak is said to have »borrowed« or »stolen« its intensity from the parent peak.

The results of the complete LCOAO-CI calculation for the π system of butadiene are illustrated graphically in Figure 3, with indication of the recorded photoelectron curve²⁹. Configuration interaction has a significant impact on the calculated spectrum, leading to splitting of the second Koopmans' transition into two 2A_u components, as discussed above. The results are consistent with those of several previous studies^{13,18-21,30-32} (including a non-empirical Green's function investigation³⁰). Experimental observation of the 2A_u satellite predicted close to 14 eV is impossible because of overlap with σ bands in the same energy region (note that transitions involving σ orbitals are not considered in the present theoretical treatment). However, both 2A_u states are apparently observed in the electronic absorption spectrum of the radical cation, giving rise to two prominent ${}^2B_g \rightarrow {}^2A_u$ absorption bands^{12,13,32}. Indeed, the second ${}^2B_g \rightarrow {}^2A_u$ transition, the one corresponding to the photoelectron satellite, is apparently the most intense optical transition in the near-uv/visible, illustrating the different selection rules in optical absorption and photoelectron spectroscopy.

In order to resolve the 2A_u satellite in the photoelectron spectrum of a butadiene derivative, the σ onset must be shifted towards higher and/or the satellite towards lower binding energies. Both shifts seem to take place in the case of 1,1,4,4-tetrafluorobutadiene²⁹. The weak feature at 13.4 eV in the photoelectron spectrum of this compound (Figure 3) has been assigned to the 2A_u shake-up state¹⁸⁻²⁰. The high binding energy shift of the σ onset relative to

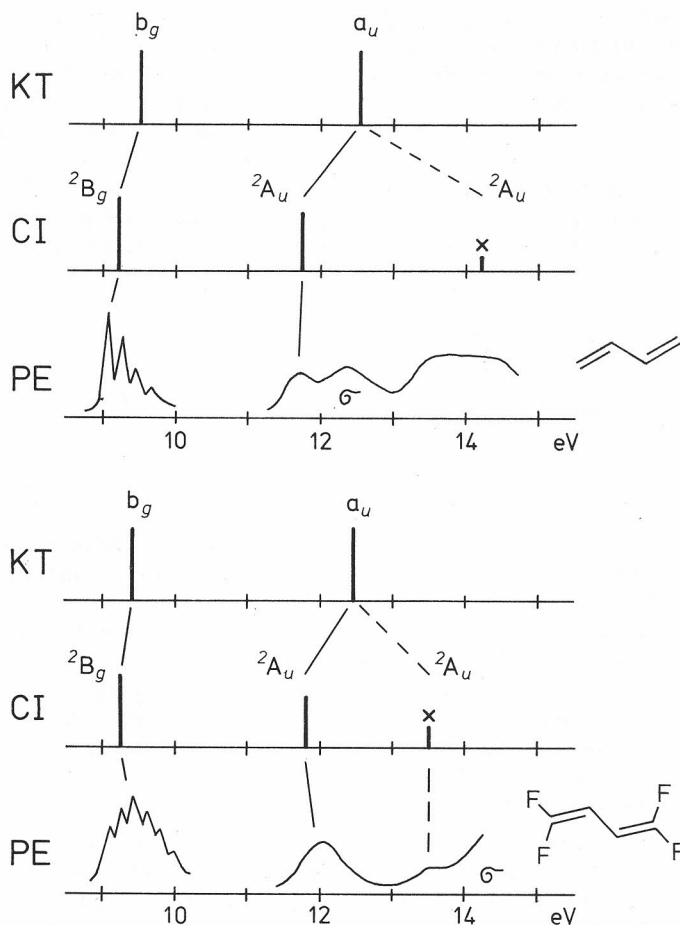


Figure 3. Calculated and observed²⁹ photoelectron spectra for butadiene (top) and 1,1,4,4-tetrafluorobutadiene (bottom). The lines in the theoretical spectra indicate predicted π bands and correspond to results obtained using Koopmans' theorem (KT), with indication of orbital symmetries, and to results of a restricted open-shell calculation on the radical cation with inclusion of configuration interaction (CI). The length of the lines is proportional to the predicted Koopmans' character and indicates the relative photoelectron intensity; transitions with relative intensity less than 0.6 are labeled with an »x« (see Section 2 and the Appendix).

the π levels is known as the fluoro effect, and can be explained by the inductive effect of the fluorine atoms and by the tendency of inductive and conjugative effects to cancel for the π levels. On the other hand, the low-energy shift of the π satellite relative to the main π levels can be explained by the circumstance that the π^* orbitals are much less affected by destabilizing conjugative interactions than the π orbitals, because of the much larger distance in energy to the fluorine 2p functions. As a result, the HOMO-LUMO gap is decreased and the non-Koopmans' configurations are stabilized by the fluorine substitution.

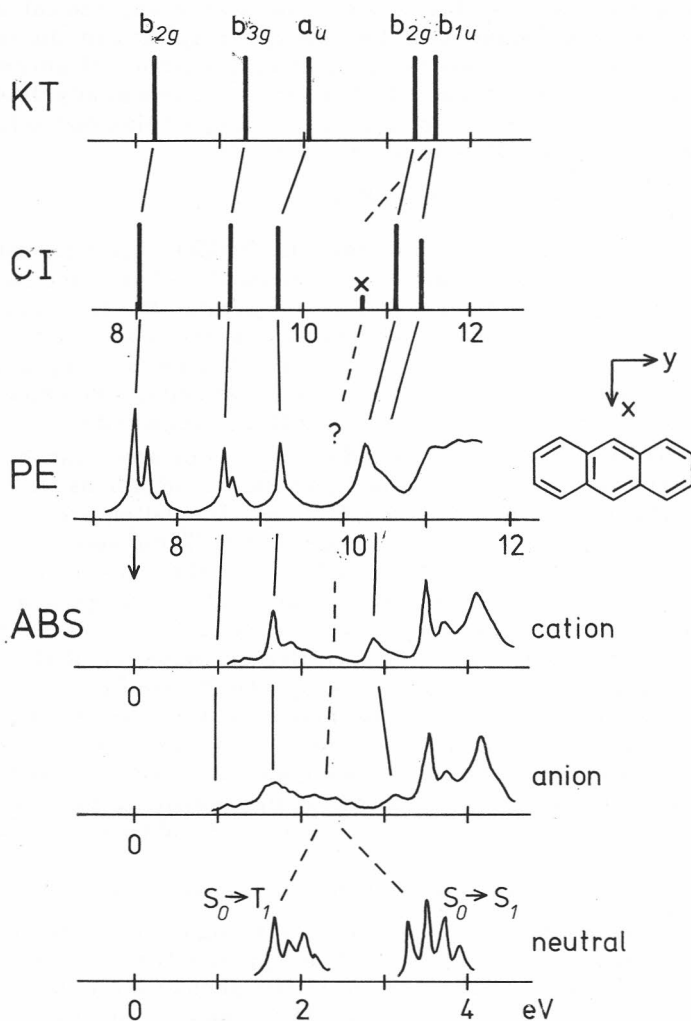


Figure 4. Top to bottom: Calculated and observed^{5,33} photoelectron spectra of anthracene (see legend to Figure 3), general outline of the observed optical absorption spectra of the anthracene radical cation and anion³⁴, and of the lowest singlet-singlet and singlet-triplet absorption bands for neutral anthracene³⁵.

We shall conclude this introduction with a brief consideration of the spectrum of a much larger system, namely the photoelectron spectrum of anthracene. The calculated spectrum is indicated in Figure 4. The fourth cation state can be described as a ${}^2B_{1u}$ HOMO-LUMO shake-up state. The predicted photoelectron intensity is weak and the state is apparently not observed in the experimental spectrum. However, the state seems to be observed in the optical absorption spectrum of the radical cation, where the feature close to 2.4 eV has been assigned to it³⁴ (note that the neighbouring ${}^2B_{2g} \rightarrow {}^2B_{2g}$ transition is forbidden by symmetry in one-photon absorption spectroscopy). A

corresponding transition is observed for the anthracene radical anion³⁴ (Figure 4). The obvious similarity of the absorption spectra of the positive and negative ions can be explained by the pairing properties of alternant hydrocarbons. The assignment of the 2.4 eV band to an essentially HOMO-LUMO type transition is supported by application of a simple relationship for alternant hydrocarbons derived by Haselbach, Wirz *et al.*¹⁷

$$E(D_1) \approx [E(S_1) \cdot E(T_1)]^{1/2}$$

This approximate relation states that the HOMO-LUMO transition energy $E(D_1)$ for the doublet cation or anion is intermediate between the corresponding singlet-singlet and singlet-triplet transition energies for the neutral species. The relevant absorption bands are indicated in the lower half of Figure 4; the large $S_1 - T_1$ energy splitting and the considerable lowering of $E(D_1)$ relative to $E(S_1)$ is characteristic for alternant systems and can be explained by the large HOMO-LUMO exchange integrals for these compounds³⁶.

The photoelectron spectra of butadiene and anthracene can be considered as characteristic for those of »normal« polyenes, in so far as there is a clear distinction between parent and satellite lines. The latter are weak and are easily obscured by overlap with the stronger bands. These photoelectron spectra can usually be satisfactorily interpreted within the one-electron picture of ionization; the interaction between Koopmans' and non-Koopmans' configurations is small relative to their separation in energy and configuration interaction can be considered as a minor perturbation. However, if the cross terms become large relative to the separations in energy, configuration interaction becomes essential. In this case, the distinction between parent lines and satellites is ambiguous or impossible, and the one-electron picture of ionization breaks down: there is no longer a one-to-one correspondence between molecular orbitals and photoelectron bands. In the remaining part of this paper, we shall consider some possible candidates for such »abnormal« behaviour.

3. *p*- AND *o*-QUINODIMETHANES AND RELATED COMPOUNDS

In 1975 Koenig *et al.*¹⁵ published an investigation of the photoelectron spectrum of *p*-quinodimethane, which was generated in the spectrometer by pyrolysis of [2.2](1,4)cyclophane. The measured photoelectron curve is outlined in Figure 5. The most remarkable result of the analysis by Koenig *et al.* was the assignment of the diffuse shoulder around 10.2 eV to an ionization process with large non-Koopmans' character and correspondingly weak photoelectron intensity. The resolution of the band is greatly improved in the spectrum of 3,7-dimethyl-*p*-quinodimethane¹⁶ (Figure 5), as a result of the different substituent effects for Koopmans' and non-Koopmans' configurations. The interpretation by Koenig *et al.* was highly unconventional. In two contemporary analyses³⁷, the spectrum of *p*-quinodimethane was discussed under the traditional assumption of Koopmans' approximation, with no reference to shake-up contributions, and in a more recent paper by Dewar²² the assignment of Koenig *et al.* is firmly rejected. However, an increasing body of calculational evidence¹⁹⁻²¹ seems to support the original assumptions of Koenig *et al.*^{15,16} The results shown in Figure 5 indicate strong, essentially first order interaction between the first HOMO-LUMO shake-up configuration and the third Koopmans' configuration, resulting in the prediction of two states with about equal

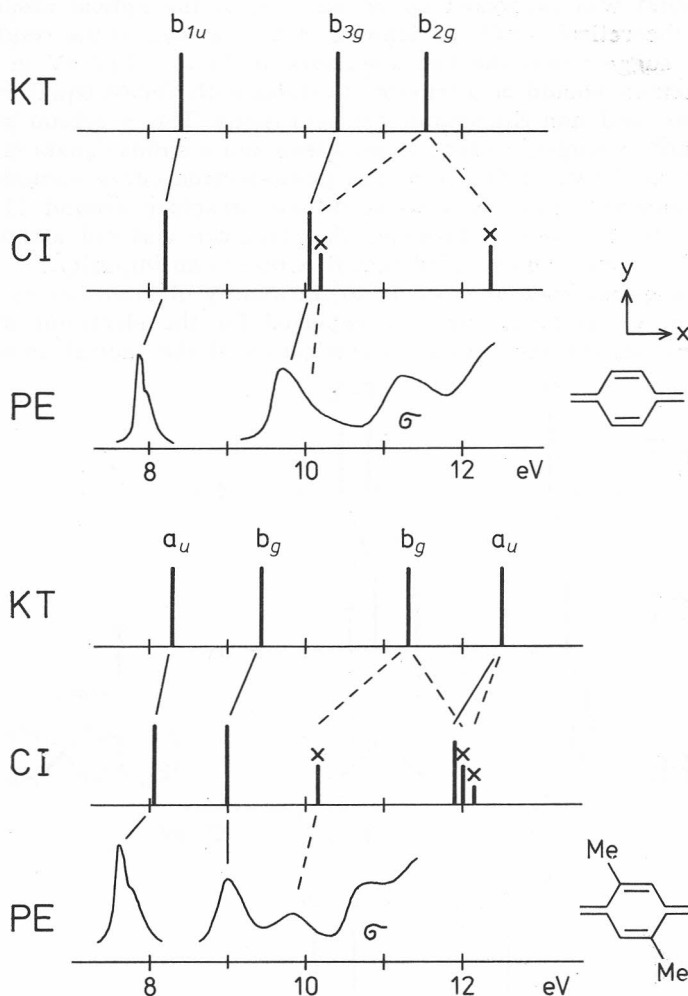


Figure 5. Calculated and observed¹⁵⁻¹⁶ photoelectron spectra for *p*-quinodimethane (top) and its 3,7-dimethyl derivative (bottom); see legend to Figure 3.

admixtures of Koopmans' and non-Koopmans' contributions. This situation corresponds to complete invalidity of the one-particle picture for these ionization processes. The reason for the predicted breakdown is a low HOMO-LUMO excitation energy, leading to near-degeneracy of Koopmans' and non-Koopmans' configurations in the low energy region, and a large cross term, which can be understood in terms of the orbital topology (the orbitals involved in the pertinent three-orbital integral all tend to have large amplitudes on the methylene groups²¹).

A similar breakdown is predicted for *o*-quinodimethane²⁰. Its photoelectron spectrum is unknown, but the spectrum of the derivative 2,2-dimethylisoidene has been measured and discussed by Haselbach *et al.*^{12,17} They assigned the lowest excited state of the cation to a state with large non-Koopmans' character;

this assignment was supported by an analysis of the optical absorption spectrum. The theoretical results of Schweig *et al.*²⁰ as well as the results outlined in Figure 6 suggest that the two shoulders at 9.4 and 10.2 eV in the photoelectron spectrum should be attributed to states with almost equal participation of Koopmans' and non-Koopmans' configurations. The π orbital structure of benzo[c]furan³⁸ is similar to that of isoindene and a similar shake-up structure is predicted, as shown in Figure 6. The photoelectron curve published by Palmer and Kennedy³⁸ exhibits a weak diffuse structure around 11 eV which may be due to a satellite. However, the structure was not assigned by the authors and it cannot be excluded that it is due to an impurity.

p- and *o*-quinodimethane belong to the family of alternant hydrocarbons, and a mirror image relationship is expected for the electronic structure of paired radical anions and cations. Investigation of the radical anions of these

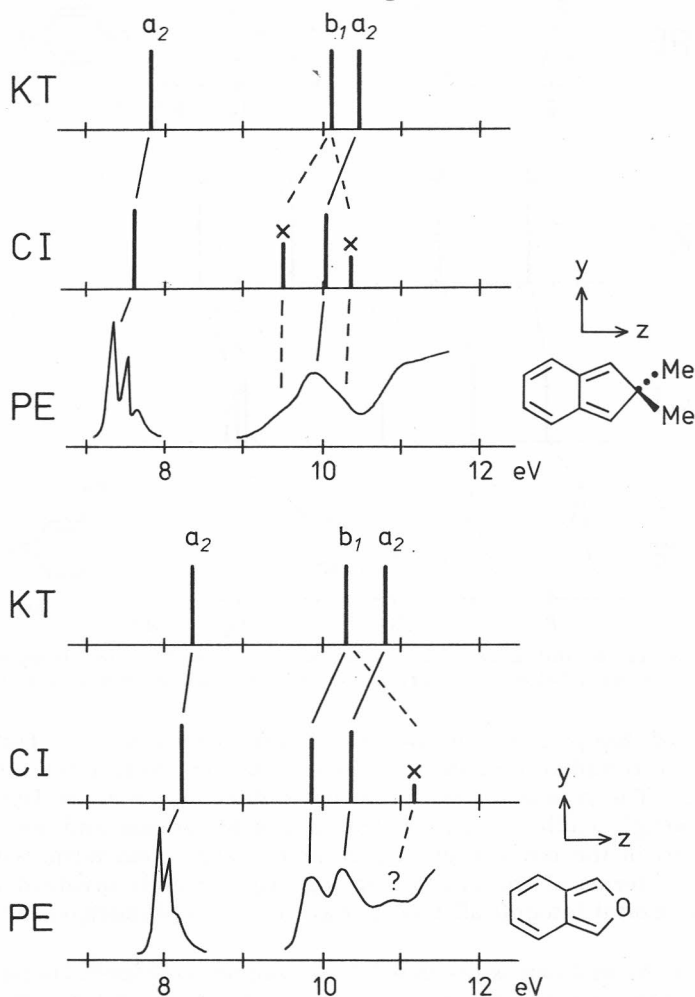


Figure 6. Calculated and observed^{17,38} photoelectron spectra for 2,2-dimethyl-isoindene (top) and benzo[c]furan (bottom); see legend to Figure 3.

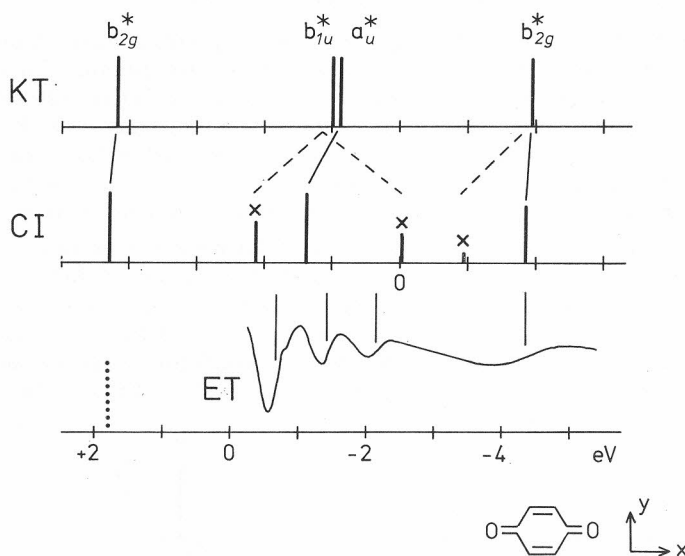


Figure 7. Calculated and observed^{41,42} electron affinities for *p*-benzoquinone. The theoretical energies are calculated and diagrammed in complete analogy to the treatment of the photoelectron energies (see legend to Figure 3). The experimental electron transmission spectrum is indicated in the form of the derivative of the transmitted current^{41,42}.

species, *e.g.* by electron transmission spectroscopy, would complement the photoelectron spectroscopic investigations^{39,40}. The electron transmission spectrum of *p*-benzoquinone, an oxa-analogue of *p*-quinodimethane, has been published recently by Allan⁴¹ and by Modelli and Burrow⁴². The electron transmission derivative curve is outlined in Figure 7. Note that the ground state of the anion, corresponding to electron capture by the b_{2g} (π^*) LUMO, is a stable anion state (positive electron affinity ≈ 1.8 eV) and is inaccessible to electron transmission spectroscopy³⁹. Four individual excited anion states are observed with attachment energies equal to 0.7, 1.4, 2.1, and 4.4 eV. However, only three virtual orbitals seem available in this region, suggesting a failure of the orbital picture of electron capture. Modelli and Burrow⁴² assigned the features at 0.7, 1.4, and 4.4 eV to the three available Koopmans' anion configurations, and assigned the additional resonance at 2.1 eV to a »core excitation« (corresponding to a non-Koopmans' anion configuration). Allan⁴¹, however, considers the large intensity of the 2.1 eV feature in electron transmission and vibrational excitation an indication of a »shape« resonance character (corresponding to a Koopmans' anion contribution). The calculated results outlined in Figure 7 suggest the assignment of the two resonances observed at 0.7 and 2.1 eV to two ${}^2B_{1u}$ anion states resulting from strong interaction between the second Koopmans' and the first non-Koopmans' π electron configuration. Because of the profound mixing, the assignment of »shape« and »core excitation« (*i. e.*, Koopmans' and non-Koopmans') character to these anion states is ambiguous. The situation is thus completely analogous to the one predicted for the corresponding ${}^2B_{2g}$ cation states of *p*-quinodimethane (Figure 5).

4. NON-ALTERNANT POLYENES

Non-alternant unsaturated hydrocarbons frequently have small HOMO-LUMO gaps, thereby increasing the density of non-Koopmans' ion configurations in the low energy region. Fulvene is one of the most investigated simple non-alternants, and fulvene derivatives have been discussed with respect to the applicability of Koopmans' approximation, in particular concerning the »frozen orbital« assumption^{5,43}. In this section we shall have a brief look at the photoelectron spectra of some compounds more or less related to fulvene.

The calculated and observed⁴⁴ spectra of fulvene are shown in Figure 8. A weak HOMO-LUMO type satellite is predicted in the region of the first σ band, gaining its intensity from the Koopmans' configuration corresponding to the lowest occupied π orbital. In the case of 6-vinyl-fulvene (Figure 8), the third Koopmans' and the first non-Koopmans' configurations are predicted to be near-degenerate, but the coupling is only modest, leading to the prediction

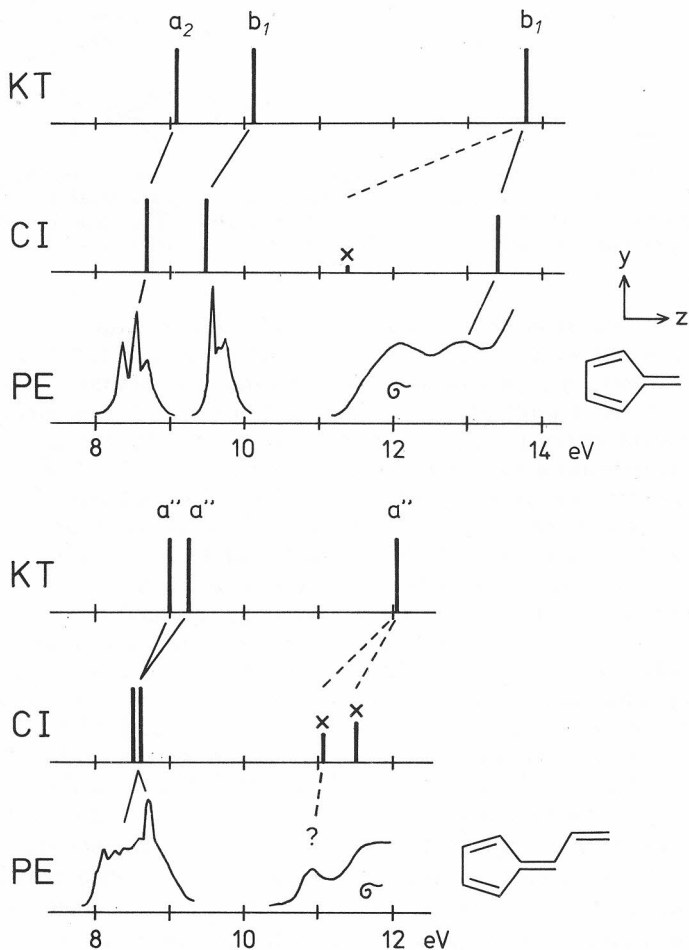


Figure 8. Calculated and observed^{5,45} photoelectron spectra for fulvene (top) and 6-vinyl-fulvene (bottom); see legend to Figure 3.

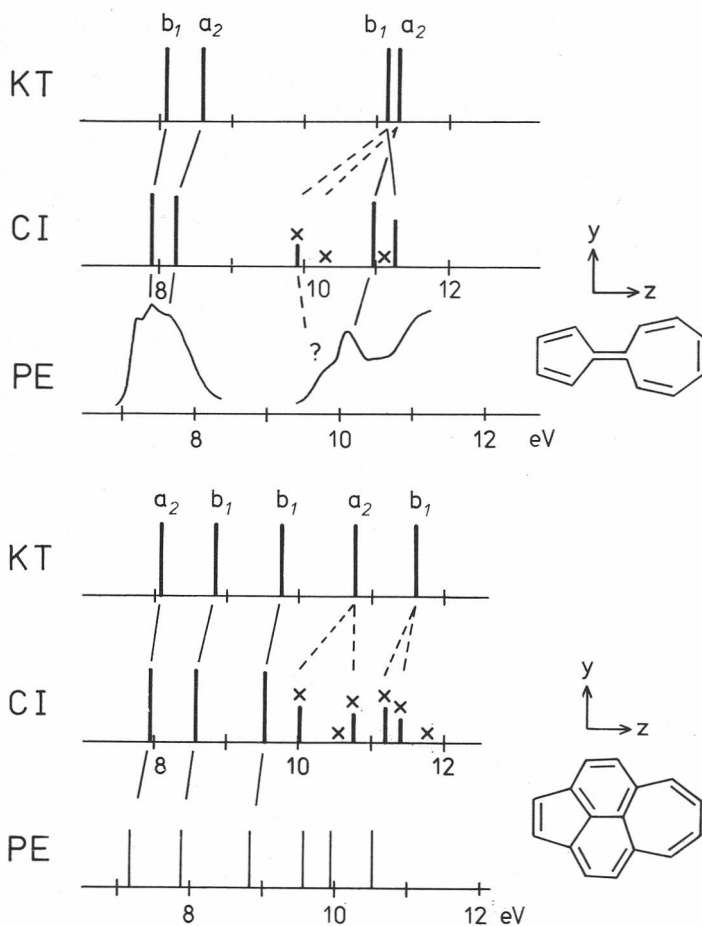


Figure 9. Calculated and observed^{5,45} photoelectron spectra for sesquifulvalene (top) and acepleiadylene (bottom); see legend to Figure 3. In the case of acepleiadylene, observed ionization energies⁴⁵ are indicated.

of two closely spaced transitions. The relatively low intensity of the third photoelectron band close to 11 eV⁵ can probably be explained by a shake-up contribution.

At least three low energy satellites are predicted for sesquifulvalene (Figure 9). The weak shoulder at 9.8 eV⁵ was assigned to a 2A_2 Koopmans' configuration by Heilbronner and Maier⁵, but was left unassigned by Marschner and Pohle³⁷. According to the present results, this feature can probably be assigned to a 2B_1 satellite. On the basis of a correlation of the observed first ionization energy with the Hückel orbital energy coefficient χ_{HOMO} for a series of π systems including sesquifulvalene, Heilbronner and Maier⁵ predicted an extremely drastic failure of the »frozen orbital« approximation for this compound (*i.e.*, the assumption of the same set of orbital functions for sesquifulvalene and its radical cation). The results of the present SCF-based calculations do not support this view. Actually, the calculated »Koopmans' defect«

for the first ionization energy of sesquifulvalene is comparatively small. The results of Heilbronner and Maier⁵ probably signify a shortcoming of the standard Hückel approximation, rather than a striking invalidity of the »frozen orbital« assumption (see also the discussions in Ref. 43).

A complicated spectrum is predicted in the case of acepleiadylene, as shown in Figure 9. In the region above the first three cation states, coupling between Koopmans' and non-Koopmans' configurations leads to the prediction of several states with fractional photoelectron intensity. Measured ionization energies has been published by Boschi, Clar, and Schmidt⁴⁵ and are indicated in Figure 9. Unfortunately, the photoelectron curve was not published, thereby complicating a verification of the predicted trends.

We finally consider the spectra of aceheptylene and dicyclopenta[*ef, kl*]-heptalene. The spectrum predicted for aceheptylene is dominated by the Koopmans' contributions, as shown in Figure 10. Several low-energy satellites are

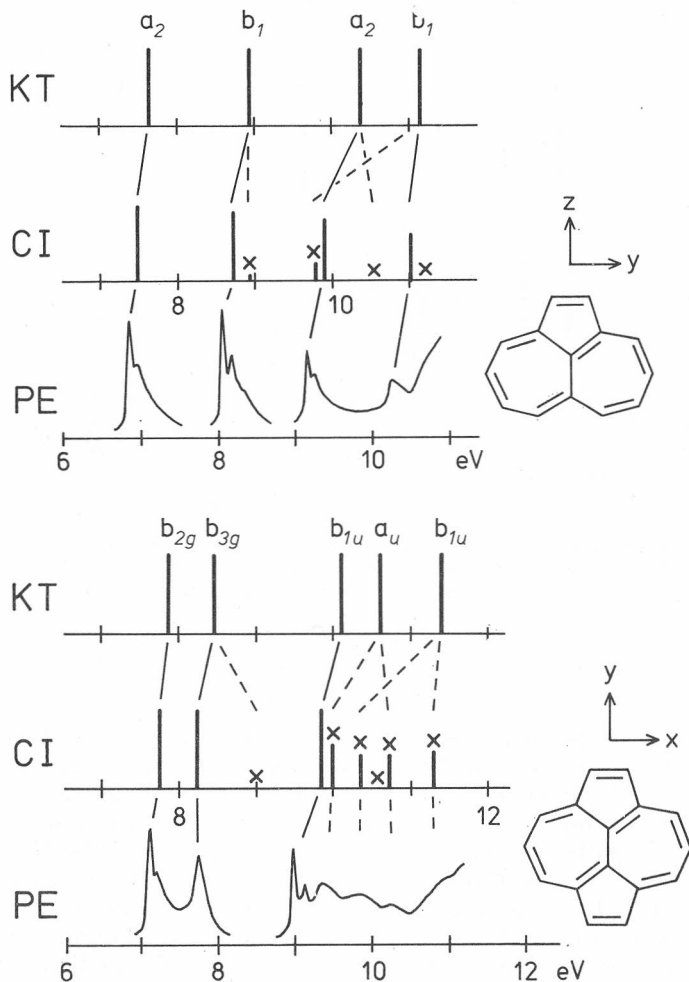


Figure 10. Calculated and observed^{46,47} photoelectron spectra for aceheptylene (top) and dicyclopenta[*ef, kl*]heptalene (bottom); see legend to Figure 3.

predicted, but they are all fairly weak and tend to overlap with the intenser main transitions. This prediction is consistent with the experimental spectrum^{46,47}, which looks much as expected for a »normal« polyene. Similarly »normal« spectra are predicted⁴⁸ (and observed⁴⁷) for several non-alternant polyenes, in spite of the presence of low-lying shake-up configurations, for example for pentalene, azulene, and cyclopent[*cd*]azulene. In contrast, a complex spectrum is predicted for dicyclopenta[*ef, kl*]heptalene (Figure 10) with complete scrambling of Koopmans' and non-Koopmans' contributions in the region above the third main band. The diffuse structures observed in this region of the experimental spectrum⁴⁷ seem quite consistent with the prediction.

5. BRIDGED ANNULENES

Another class of polyenes with potentially very small HOMO-LUMO gaps are the annulenes, particularly $[4n]$ annulenes, but also medium to large sized $[4n + 2]$ annulenes, provided they are fixed in a reasonably planar conformation.

In Figure 11 are shown the calculated and observed photoelectron spectra for two alkyl bridged $[14]$ annulenes, namely 1,6:8,13-ethanediylidene $[14]$ annulene and trans-15,16-dimethyl-dihydropyrene. As expected from the low excitation energies of the neutral compounds⁴⁹⁻⁵¹, several low-energy shake-up states are predicted for the cations. For 1,6:8,13-ethanediylidene $[14]$ annulene and related anthracene shaped annulenes Batich, Heilbronner, and Vogel⁵² recorded a »rather broad and ill-defined« band close to 9.7 eV which could not easily be assigned to a Koopmans' configuration. This band can probably be explained by the considerable shake-up activity predicted in this region. A similar situation is encountered in the case of the pyrene shaped annulene, as indicated in Figure 11. The weak and diffuse shoulder characterizing the onset of the third main band⁵³ can probably be assigned to one or two satellites, borrowing photoelectron intensity from the fourth and fifth Koopmans' configurations. Relative to the previously published CNDO/S results⁵¹, the present LCOAO calculation predicts an additional $b_g(\pi)$ orbital in the frontier region with considerable alkyl participation, thereby leading to an improved prediction and an alternative assignment of the third peak around 9.1 eV. This and other results⁴⁸ (e. g., Figures 5 and 6) seem to indicate a realistic representation in the LCOAO model of the hyperconjugative effect of alkyl groups.

In Figure 12 are indicated the results for cycl[3,2,2]azine, which can be considered as a $[10]$ annulene bridged by three bonds to a central nitrogen atom. A fairly »normal« photoelectron spectrum is predicted, in consistency with the observed spectrum⁵⁴. A more interesting case is presented by cycl-[3,3,3]azine, which can be considered as a perturbed $[12]$ annulene. This »anti-aromatic« compound has an extremely low-energy forbidden HOMO-LUMO transition in the near-infrared (~ 1.0 eV) and intense absorption in the visible region (~ 2.7 eV)⁵⁵; no wonder that a rich low-energy shake-up structure is predicted for the photoelectron spectrum, as shown in Figure 12. Most significantly, the doubly degenerate ${}^2E''$ Koopmans' configuration derived by ionization from the second highest occupied orbital level interacts strongly with a nearby non-Koopmans' configuration (corresponding to the visible absorption band for the neutral species), leading to the prediction of two low-energy ${}^2E''$ cation states with comparable photoelectron intensities. Comparison with the recorded photoelectron spectrum⁵⁴ seems to support the prediction (Figure

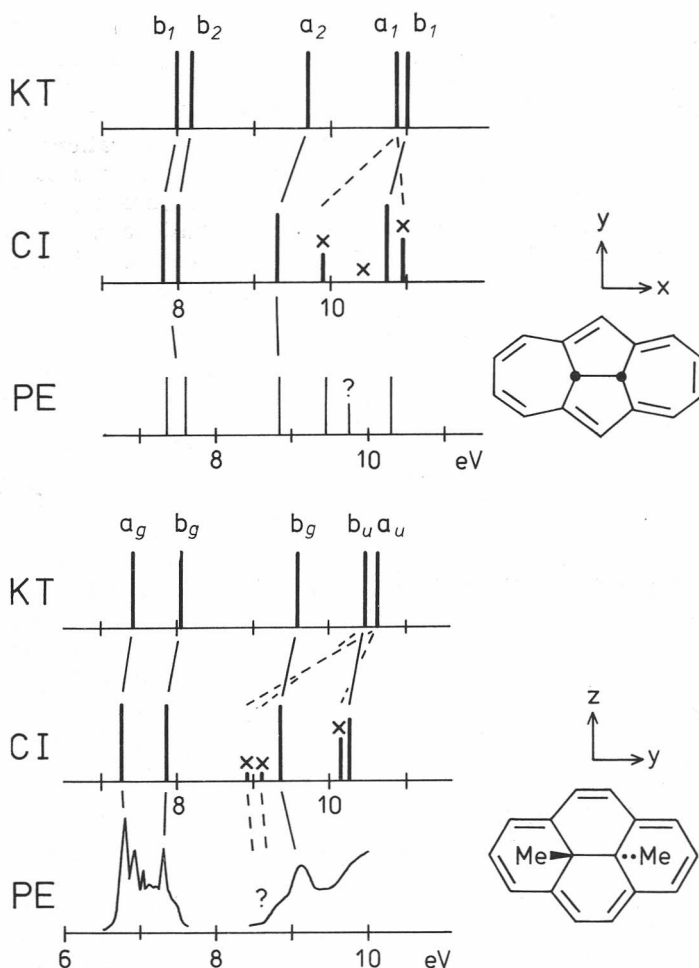


Figure 11. Calculated and observed^{52,53} photoelectron spectra for 1,6:8,13-ethanediylidene[14]annulene (top) and trans-15,16-dimethyldihydropyrene (bottom); see legend to Figure 3. In the case of 1,6:8,13-ethanediylidene[14]annulene, observed ionization energies⁵² are indicated.

12). Introduction of configuration interaction leads to a pleasing agreement with the number and spacing of the observed photoelectron maxima. On the other hand, the results for a »biradicaloid« species such as cycl[3,3,3]azine may be sensitive to the CI expansion. A more detailed investigation of the cation states of cyclazines is in progress²⁴.

6. CONCLUSIONS

The results of this and a number of recent investigations¹²⁻²¹ indicate that the contribution of shake-up processes to the photoelectron spectra of hydrocarbon π systems may be more significant than previously assumed, leading in several cases to inapplicability of the one-electron picture of ionization even

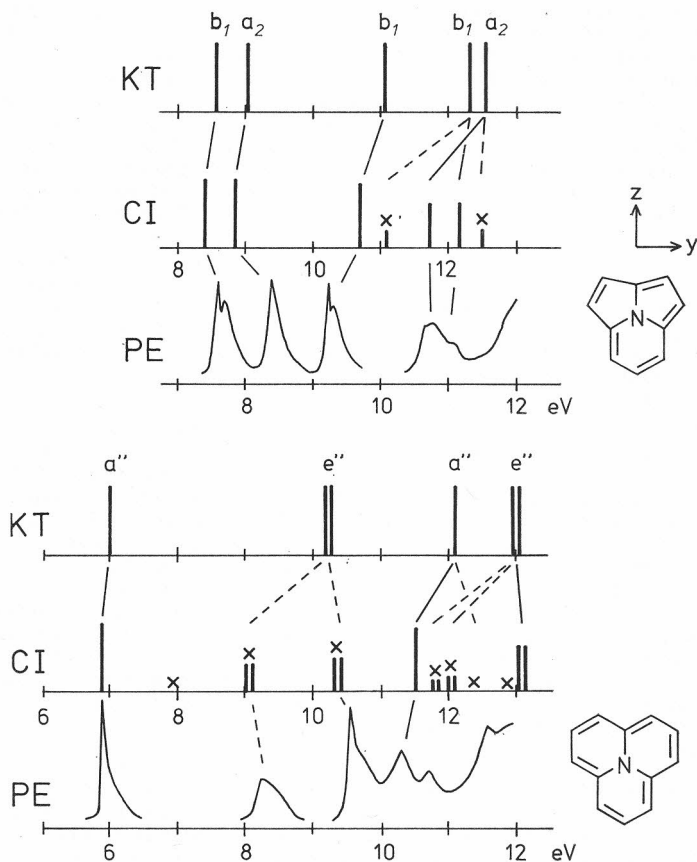


Figure 12. Calculated and observed⁵⁴ photoelectron spectra for cycl[4,2,2]azine (top) and cycl[3,3,3]azine (bottom); see legend to Figure 3.

in the region of lowest binding energy. A similar situation probably applies to the corresponding picture of electron affinity, as indicated by the electron transmission spectrum of *p*-benzoquinone. The results of approximate semi-empirical models, such as those applied by Schweig and his co-workers²⁰ for many years, suggest that useful predictions can be obtained within a limited configuration interaction framework. It is thus likely that simple CI models will find increased application within the fields of photoelectron and electron transmission spectroscopy, thereby introducing a more realistic electronic state picture than the one implied by a rigid application of Koopmans' theorem, equivalent to the conceptual model³⁶ prevailing for decades within the related fields of electronic absorption and emission spectroscopy.

APPENDIX: CALCULATIONAL

The photoelectron spectra were calculated at two levels of approximation: 1) by application of Koopmans' theorem⁶ to the results of a molecular orbital SCF calculation on the closed-shell ground configuration, and 2) by an open shell mono-excited configuration interaction (CI) calculation for the radical cation, using restricted open-

-shell SCF theory and the canonical ensemble average CI approximation discussed by Jørgensen²⁵. At the first level, only Koopmans' states are predicted; at the second the manifold is expanded by the inclusion of non-Koopmans' contributions, as considered in detail in Section 2, leading to the prediction of additional ionic states. The two levels of approximation refer to slightly different sets of orbital functions and the results are not strictly comparable. However, the overlap integrals between corresponding functions of the two sets of orbitals are in all cases very close to unity (≈ 0.99), and states predicted by the open-shell CI treatment can thus be directly related to the »parent states« obtained by the application of Koopmans' theorem, as indicated by the correlation lines in the diagrams. The relative photoelectron intensities indicated in the calculated spectra correspond to the sum of squared coefficients for Koopmans'-type configurations in the CI wave functions (see Section 2); states with intensities less than 0.6, corresponding to less than 60% Koopmans' character, are labeled with an »x«. With the exception of the case of the non-planar compounds in Figure 11, only $\pi \rightarrow \pi^*$ transitions were included in the CI expansion. All calculations were based on singlet ground state geometries predicted by the MNDO method²⁶, except for the compounds in Figure 11 for which structures were selected as previously described²¹.

Approximate canonical molecular orbitals were calculated in an all-valence-electrons basis of Löwdin orthogonalized atomic orbitals²⁷ according to a previously published prescription²³. The recently developed implementation of this »Linear Combination of Orthogonalized Atomic Orbitals« (LCOAO) method will be discussed in a forthcoming publication²⁴. The LCOAO-CI procedure is designed to predict electronic absorption and magnetic circular dichroism data for closed- and open-shell organic π systems, with particular emphasis on the reproduction of the fundamental pairing properties observed for alternant hydrocarbons²³. The application of different scaling factors²¹⁻³¹ for Koopmans' and non-Koopmans' configurations is avoided. However, the method is not parametrized to the prediction of photoelectron (or electron transmission) spectra and does not generally predict differences in ground state energy between neutral compounds and their ions; in the diagrams, the energy scale of the calculated electron spectrum is, therefore, in some cases shifted relative to that of the observed spectrum (as indicated in the Figures), to facilitate comparison of predicted and observed trends.

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SAŽETAK

Slom jednoelektronske slike kod ionizacije π -elektronskih ugljikovodika

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Analizirani su fotoelektronski spektri niza karakterističnih π -elektronskih ugljikovodika. Pri tome je uzeta u obzir Koopmansova aproksimacija, a doprinosi Koopmansovu defektu procijenjeni su s pomoću ograničene konfiguracijske interakcije (CI). Rezultati dobiveni za kvinodimetane, fulvene, anulene i neke srodne sustave nedvosmisleno pokazuju da jednoelektronska slika ionizacije ne vrijedi čak ni za vanjske valentne elektrone. Slična se situacija pojavljuje kod odgovarajućih spektara aniona. Ova kao i nedavne slične studije upućuju na potrebu uvođenja realističnijeg koncepta pobuđenog stanja od onoga koji se implicite nalazi u Koopmansovoj aproksimaciji.