

and is substantially impermeable to water. Samples were placed inside the Dewar and equilibrated with nitrogen gas that was used for temperature control. ESR spectra were obtained with a Varian E-109 X-band spectrometer with Varian temperature control accessories and Varian E-231 multipurpose cavity (rectangular TE₁₀₂ mode). The sample was thoroughly deoxygenated in order to obtain correct line shapes of ESR spectrum and to prevent possible oxidation of lipids.

Synthesis of Phospholipid 3. Dipalmitoyl glycerol and 3-phosphoric acid bromoethyl ester³⁵ (300 mg, 0.377 mmol) were mixed with 4 mL of (dimethylamino)ethyl methacrylate and stirred in an oil bath for 40

h at 50 °C. Upon cooling the solution to room temperature, 30 mL of acetone was added. A colorless precipitate was formed on standing at -10 °C for 4 h. This crude product (307 mg) was then chromatographed on silica gel using conditions similar to those previously described,² to give 192 mg (0.231 mmol) of **3** having the expected IR and NMR spectrum.² Anal. Calcd for **1**: N, 1.68; P, 3.72. Found: N, 1.71; P, 3.75.

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(34) Popp, C. A.; Hyde, J. S. *J. Magn. Reson.* **1981**, *43*, 249.

(35) Eibl, H. *Chem. Phys. Lipids* **1980**, *26*, 239.

Low Non-Koopmans' Ion States of Unsaturated Hydrocarbons. Semiempirical PERTCI Calculations¹

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Abstract: A theoretical approach to the question of low shake-up ionizations in the photoelectron spectra of unsaturated polyene-like hydrocarbons is made. PERTCI calculations including all singles and doubles with respect to the Koopmans' configurations as well as to the shake-up configurations were made using semiempirical MNDO, CNDO/S, and LNDO/S wave functions. The method was applied to butadiene, 1,1,4,4-tetrafluorobutadiene, *p*-xylylene, *o*-xylylene, isobenzofulvene, isobenzofulvenallene, 2,2-dimethylisoidene, and benzocyclobutadiene. Calculated ionization spectra for all of these systems are presented. They are compared with the UV photoelectron spectra of the molecules and, for 2,2-dimethylisoidene, with the UV/VIS spectrum of its cation. The results show that in all cases where photoelectron bands or shoulders of low intensity were ascribed to shake-up ionizations (e.g., tetrafluorobutadiene and *p*-xylylene) this was done for good reasons. The results further encompass new cases (e.g., isobenzofulvene, isobenzofulvenallene, and benzocyclobutadiene), for which low shake-up ionizations are predicted that cannot be observed in the photoelectron spectra due to their low intensities. These cases call for prompt measurements of the UV/VIS spectra of the corresponding cations.

Introduction

The interpretation of UV photoelectron (outer valence) spectra is usually based on the one-electron model of ionization, i.e., Koopmans' approximation, neglecting effects of electron correlation and reorganization. This is true for the overwhelming majority of ab initio as well as semiempirical calculations although it is known that Koopmans' approximation leads to wrong results for strongly localized molecular orbitals.² Two prominent examples of this failure are the ion state sequences of 1,4- and 1,2-benzoquinones.^{3,4} These can correctly be obtained only as n,n,π,π and n,π,n,π , respectively, if configuration interaction is admitted. In the inner valence region, the one-electron description is often effectively useless due to strong mixing between Koopmans' and non-Koopmans' configurations.⁵ As a consequence, numerous satellite bands emerge in the calculated photoelectron spectra. The interaction between Koopmans' and non-Koopmans' configurations can be so pronounced that a distinction between main bands and satellite bands is no longer possible. In addition, strong interaction between Koopmans configurations via non-Koopmans configura-

tions has recently been demonstrated.⁶

In accordance with these experiences all ion state calculations and thus interpretation of photoelectron spectra in our group have therefore been based on a large-scale configuration interaction treatment as a routine for many years, even in the low-energy (outer valence) region. Such a procedure guarantees that non-Koopmans' effects such as alterations in ion state sequences due to electron reorganization, correlation or Koopmans' state interactions via non-Koopmans' state interactions, and the appearance of low excited non-Koopmans' ion states (satellites or shake-up bands in the photoelectron spectra) are automatically taken into account.

Below we apply our configuration interaction approach in conjunction with semiempirical wave functions to unsaturated hydrocarbons, thus either confirming or predicting the existence of low shake-up ion states for these molecules.⁷ Transitions to such states may show up in the photoelectron spectra of these systems and/or the UV/VIS absorption spectra of the corresponding cations. The results clearly demonstrate the importance and the advantage of a many-electron approach to the prediction

(1) Part 99 of Theory and Application of Photoelectron Spectroscopy. For Part 98, see Schulz, R.; Schweig, A. *J. Electron Spectrosc. Relat. Phenom.* **1982**, *28*, 33.

(2) See, e.g., Lauer, G.; Schulte, K.-W.; Schweig, A. *Chem. Phys. Lett.* **1975**, *32*, 163, and references quoted therein.

(3) Lauer, G.; Schäfer, W.; Schweig, A. *Chem. Phys. Lett.* **1975**, *33*, 312.

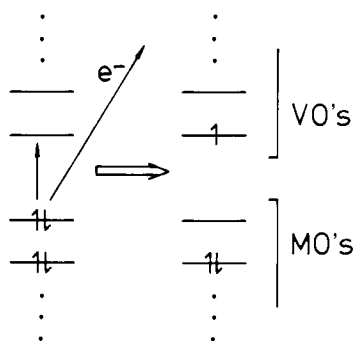
(4) Eck, V.; Lauer, G.; Schweig, A.; Thiel, W.; Vermeer, H. *Z. Naturforsch.* **1978**, *33a*, 383.

(5) Cederbaum, L. S.; Domcke, W.; Schirmer, J.; von Niessen, W.; Dircksen, G. H. F.; Kraemer, W. P. *J. Chem. Phys.* **1978**, *69*, 1591.

(6) von Niessen, W.; Bieri, G.; Schirmer, J.; Cederbaum, L. S. *Chem. Phys.* **1982**, *65*, 157.

(7) Semiempirical SECI estimations of shake-up ionizations in the photoelectron spectra of polyene-like molecules were also made (a) by Koenig, T., personal communication, 1981, and Koenig, T.; Klopfenstein, C. E.; Southworth, S.; Hoobler, J. A.; Wilesek, R. A.; Balle, T.; Shell, W.; Imre, D. *J. Am. Chem. Soc.* **1983**, *105*, 2256, for *p*-xylylene, its dimethyl and perfluoro derivatives and tetrafluorobutadiene, and (b) by Kluge, G.; Scholz, M. *Int. J. Quant. Chem.* **1981**, *20*, 669, for butadiene.

Scheme I



of ion states, even for hydrocarbons.

Method of Calculation

The molecular ground- and the ion-state calculations were performed using the PERTCI method and program system.⁸ For the ground-state calculations mixing of the closed-shell configuration was admitted with all singly and doubly excited configurations which can be generated from the closed-shell configuration, limiting the number of orbitals to the 12 highest occupied orbitals (MO's) and the 12 lowest virtual orbitals (VO's). Making use of the same assumption, each Koopmans' configuration was treated as follows: (1) all singly and doubly excited configurations with respect to the main configuration (i.e., the Koopmans' configuration chosen) were generated; (2) a PERTCI calculation based on the main and the generated singles and doubles was performed; (3) the resulting lowest-energy CI vector is inspected; if no non-Koopmans' interaction was revealed (i.e., no shake-up or other Koopmans' configuration occurred with sizable coefficients) the PERTCI ion-state calculation (based on the selected Koopmans' configuration) was finished; if, however, a shake-up configuration with an appreciable coefficient occurred, the following step was taken; (4) the configurations with the largest coefficients were gathered and considered to be the main configurations for a final PERTCI treatment; in this treatment, all singles and doubles from the main configurations (i.e., of the Koopmans' and shake-up type) were generated; (5) the final PERTCI calculation based on the main configurations and all the singles and doubles with respect to these main configurations was carried out. The selection parameter T^8 for both PERTCI treatments was chosen to be in the range of 0.008–0.02 eV.

For the molecules investigated in the present work two cases arose. Either one low-lying shake-up configuration (or state) occurred with practically no mixing to a Koopmans' configuration or strong configurational mixing occurred between one shake-up configuration and one Koopmans' configuration leading again to one low-lying shake-up state. In both cases, the shake-up configuration involved is the HOMO–LUMO one, as illustrated in Scheme I.

Our PERTCI approach to the calculation of non-Koopmans' effects can be based on either ab initio or semiempirical wave functions. Since in the present case rather large organic molecules are involved, we chose semiempirical ones, namely CNDO/S,⁹ MNDO,¹⁰ and LNDO/S¹¹ wave functions. Our group has experience over the years with the suitability of the combinations CNDO/S PERTCI, MNDO PERTCI, and LNDO/S PERTCI for the calculation of ion states of all sorts of organic systems.¹² A detailed comparison of methods (between CNDO/S SCF, MNDO SCF, LNDO/S SCF as well as CNDO/S PERTCI, MNDO PERTCI, and LNDO/S PERTCI) has been carried out.¹³ Since the LNDO/S method was parametrized both in the combined form LNDO/S PERTCI (i.e., with inclusion of electron correlation) and for reproducing ion and electronically excited states simultaneously, it appears to be most appropriate for the calculation of shake-up states.

In the subsequent section the calculated ion states are represented in the form of ionization spectra where the value of each bar on the abscissa

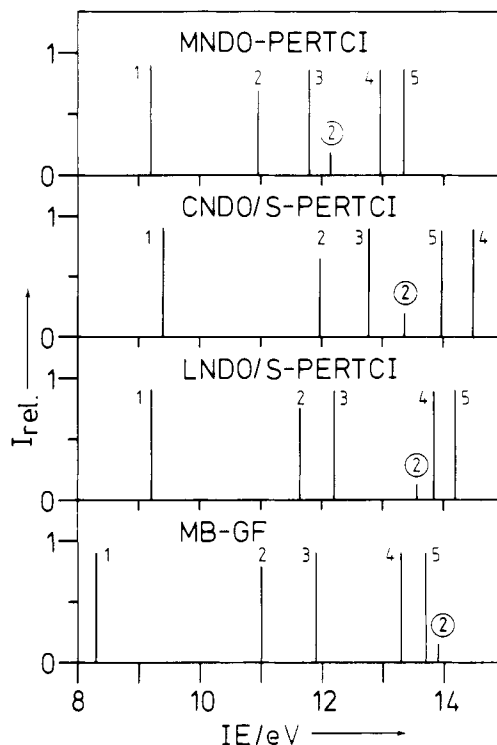


Figure 1. Ionization spectrum of *trans*-butadiene obtained using the semiempirical MNDO PERTCI, CNDO/S PERTCI, LNDO/S PERTCI, and ab initio MB-GF⁵ methods. The Koopmans' ionizations are numbered in the order of increasing energy, and a shake-up ionization is marked by encircling the number of the Koopmans' state to which it is predominantly coupled. The assignments are: (1) ${}^2B_g(\pi)$; (2) ${}^2A_u(\pi)$; (3) ${}^2A_g(\sigma)$; (encircled 2) ${}^2A_u(\sigma)$; (4) ${}^2B_u(\sigma)$; (5) ${}^2A_g(\sigma)$.

gives the vertical ionization energy and the height of the bar the intensity of that ionization. The intensity of each ionization was assumed to be proportional to the sum of the squared coefficients of the Koopmans' configurations that are contained in the corresponding CI vector. The Koopmans' ionizations in the ionization spectra shown are numbered and a shake-up ionization is marked by encircling the number of the Koopmans' state to which it is predominantly coupled and to which it owes most of its intensity. In cases where a low shake-up is predicted, but of practically no intensity, its location is marked by an arrow.

Results and Discussion

The examples considered are butadiene (1), 1,1,4,4-tetrafluorobutadiene (2), *p*-xylylene (3), *o*-xylylene (4), isobenzofulvene (5), isobenzofulvenallene (6), 2,2-dimethylisoidene (7), and benzocyclobutadiene (8); 1 is almost a classical example,⁵ 3 has been controversially discussed in ref 14 and 15; 2¹⁶ and 7¹⁷ have only recently been discussed in the context of shake-up processes. For 5, 6, and 8 low non-Koopmans' states are predicted for the first time in the present work.

Butadiene. *trans*-Butadiene (1) was chosen as a test for our



calculational approach since several other workers^{5,7b,16} have previously postulated a shake-up satellite at 13 to 14 eV in the photoelectron spectrum of this compound. Unfortunately, because of strongly overlapping bands in this region the prediction cannot be verified experimentally.

Figure 1 shows the MNDO PERTCI, CNDO/S PERTCI, and LNDO/S PERTCI ionization spectra of 1 along with the cor-

(8) Hase, H. L.; Lauer, K. G.; Schulte, K.-W.; Schweig, A. *Theoret. Chim. Acta* **1978**, *48*, 47.

(9) Schulte, K.-W.; Schweig, A. *Theor. Chim. Acta* **1974**, *33*, 19, and references cited therein; the present calculations were performed using the PSS1 parametrization scheme.

(10) Dewar, J. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899.

(11) Lauer, G.; Schulte, K.-W.; Schweig, A. *J. Am. Chem. Soc.* **1978**, *100*, 4925.

(12) See, e.g., Schulz, R.; Schweig, A. *J. Electron Spectrosc. Relat. Phenom.* **1982**, *28*, 33, and preceding parts in this series of papers.

(13) Schulz, R.; Schweig, A., manuscript in preparation, 1982.

(14) Koenig, T.; Wielesek, R.; Shell, W.; Balle, T. *J. Am. Chem. Soc.* **1975**, *97*, 3225.

(15) Dewar, M. J. S. *J. Am. Chem. Soc.* **1982**, *104*, 1447.

(16) Herrick, D. J. *Chem. Phys.* **1981**, *74*, 1239.

(17) Forster, P.; Gschwind, R.; Haselbach, E.; Klemm, U.; Wirz, J. *Nouv. J. Chim.* **1980**, *4*, 365.

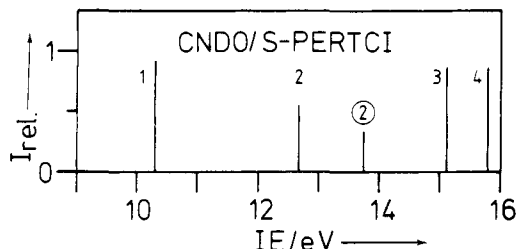


Figure 2. Ionization spectrum of 1,1,4,4-tetrafluorobutadiene obtained using the CNDO/S PERTCI method. The assignments of the Koopmans' ionizations (marked by numbers) and of the shake-up ionization (encircled number; for its meaning, see the caption of Figure 1) are: (1) ${}^2B_g(\pi)$; (2) ${}^2A_u(\pi)$; (encircled 2) ${}^2A_u(\pi)$; (3) ${}^2A_g(\sigma)$.

responding MB-GF spectrum taken from ref 5. The ${}^2B_g(\pi)$ state is considerably better reproduced by the semiempirical PERTCI methods (8.9 to 9.4 eV, measured at 9.1 eV) than by the *ab initio* MB-GF approach. Except for the CNDO/S PERTCI approach that predicts the order of σ states ${}^2A_g(\sigma)$ followed by ${}^2B_u(\sigma)$, the predicted sequences of all calculations agree with one another as well as with the experimental assignments. Particularly noteworthy is the ${}^2A_u(\pi)$ shake-up state which arises from mixing the lowest shake-up [HOMO (b_g)-LUMO(a_u)] configuration with the a_u -Koopmans' configuration. Both the CNDO/S PERTCI and the LND0/S PERTCI methods predict this state to be located at 13.5 eV with a relative intensity of 0.1 to 0.2.

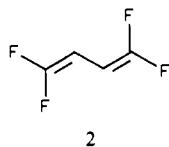
The MNDO PERTCI method yields 12.15 eV for the shake-up state, a distinctly lower value than all other approaches gave or as can be estimated from a simple relationship valid for the HOMO-LUMO shake-up state of alternant hydrocarbons¹⁷

$$E(\text{shake-up}) = IE_1 + [E(S_1) \cdot E(T_1)]^{1/2}$$

where $E(\text{shake-up})$ is the energy of the shake-up state, IE_1 the energy of the ion ground state, and $E(S_1)$ and $E(T_1)$ the energies of the lowest singlet and triplet excited states, respectively. With $IE_1 = 9$ eV,¹⁸ $E(S_1) = 5.92$ eV,¹⁹ and $E(T_1) = 3.22$ eV,¹⁹ we obtain $E(\text{shake-up}) = 13.4$ eV. The failure of the MNDO wave functions to correctly predict the shake-up energy is understandable if one is aware of the fact that MNDO PERTCI (or variants of it) excellently reproduce Koopmans' ion states, whereas electronically excited states are, as a rule, strongly underestimated.²⁰

To summarize, our results on *trans*-butadiene clearly support previous predictions of a hidden shake-up satellite at ca. 13.5 eV in the photoelectron spectrum of **1**. They further demonstrate the potential of the CNDO/S PERTCI and LND0/S PERTCI approaches for the prediction and localization of such states in cases which are more controversial or even uninvestigated.

1,1,4,4-Tetrafluorobutadiene. It has been proposed¹⁶ that a band of very low intensity in the photoelectron spectrum of 1,1,4,4-tetrafluoro-*trans*-butadiene (**2**) at ca. 13.5 eV is to be assigned



to the ${}^2A_1(\pi)$ satellite for this molecule which was discussed above in detail for the parent *trans*-butadiene (**1**). This very interesting proposal induced us to seek some calculational confirmation using our PERTCI approaches.

Figure 2 presents the CNDO/S PERTCI ionization spectrum of **2**. Note especially the ${}^2A_u(\pi)$ shake-up state at 13.7 eV. This result as well as the ionization spectrum from the corresponding MNDO PERTCI approach nicely corroborates the ad hoc pro-

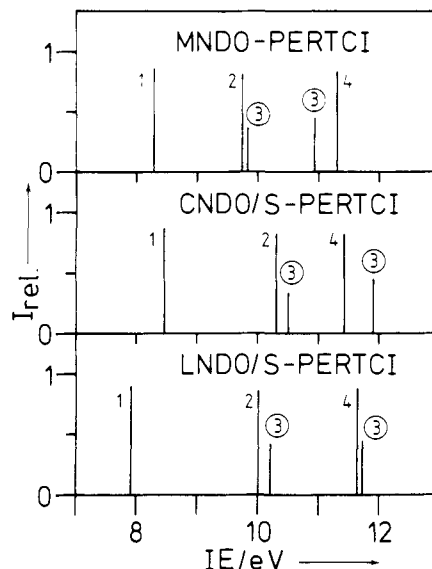


Figure 3. Ionization spectrum of *p*-xylylene calculated using the MNDO PERTCI, CNDO/S PERTCI, and LND0/S PERTCI approaches. The assignments of ionizations are as follows: (1) ${}^2B_{3u}(\pi)$; (2) ${}^2B_{1g}(\pi)$; (encircled 3) ${}^2B_{2g}(\pi)$; (4) ${}^2B_{3g}(\sigma)$; (encircled 3) ${}^2B_{2g}(\pi)$. The numbers designate the Koopmans' ionizations and the two encircled numbers signify a nearly perfect mixing of the [${}^2A_2(\pi)$] Koopmans' and shake-up configurations no longer allowing us to strictly classify one ionization as Koopmans' and the other one as shake-up ionization. The Cartesian coordinates were chosen such that the molecule is in the *yz* plane with *z* being the long axis (according to ref 14).

posal of ref 16 (note that LND0/S PERTCI calculations could not be made since the parameters of the fluorine atom have not yet been determined). Thus the present result strongly supports the idea of ref 16 and makes it very likely indeed that the shake-up predicted to exist in the photoelectron spectrum of *trans*-butadiene (but hitherto not proved by experiment) does really exist.

It is to be added, however, that the CNDO/S PERTCI treatment overemphasizes the relative intensity of the shake-up ionization (0.32) to some extent and this even more so for the MNDO PERTCI approach (results: shake-up energy = 12.13 eV relative intensity 0.4). An argument for the low MNDO shake-up energy has been given above.

***p*-Xylylene.** An original interpretation of the shoulder at 9.8 eV in the photoelectron spectrum of *p*-xylylene (**3**) assigned it the



HOMO-LUMO shake-up state from the very beginning of the photoelectron spectral study of this compound.¹⁴ This interpretation was later supported by a photoelectron spectral study of the 2,5-dimethyl derivative of **3**.²¹ Most recently this assignment was rejected on the base of MNDO-SCF calculations and the spectral feature in question was ascribed to an impurity.¹⁵ This controversy makes it most timely to present the results of our PERTCI calculations of the ion state of **3**. The calculations showed that dramatic changes of ion-state energies occur as referenced to the Koopmans' values when configuration interaction is admitted.

Figure 3 exhibits the MNDO PERTCI, CNDO/S PERTCI, and LND0/S PERTCI ionization spectra of **3**. All three procedures predict strong mixing between the HOMO-LUMO b_{2g} shake-up configuration (energy: MNDO = 11.16 eV, CNDO/S = 11.23 eV, and LND0/S = 11.85 eV) and the adjacent Koopmans' configuration of the same symmetry (energy: MNDO

(18) Beez, M.; Bieri, G.; Bock, H.; Heilbronner, E. *Helv. Chim. Acta* **1973**, *56*, 1028.

(19) Mosher, O. A.; Flicker, W. A.; Kuppermann, A. *J. Chem. Phys.* **1973**, *59*, 6502.

(20) Schweig, A.; Thiel, W. *J. Am. Chem. Soc.* **1981**, *103*, 1425.

(21) Koenig, T.; Southworth, S. *J. Am. Chem. Soc.* **1977**, *99*, 2807.

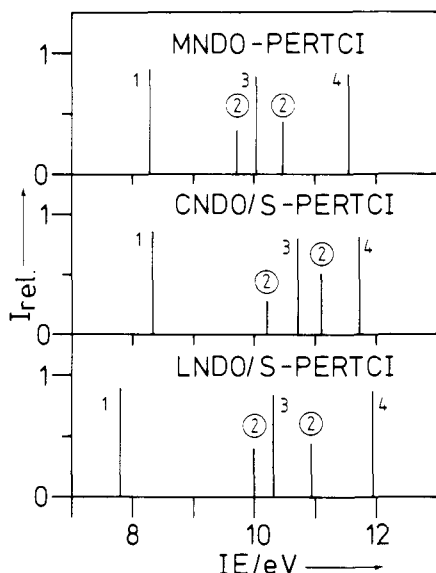


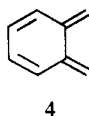
Figure 4. Ionization spectrum of *o*-xylene calculated using the MNDO PERTCI, CNDO/S PERTCI, and LNDO/S PERTCI methods. The assignments of ionizations are: (1) ${}^2A_2(\pi)$; (encircled 2) ${}^2B_1(\pi)$; (3) ${}^2A_2(\pi)$; (encircled 2) ${}^2B_1(\pi)$; (4) ${}^2A_1(\sigma)$. For the designation of ionizations, see the caption of Figure 3.

= 10.73 eV, CNDO/S = 11.54 eV, and LNDO/S = 11.37 eV). As a result of this coupling all three procedures predict the first non-Koopmans' ionization to occur at ca. 10 eV, i.e., at the high-energy flank of the second band in the photoelectron spectrum of **3**. According to the data obtained, the second mixed state should occur near the third Koopmans' state at 11 to 12 eV. Thus the present results fully confirm the original assignments of ref 14 and 21.

The energy of the shake-up configuration was estimated in ref 15 to be higher than 12 eV. As shown above, strong configurational interaction reduces this value appreciably.

The occurrence of low non-Koopmans' ionizations is by no means confined to **3**. We present the full PERTCI ionization spectra of *o*-xylene, isobenzofulvene, isobenzofulvenallene, 2,2-dimethylisoidene, and benzocyclobutadiene. Among these, shake-up states have not been discussed before for isobenzofulvene, isobenzofulvenallene and benzocyclobutadiene.

***o*-Xylene and Isoindene Derivatives.** The structure of *o*-xylene (**4**) makes the occurrence of low non-Koopmans' ion states



very probable. Comparison with structure-related compounds leads us to expect a low ${}^2A_2(\pi)$ ion ground state at ca. 7.5 eV. The lowest electronically excited state (1B_2) of the molecule has been determined to be at 3.4 eV above the ground state.²² The photoelectron spectrum of **4** is still unknown. Attempts to generate and detect **4** in VTPES²³ experiments failed;^{24,25} instead of **4** benzocyclobutene was obtained. Because of the low activation energy of the unimolecular consecutive reaction ($E_a = 26.9$ kcal/mol,²⁶ $A = 2.1 \times 10^{12} \text{ s}^{-1}$)²⁶ "cold methods" should be tried for the generation and photoelectron spectral detection of **4**. The photoelectron spectrum of **4** and the UV/VIS spectrum of the

(22) Tseng, K. L.; Michl, J. *J. Am. Chem. Soc.* **1977**, *99*, 4840.

(23) Schweig, A.; Vermeer, H.; Weidner, U. *Chem. Phys. Lett.* **1974**, *26*, 229; Schäfer, W.; Schweig, A. *Z. Naturforsch.* **1975**, *30a*, 1785.

(24) E.g., from isochromanone: Eck, V.; Schweig, A., unpublished results; Eck, V. Thesis, Marburg, 1979.

(25) Koenig, T.; Imre, D.; Hoobler, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 6446.

(26) Roth, W. R.; Scholz, B. P. *Chem. Ber.* **1981**, *114*, 3741.

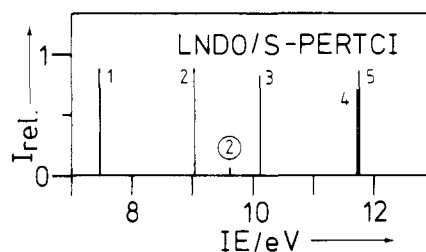


Figure 5. Ionization spectrum of isobenzofulvene obtained by use of the LNDO/S PERTCI treatment. The assignments of ionizations are: (1) ${}^2A_2(\pi)$; (2) ${}^2B_1(\pi)$; (encircled 2) ${}^2B_1(\pi)$; (3) ${}^2A_2(\pi)$; (4) ${}^2B_1(\pi)$; (5) ${}^2A_1(\sigma)$. For the designation of ionizations, see the caption of Figure 1.

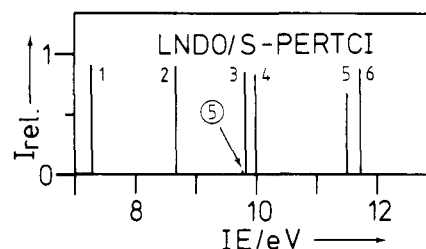


Figure 6. Ionization spectrum of isobenzofulvenallene calculated by use of the LNDO/S PERTCI treatment. The assignments of ionizations are: (1) ${}^2A_2(\pi)$; (2) ${}^2B_1(\pi)$; (encircled 5) ${}^2B_1(\pi)$; (3) ${}^2B_2(\sigma)$; (4) ${}^2A_2(\pi)$; (5) ${}^2B_1(\pi)$; (6) ${}^2A_1(\sigma)$. For the designation of ionizations, see the caption of Figure 1.

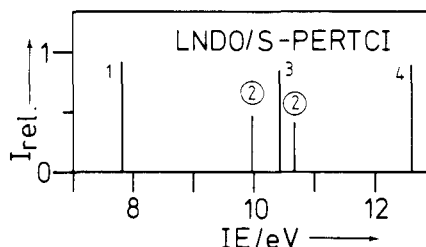
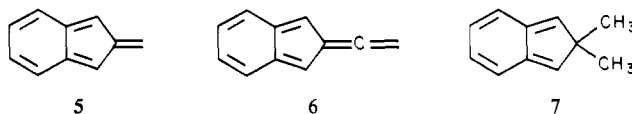


Figure 7. Ionization spectrum of 2,2-dimethylisoidene computed using the LNDO/S PERTCI method. The assignments of ionizations are: (1) ${}^2A_2(\pi)$; (encircled 2) ${}^2B_1(\pi)$; (3) ${}^2A_2(\pi)$; (encircled 2) ${}^2B_1(\pi)$; (4) ${}^2B_2(\sigma)$. For the designation of ionizations, see the caption of Figure 3.

corresponding cation are very much desired in order to examine the predictions made below.

Figure 4 displays the MNDO PERTCI, CNDO/S PERTCI, and LNDO/S PERTCI ionization spectra of **4**. In accordance with the open-shell PPP CI results of ref 17 the PERTCI calculations predict that already the first excited ion state of **4** is heavily mixed with the HOMO-LUMO shake-up configuration. The PERTCI results are different, however, in two respects. First, PERTCI yields a higher contribution of the Koopmans' configuration to the 2B_1 shake-up state than the PPP CI approach, and secondly, the PERTCI energy of the first non-Koopmans' state amounts to 10 eV as compared to 8.6 eV derived from the PPP CI treatment.

The electronic structure of the isoindene derivatives isobenzofulvene (**5**), isobenzofulvenallene (**6**) and 2,2-dimethylisoidene (**7**) is similar to the electronic structure of *o*-xylene (**4**).



Thus these compounds, which are more easily accessible, could be useful for finding some experimental support for the existence of a low shake-up state in the ionization spectrum of **4**.

Figures 5 and 6 present the LNDO/S PERTCI ionization spectra of **5** and **6**. Unfortunately, the relative intensities of the respective ${}^2B_1(\pi)$ non-Koopmans' ionizations of **5** and **6** amount only to 0.04 and 0.02, respectively. Thus the corresponding

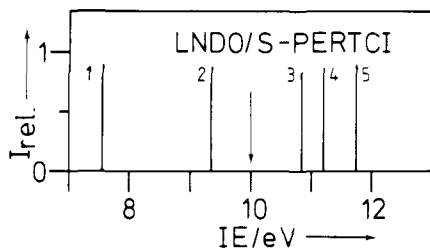


Figure 8. Ionization spectrum of benzocyclobutadiene using the LNDO/S PERTCI method. The assignments of ionizations are: (1) ${}^2B_1(\pi)$; (2) ${}^2A_2(\pi)$; (\rightarrow) ${}^2A_2(\pi)$; (3) ${}^2B_1(\pi)$; (4) ${}^2A_1(\sigma)$; (5) ${}^2B_2(\sigma)$. The numbers mark the Koopmans' ionizations and the arrow indicates the location of the shake-up ionization of very low intensity.

shake-up satellite cannot be seen in the photoelectron spectra of these compounds. This is in accord with our results obtained previously; the photoelectron spectra of **5**²⁷ and **6**²⁸ are fully understood in terms of Koopmans' states only.

The situation is much more favourable for 2,2-dimethylisoidene (**7**). Figure 7 shows the LNDO/S PERTCI ionization spectrum of **7**. Accordingly, it is expected that the ${}^2A_2(\pi)$ band calculated at 10.43 eV ($I_{rel} = 0.85$) will have a ${}^2B_1(\pi)$ shoulder on each side due to strong mixing of the ${}^2B_1(\pi)$ Koopmans' and HOMO-LUMO shake-up configurations (relative intensities of the shoulders = 0.47 and 0.41, respectively). Compared to the ionization spectrum of Figure 7, the measured photoelectron spectrum¹⁷ is shifted by 0.5 eV to lower ionization energies. Corresponding shifts are found for other alkyl-substituted unsaturated systems (due to an underestimation of alkyl-group effects by semiempirical valence electron methods). When this shift is taken into account the calculated ionizations and the measured photoelectron spectrum of **7** correspond to each other if the shoulders of the second photoelectron band at 9.4 and 10.2 eV are attributed to the two ${}^2B_1(\pi)$ non-Koopmans' ionizations.

The UV/VIS spectrum of the cation of **7** has been measured.¹⁷ Two band systems were observed: a first one with an adiabatic transition energy of $12.85 \times 10^3 \text{ cm}^{-1}$ and a second one at ca. $20 \times 10^3 \text{ cm}^{-1}$. Both bands correspond to vertical ionizations in the photoelectron spectrum of **7** at ca. 9.1 eV (estimate based on a bandwidth of ca. 3000 cm^{-1} ; cf. the UV/VIS spectrum of ref 17) and at ca. 9.8 eV. The shape of the latter band system (strong shoulder at ca. $22 \times 10^3 \text{ cm}^{-1}$; cf. the UV/VIS spectrum of ref 17) is compatible with two transitions (${}^2A_2 \rightarrow {}^2A_2$ and ${}^2A_2 \rightarrow {}^2B_1$) being hidden under the band envelope. Taking into account a red shift of ca. 0.25 eV in the condensed phase spectrum due to solvation effects,²⁹ there is a nearly perfect reconciliation of the second band system in the photoelectron spectrum (${}^1A_1 \rightarrow {}^2B_1$, ${}^1A_1 \rightarrow {}^2A_2$, and ${}^1A_1 \rightarrow {}^2B_1$) with the first (${}^2A_2 \rightarrow {}^2B_1$) and second (${}^2A_2 \rightarrow {}^2A_2$ and ${}^2A_2 \rightarrow {}^2B_1$) band systems in the UV/VIS spectrum. We feel that these results clearly demonstrate the capability of the PERTCI approach and also the importance of including many-electron effects into the calculation of ionization energies.

Benzocyclobutadiene. Recently, the photoelectron spectrum of benzocyclobutadiene (**8**) was recorded.²⁵ Neither the spectrum



8

(27) Gross, G.; Schulz, R.; Schweig, A.; Wentrup, C. *Angew. Chem.* **1981**, *93*, 1078; *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 1021.

(28) Schulz, R.; Schweig, A.; Wentrup, C.; Winter, H.-W. *Angew. Chem.* **1980**, *92*, 846; *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 821.

(29) Haselbach, E.; Bally, T.; Gschwind, R.; Klemm, U.; Lanyiova, Z. *Chimica* **1979**, *33*, 405.

nor HAM/3 CI^{25,30} calculations offered any hints of shake-up contributions. In accord with this result the LNDO/S PERTCI method perfectly reproduces the measured vertical ionization energies and confirms that the first five bands in the spectrum can be satisfactorily attributed to one-electron ionization processes. The relative intensities of these bands are all larger than 0.8. Nonetheless, LNDO/S PERTCI predicts a shake-up state at 9.94 eV in addition, which is more than 80% determined by the $b_1^{-2}a_2^{-1}$ shake-up configuration and therefore is not seen (intensity less than 0.005) in the photoelectron spectrum. For these results see the LNDO/S PERTCI ionization spectrum of Figure 8. It is to be noted that the MNDO PERTCI and CNDO/S PERTCI approaches lead to an identical result. This result also calls for measuring the UV/VIS spectrum of the cation of **8**.

Conclusion

Several years ago a general configuration interaction approach to the calculation of the electronic structure of molecules and ions was developed. Since that time all calculations of ion states in conjunction with photoelectron spectral studies in our group were principally performed—irrespective of whether ab initio or semiempirical wave functions were used—using the PERTCI approach. Such an approach automatically avoids any Koopmans' defects (i.e., incorporates all non-Koopmans' effects) caused by otherwise neglecting electron correlation and reorganization. Over the years several particular non-Koopmans effects have become known. One of these, namely the occurrence of low-lying shake-up ionization states in the low energy (outer valence) region of the UV photoelectron spectra of unsaturated hydrocarbons, has been particularly striking (and until now was the subject of little investigation) as controversial discussions have recently made clear.

Therefore our MNDO PERTCI, CNDO/S PERTCI, and LNDO/S PERTCI approaches were applied to this problem. Among these methods MNDO PERTCI was shown to be the least suitable because of the incapability of the MNDO method for the calculation of electronically excited states (in contrast to its brilliant capability for the calculation of Koopmans' ion states), and LNDO/S PERTCI was considered the most suitable due to its capability to calculate ion and electronically excited states simultaneously.

The calculations have clearly established the phenomenon of low-lying shake-up bands in the ionization spectra (UV photoelectron spectra) of unsaturated hydrocarbons. Where such ionizations have previously been seen and assigned as shake-up ionizations (for tetrafluorobutadiene, *p*-xylylene, and 2,2-dimethylisoidene), our calculations provide full confirmation. In addition, low-lying shake-up states are predicted for the first time to occur for isobenzofulvene, isobenzofulvenallene, and benzocyclobutadiene. Since it is established that the corresponding shake-up bands cannot be seen in the UV photoelectron spectra (because of too low intensity), these results call for measurements of the UV/VIS spectra of the corresponding cations.

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(30) Åsbrink, L.; Fridh, C.; Lindholm, E. *Chem. Phys. Lett.* **1977**, *52*, 69. Åsbrink, L.; Fridh, C.; Lindholm, E.; de Bruijn, S.; Chong, D. P. *Phys. Scr.* **1980**, *22*, 475.