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Partial channel photoionization cross sections of polyenes

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We present calculations of partial channel photoionization cross sections and photoelectron spectra of polyenes in the ultraviolet wavelength region. The dependences on molecular size, up to $C_{16}H_{18}$, on photon energy, including He I and He II spectra, and on the particular ionization channel have been investigated using the independent-channel static exchange method. The channel dependence of the He I cross sections, which is quite strong for ethylene, diminishes, as the molecular length is increased, and becomes weak in the He II region. The energy dependence, which is strong in the He I region for all molecules and/or channels, is also insignificant for He II excitation, with the cross sections of all channels being close to each other. The cross sections are remarkably constant for the different π levels at any given photon energy. Spectral analyses for the first three smallest molecules—ethylene, butadiene, and hexatriene—show that the independent-channel approach is able to reproduce experimental data quite well. [S0163-1829(97)04915-1]

I. INTRODUCTION

Although several computational methods have been developed and applied to describe photoionization processes in small molecules, comparatively little has been accomplished with methods that are scalable toward larger species. This is unfortunate from the point of view that ultraviolet photoelectron spectroscopy (UPS) has increasingly been employed as a diagnostic tool for extended species of technological interest, such as polymers, polymer interfaces, and surface adsorbates.[1–4] With synchrotron radiation sources, UPS spectroscopy has been extended into the far-ultraviolet region, making recordings of a broad continuous region of photon energies possible, thereby increasing the informational content and diagnostic capability of the spectroscopy even more.

Most analysis in the context of UPS spectra of larger species has been based only on ionization energies, often utilizing Koopmans theorem, whereas absolute, total, or partial cross sections and the energy dependence of the cross sections have not been investigated to the same extent. Some of this mismatch can be ascribed to the problem of computing continuum photoelectron functions in the anisotropic molecular potential and to special many-body features of the cross sections, but the computational problems in handling extended systems have also been a limiting factor.

In the present work we explore the utility of the static exchange method (STEX) for valence UPS cross sections of larger molecular systems. Being an independent-particle, independent-channel, scheme and a scalable size-consistent method, it is a suitable candidate method to explore UPS spectra of more extended molecules. Its merits and limitations are already well established for photoionization of small molecules; it includes intrachannel but excludes interchannel coupling, and lacks gauge invariance in the limit of a full one-particle basis set. The applicability to larger species stems from the fact that it can be implemented with so-called integral direct and basis set augmentation techniques, and has as such now been applied quite extensively for core excitations in the x-ray region (near-edge x-ray-absorption spectra, NEXAFS).[5–7] Although a strict approximation to the random-phase-approximation method, which also is scalable for extended species, the STEX method is advantageous in that it gives partial-channel cross sections in a well-defined way. The partial-channel cross sections and their energy dependences are indeed the experimentally interesting quantities obtained from UPS spectra.

In contrast to core excitations, the role of interchannel coupling cannot be *a priori* neglected for valence excitations. Especially toward the inner-valence region there are strong hole-mixing and breakdown effects which make state-by-state cross sections obtained from independent particle calculations of little use. For larger species the intermediate- and inner-valence regions of the UPS spectra are poorly resolved, and the STEX technique might conceivably be used only for the gross shape of the spectra in this region. Toward the outer-valence region, which still can be well resolved for larger species, the independent or quasiparticle pictures are known to hold better, and there is accordingly more hope for applicability of an independent-channel approach like STEX. Tests on small molecules do, however, show some interchannel coupling effects even in the outer-valence region.[8–10] In the present work we nevertheless take a pragmatic approach and compare STEX results for the polyenes for which experimental data are available. We then explore trends with respect to molecular size, electronic levels, and band formation, and investigate the photon energy dependence of the absolute and relative photoionization cross sections. In Sec. II we first briefly address some computational aspects of the STEX method applied to valence photoionization. In Sec. III we present and discuss the computed He I and He II UPS spectra and the energy-dependent partial photoionization

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cross sections for valence levels of $C_{2n}H_{2(n+1)}$ with $n=1,2,3,5$, and 8, and in the final section, Sec. IV, we summarize and discuss the results.

II. CALCULATION DETAILS

In the static-exchange approach a one-hole potential, with appropriate spin coupling of ion electrons and photoelectron, is constructed and diagonalized to yield a primitive photoexcitation spectrum of transition energies and transition moments. The potential can be given by ground-state frozen orbitals or by state-specific orbitals which are optimized for each particular hole state. For both computational and formal reasons the former approach is to prefer in the case of ionization of valence shells. The independent-channel approach is assumed in the present work, thus neglecting effects of channel interaction and neglecting photoionization satellites referring to correlation states.

The STEX approach is easily interfaced to the Stieltjes imaging technique for the continuous, photoionization, parts of the spectra. A further advantage with STEX is that it is readily implemented with a double-basis-set technique that allows computation of the spectrum close to the basis set limit.[5] The bound orbitals and the potential are constructed in a limited basis set, while the full spectrum is obtained in an augmented basis set containing many diffuse functions. The direct self-consistent-field program DISCO (Ref. 11) modified for STEX calculations[5] has been employed throughout; only a few computational details are given in the following.

A. Augmentation of the basis set

A problem encountered in the present applications, which is not severe either for core excitations or for valence excitations in small molecules, is the handling of the augmentation basis set describing the photoelectron function. Due to the delocalization of the valence orbitals, we have to add one basis set of this kind on each C atom. The total numbers of the basis functions and the needs of memory and CPU time for the STEX calculation increase rapidly with the length of the molecule. To make the double-basis-set technique efficient, extensive tests on the basis set dependence of the results for ethylene have been made. The augmented basis set of Gaussian functions was generated by using an even-tempered scaling of the Gaussian exponent $\alpha_n=\alpha_0\beta^{-n}$, with $\beta=1.4$. In Fig. 1 we present partial photoionization cross sections of valence shells versus photon energy obtained with different basis sets for the occupied orbitals of double ζ with polarization and higher $(5s,4p,3d)$ (CCPVTZ) (Ref. 12) quality and different augmentations. Except for the cross section of the inner channel $(2b_u)$ that is not sensitive to the size of the basis set, the cross sections of the outer valence orbitals, computed without extending the basis set (DZP-No Aug), show an unreasonable profile. The addition of $5p$ and $5d$ functions (DZP-$p5+d5$) with $\alpha_0=0.0798$ to each C basis set does give rise to a reasonable shape and asymptotic behavior of the cross sections. In fact the results obtained with a much more extended basis set (see DZP-$p10+d10$, with $\alpha_0=0.4290$) show no significant variation, which means that basis set convergence is already reached with DZP-$p5+d5$. In addition, a larger basis set (CCPVTZ) has been tested for the calculation of the ground-state occupied orbitals and of the STEX Hamiltonian; the final results agree quite well with the DZP-$p5+d5$ ones. Thus the latter basis set can be considered as having reached the basis set limit, and it was therefore adopted for all the polyenes investigated.

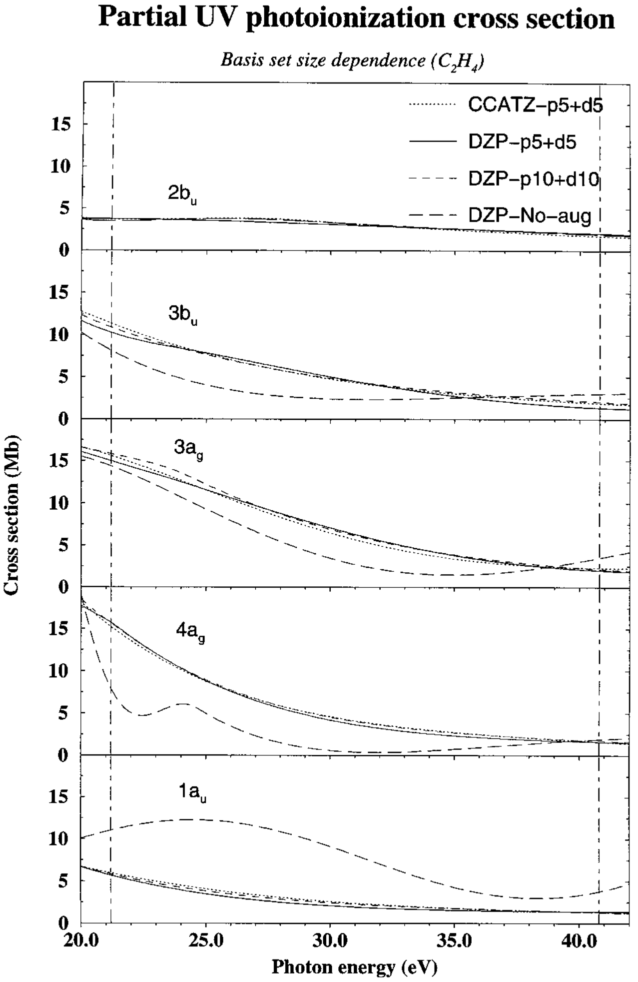

FIG. 1. Basis set size dependence of partial photoionization cross sections of valence shells of C_2H_4. The vertical dot-dashed lines at 21.2 and 40.8 eV mark the He I and *respectively* He II photon energies.

B. Gauge dependence

The STEX method is not gauge invariant, even in the limit of a complete basis set. Nevertheless, it can be interesting to check the dependence from the gauge of the relative intensities that, after all, are the quantities obtained experimentally from a UPS spectrum. In Figs. 2 and 3, we show the photoelectron spectra of C_2H_4 and $C_{10}H_{12}$, calculated adopting both length and velocity gauges, at the He I and He II photon energies. In each spectrum, the intensity of the lowest peak, $1a_u$ (C_2H_4) and $3a_u$ ($C_{10}H_{12}$), respectively, has been set to unity. Except for the $4a_g$ intensity in the He I spectrum of C_2H_4, we find only a minor dependence of the spectra from the gauge both for the short and the long molecules at the two considered photon energies. This gauge invariance of the relative intensities, that is also observed for

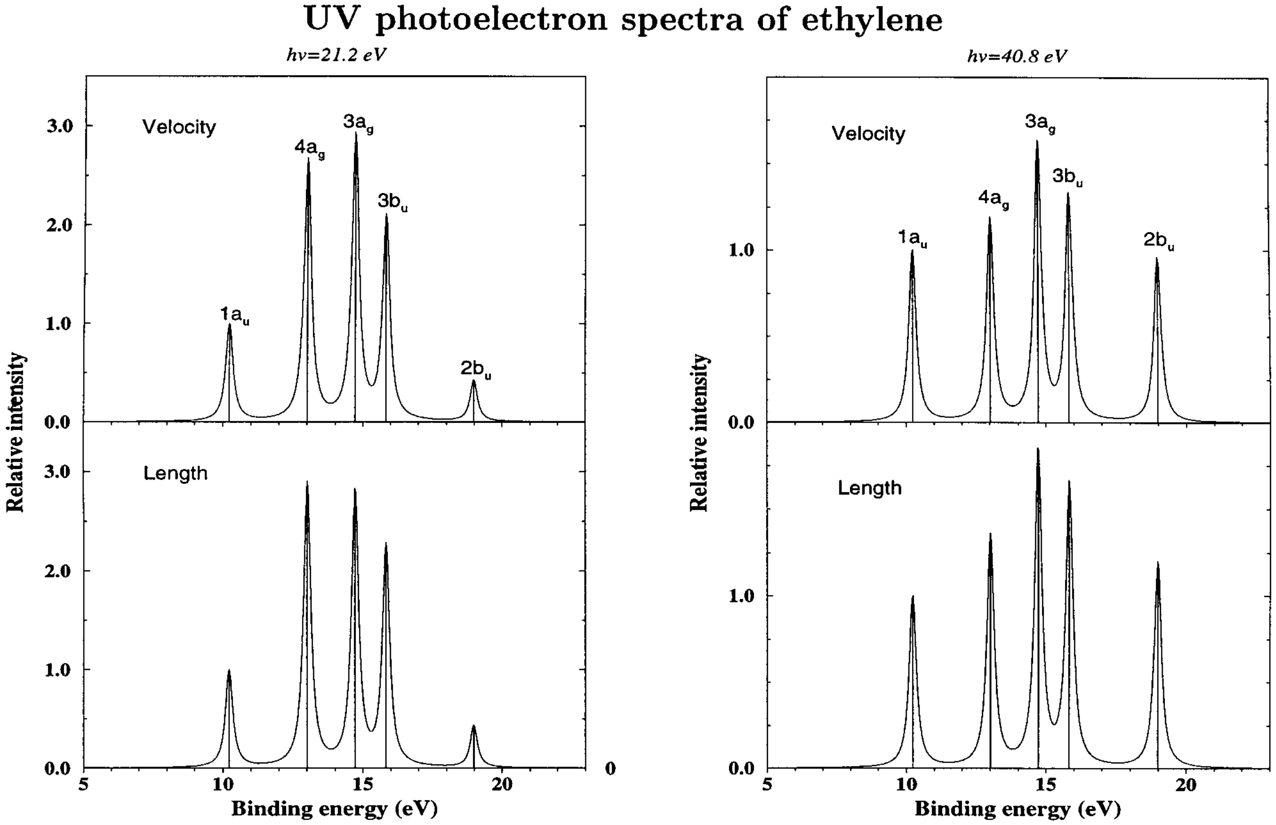

FIG. 2. Gauge dependence of the UPS spectrum of C_2H_4 at He I (21.2 eV) and He II (40.8 eV) photon energies.

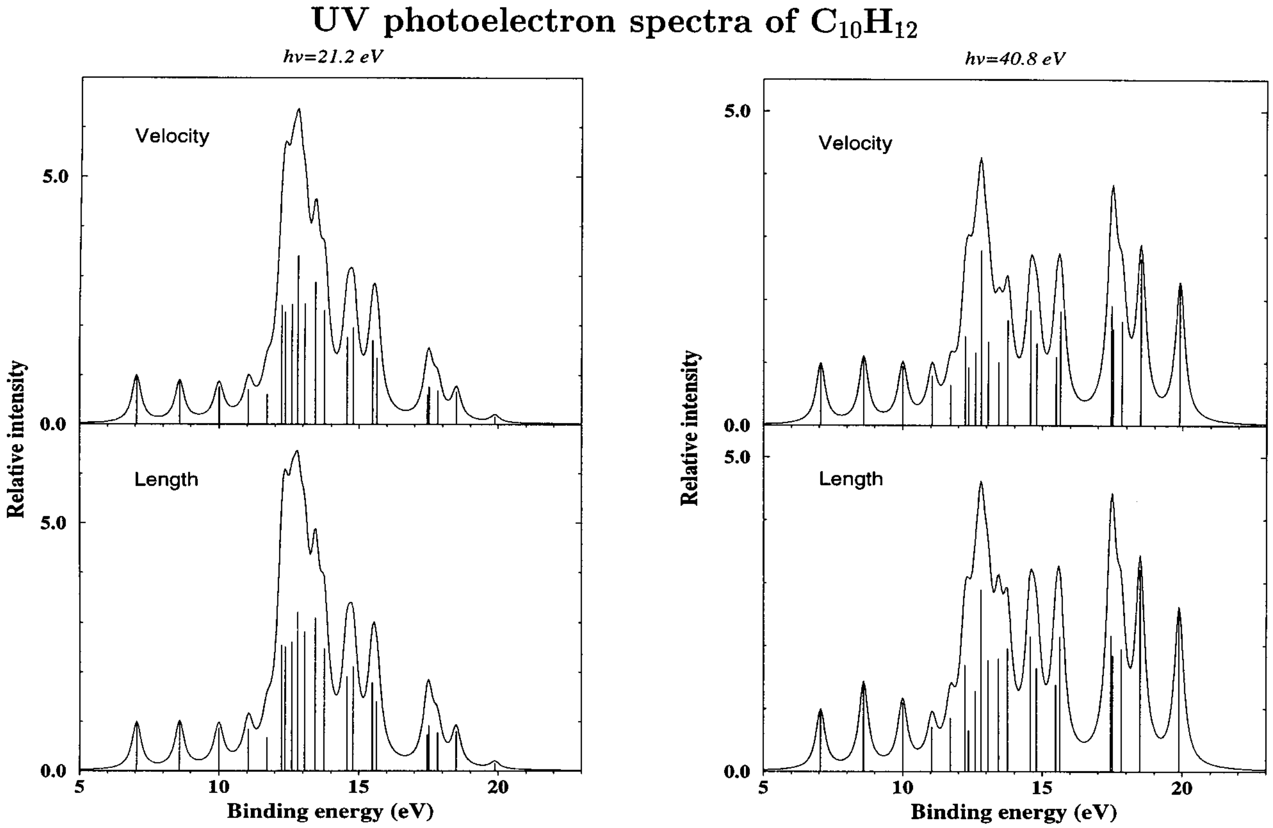

FIG. 3. Gauge dependence of the UPS spectrum of $C_{10}H_{12}$ at He I (21.2 eV) and He II (40.8 eV) photon energies.

butadience (C_4H_6) and hexatriene (C_6H_8), is remarkable considering the limits of the STEX approximation, and can be taken as an indication of the good quality of the basis sets employed. Only the results obtained in the length gauge will be presented in the following discussion.

C. Energy rescaling

The ionization thresholds here adopted are based on Koopmans theorem. It has been observed that the Koopmans energy is a reasonably good approximation for the ionization potential (IP) of the outermost valence orbitals, but that it can significantly overestimate the inner-valence orbital values, so that the total width of the valence UPS spectrum can be exaggerated.[13–15] A widely accepted way of dealing with this departure in polymer systems,[13,15] is based on a rescaling of the valence-band energy dividing by a factor of 1.3. Comparing with the experimental values, this rescaling works well for ethylene, butadiene, and hexatriene. Thus an energy rescaling of the IP's for all molecules has been adopted, and all the ionization channels with rescaled binding energy below the He I energy of 21.2 eV have been included in the calculations. However, it should be stressed that energy rescaling was employed only to make the comparison with the experimental spectra easier, while our main attention is devoted to a comparison of the intensities.

III. RESULTS

A. He I and He II UPS spectra

Figure 4(a) shows the calculated He I photoelectron spectra of $C_{2n}H_{2(n+1)}$ with $n=1$, 2, 3, and 5 including all the ionization channels open at a photon energy of 21.2 eV. Thus the innermost channels outside the reach of He I are left out in the present analysis. In order to check the energy dependence of these spectra, we have computed them also at the He II photon energy of 40.8 eV, the results obtained are shown in Fig. 4(b). The UPS spectra in Fig. 4 are presented both as bar diagrams and as continuous convoluted profiles for an easier comparison with the experimental data. Experimental spectra for ethylene, butadiene, and hexatriene[1,16,17] are reproduced for comparison in Fig. 5.

1. C_2H_4

The convoluted spectrum of ethylene consists of five distinct peaks, each of them corresponds to the ionization from an individual occupied orbital. Considering the energy sepa-

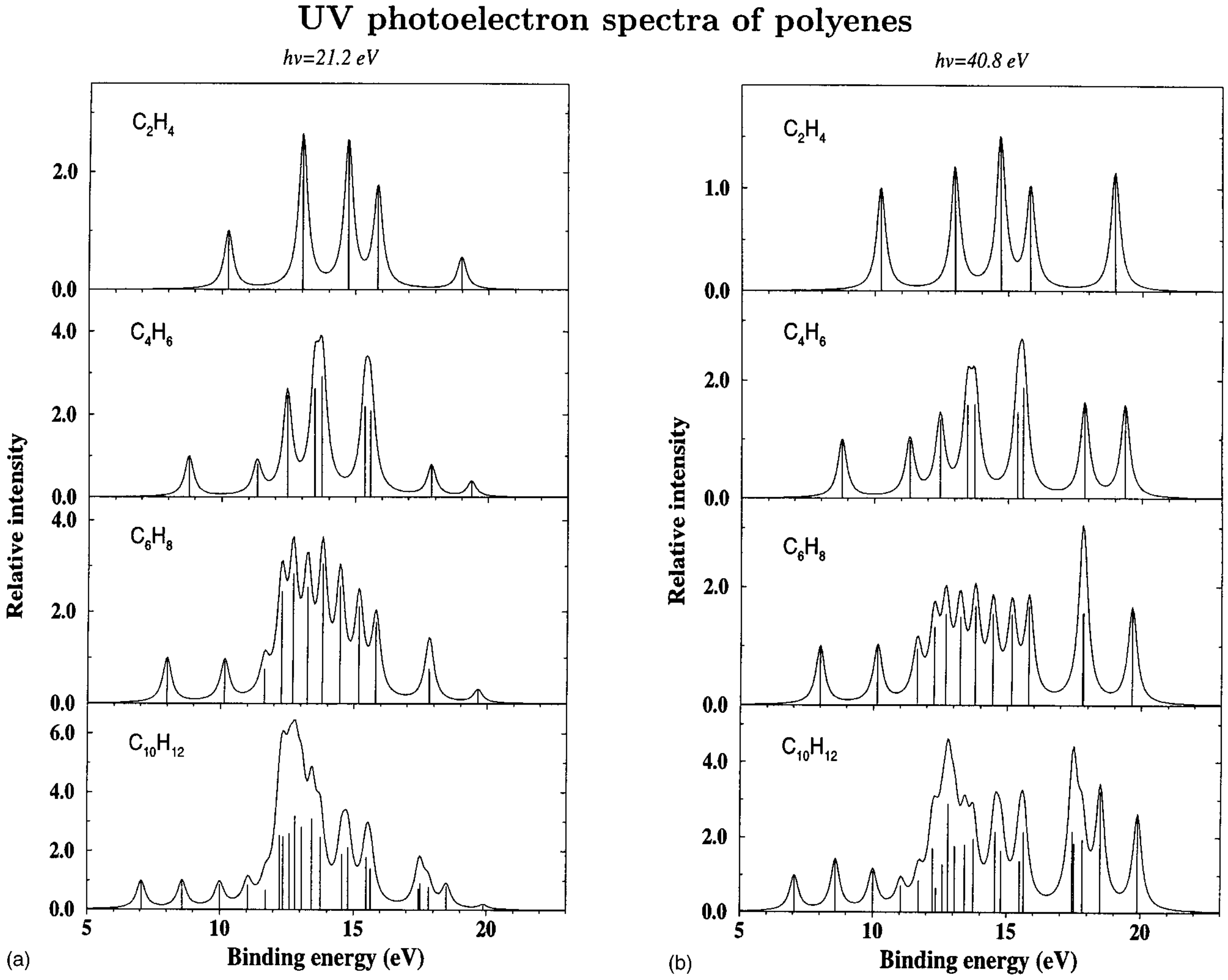

FIG. 4. Computed UPS spectra of polyenes $C_{2n}H_{2(n+1)}$ with $n=1$, 2, 3, and 5. (a) He I excitation. (b) He II excitation.

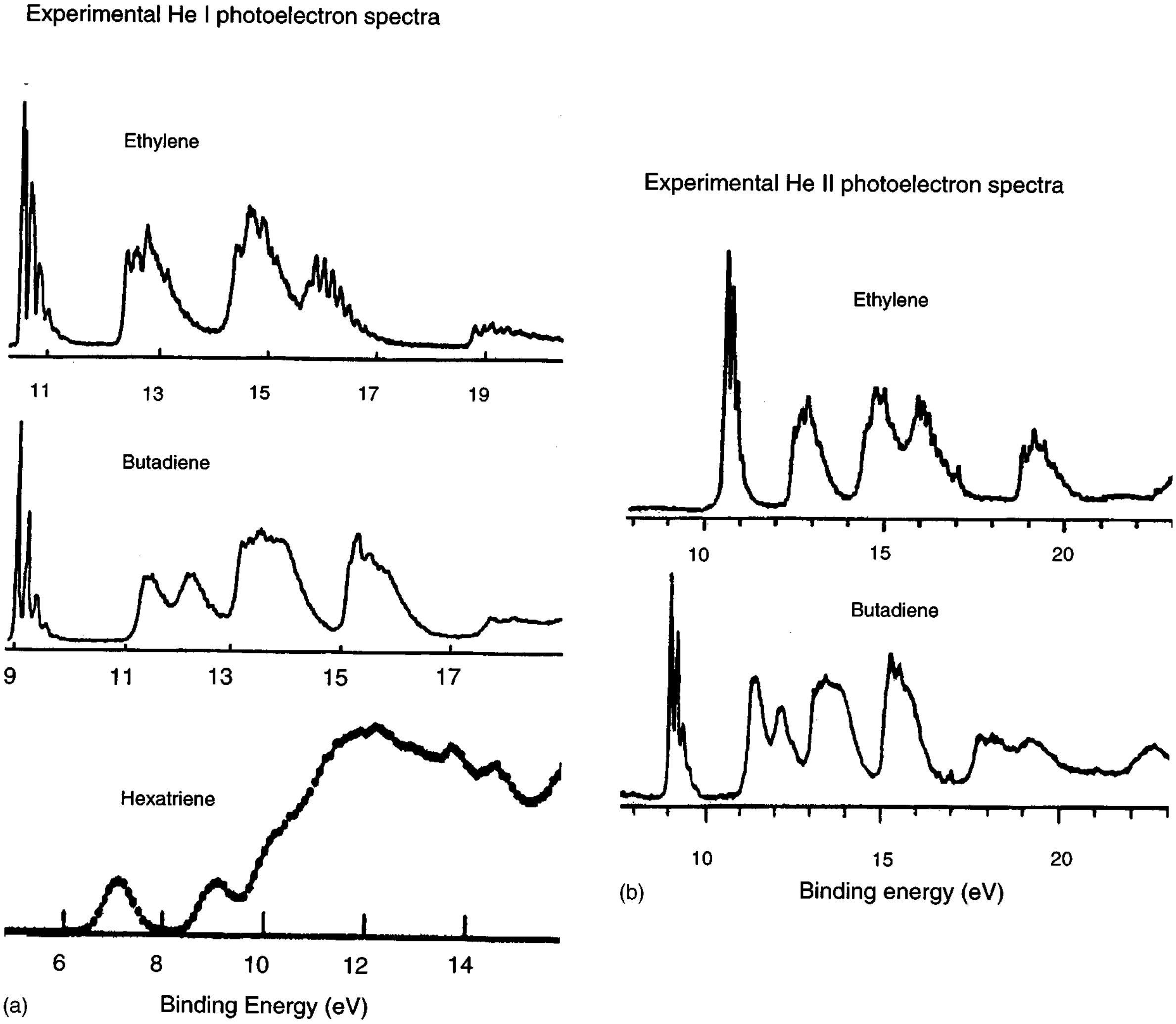

FIG. 5. Experimental UPS spectra. (a) He I spectra of ethylene, butadiene (Ref. 1), and hexatriene (Ref. 16). (b) He II spectra of ethylene and butadiene reprinted from J. Electron. Spectrosc. Relat. Phenom. **20**, 149 (1980) with kind permission of Elsevier Science.

ration and electronic composition, we can distinguish three groups of peaks, a division which seems to hold also for the other molecules here studied: The first low-binding-energy peak derives from the HOMO (highest occupied molecular orbital) of π symmetry. The second group includes three high-intensity peaks between 13 and 16 eV, corresponding to ionization from the three MO's containing in-plane C $2p$ ($4a_g$,$3a_g$, and $3b_u$). The last peak is due to the $2b_u$ orbital containing C $2s$. Note that the innermost $2a_g$ orbital falls out of the He I energy range. The intensity of the UPS spectra of ethylene shows a remarkable dependence on the photon energy, especially with an enhancement of the innermost part when passing from 21.2 to 40.8 eV for the photon energy. In the He II spectrum the absolute intensities of the second group are significantly reduced. These features are in good agreement with the experimental photoelectron spectra.[1,17] For an extensive configuration-interaction study of photoionization overlap amplitudes and of correlation states in the UPS spectra of ethylene, we refer to the recent work of Desjardins *et al.*[18]

2. C_4H_6

The UPS spectrum of butadiene can also be divided into three groups: peaks deriving from the two π orbitals ($1b_g$ and $1a_u$), from the 5-$7a_g$ and 5-$6b_u$ orbitals containing $2p$, and from the $4a_g$ and $4b_u\sigma$ orbital containing $2s$. The π peaks have almost identical intensities in both He I and He II spectra. The second group of orbitals makes up for the three-band feature that dominates both spectra. As for ethylene the largest relative change going from He I to He II is the enhancement of the third inner part containing $2s$, in full compliance with the experiment.[17]

3. C_6H_8

The UPS spectrum of hexatriene follows the trends from ethylene and butadiene. The middle part containing σ $2p$ character becomes quite complex with some seven close-lying peaks. The three π peaks have similar relative intensities in the He I and He II spectra. Similar to ethylene and butadiene, a large intensity redistribution occurs among the σ peaks in the He II spectrum. Going to higher photon energy we see that not only is the third group enhanced, but also the high-energy part of the second group containing $2p$. In the He II spectrum it is the composed C $2s$-derived structure at 18 eV that is the most intense.

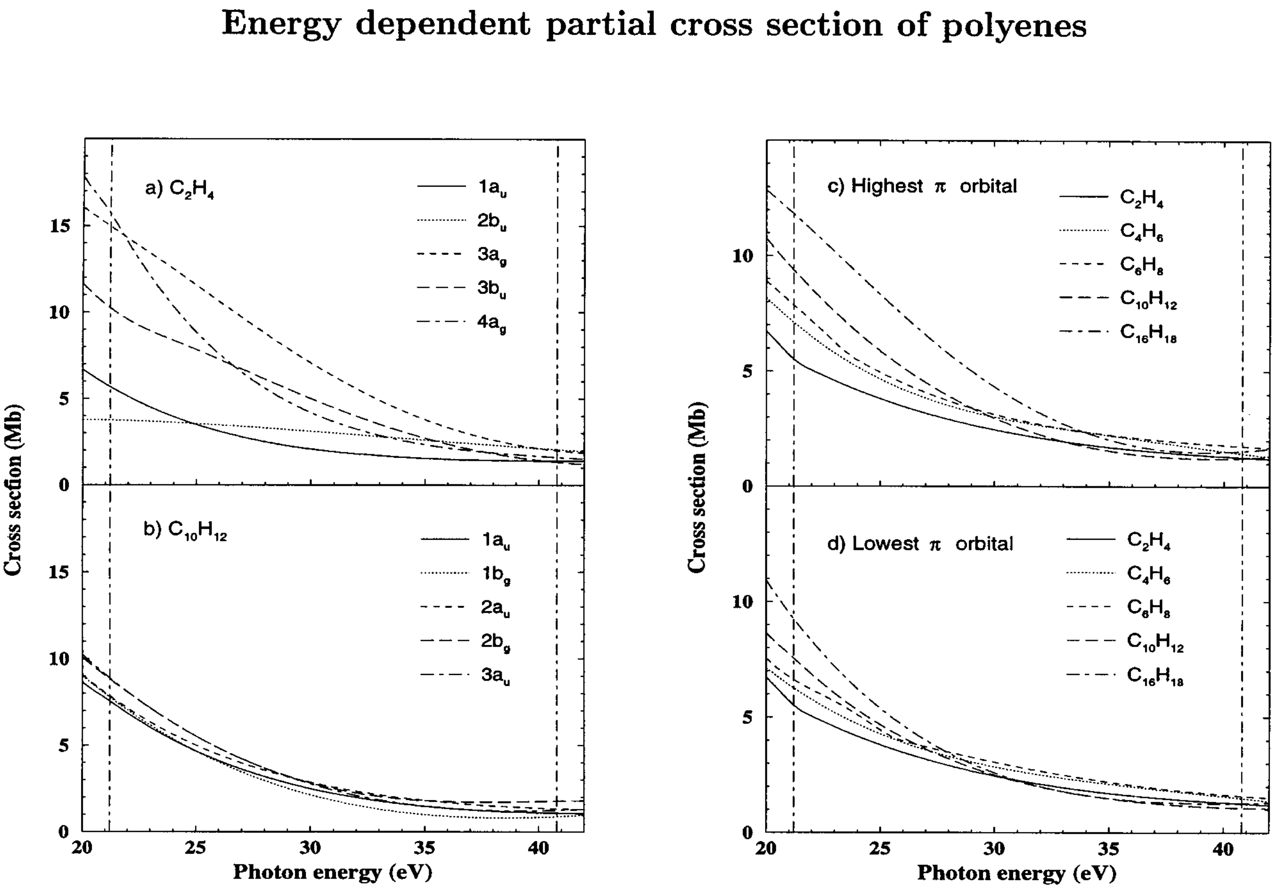

FIG. 6. Energy-dependent partial photoionization cross sections: (a) C_2H_4 all channels. (b) $C_{10}H_{12}$ all π channels. (c) HOMO π channel for $C_{2n}H_{2(n+1)}$, $n=1$, 2, 3, 5, and 8. (d) LOMO π channel for $C_{2n}H_{2(n+1)}$, $n=1$, 2, 3, 5, and 8. The vertical dot-dashed lines at 21.2 and 40.8 eV mark the He I and He II photon energies.

4. $C_{10}H_{12}$

For decapentaene the density of states is evidently pushed even higher, and the convoluted spectrum actually becomes determined mostly by the distribution of states rather than by the individual intensities. This is so because, with one or two exceptions, all cross sections within a group are of similar magnitude. As for the shorter molecules the weak band between 17 and 19 eV in the He I spectrum results from the ionization of inner valence σ orbitals. The shift of intensity from the outer to the inner part going from He I to He II is remarkable.

5. Convergence of spectra

Although the convergence with molecular length of the polyene UPS spectra is quite slow, some clear trends are observed. The UPS spectra of the polyenes consist of three well-separated parts located in the low-, medium-, and high-binding-energy regions. Increasing the size of the molecule, the He I spectrum is dominated by a large structured band, deriving from σ orbitals, located in the medium-energy region. The peaks in this range derive from the ionization from $2(n+1)\sigma$ orbitals (where n is the number of ethylene units), which are combinations of H $1s$ and the planar components of the C $2p$ atomic orbitals. At the same time, a system of weak but well-separated (and then observable) peaks corresponding to π orbitals builds up on the low-energy side, while at high binding energies there appears a more complicated group of weak peaks due to molecular orbitals with contributions from the carbon $2s$ atomic orbitals.

At the He II photon energy, the intensities of the different valence channels become comparable, which makes the He II spectrum less sharp than that of He I. We remind the reader that in the x-ray region the orbitals containing $2s$ completely dominate over the $2p$ region, something which can be rationalized in the nodal structure of the $2s$ and $2p$ atomic orbitals versus the oscillations the photoelectron function.[19,20] Increasing the length of the polyene, the density of states increases, the energy range becomes broader, and the intensity maximum of the UPS spectra shifts to lower binding energies.

B. Energy dependence of cross sections

The energy-dependent partial cross sections of C_2H_4 (all He I channels) and $C_{10}H_{12}$ (all π channels), have been collected in Figs. 6(a) and 6(b). The vertical dot-dashed lines indicate the positions of the He I and He II photon energies. We restrict the photon energy to the parts which are most used experimentally, He I and He II and the part in between, and leave out the complex onset of the continuum where autoionization and post-collision interaction effects complicate the analysis. For ethylene, the behavior of the cross sections versus the photon energy is very much channel dependent; the partial cross sections of the ''second group'' of three σ channels, $3a_g$,$3b_u$, and $4a_g$, sharply decrease with the photon energy, while the $1a_u\pi$ and, especially, the inner $2b_u\sigma$ channels decrease slowly. The variation of the cross sections are also quite channel dependent; they do converge, however, quite rapidly toward larger photon energies, and at the He II photon energy the intensity of all the channels becomes almost the same. For decapentaene the picture is different. Here the absolute cross sections and also the energy dependences of the cross sections are quite similar for all π channels over the whole energy range; see Fig. 6(b). This is in line with our previous observation that the π channels have approximately equivalent cross sections at the He I and He II photon energies. In Fig. 6(c) we have chosen the highest occupied π orbitals of $C_{2n}H_{2(n+1)}$ with $n=1$, 2, 3, 5, and 8, as representative for the molecular dependence of the cross sections. As expected from the foregoing discussion, the molecular dependence is largest at the lower excitation energies, including the He I energy.

IV. DISCUSSION

We have performed *ab initio* static exchange calculations of UPS spectra of polyenes, studying their evolution with respect to size, ionization level, and photon energy. Several salient trends have been unraveled, especially for the photon energy and the molecular length dependences of the cross sections. The energy dependence is large for the smaller species and for low, He I, photon energies, while the relative energy dependence is reduced for higher (He II) energies and/or for larger molecules. Also, the dependence on channel (ionized orbital), which is quite significant for ethylene, is significantly diminished for the large species. The π channels seem to retain rather equal cross sections independent of photon energy. This is an important verification of the assumption actually often made in the analysis of polymer UPS spectra.

A detailed analysis for the first three polyene members—ethylene, butadiene, and hexatriene—demonstrated that an independent-channel interpretation of their UPS spectra works well concerning both energies (rescaled Koopmans energies) and cross sections (independent-channel cross sections). For inner levels this contention cannot be tested on a state-by-state basis because of the high density of overlapping σ states which are vibrationally broadened and, probably, configurationally split.[18,21] From the theoretical point of view a state-by-state analysis using an independent-particle approximation becomes less meaningful in this energy region due to the breakdown and hole-mixing effects. Such effects are well established for smaller species,[18,21] and probably become more accentuated for larger molecules. Thus an analysis like the present one can, for the inner part, only claim that the gross spectral profile is reproduced, and should rather focus on the outer part of the spectra which is also the part which actually is resolved in the UPS spectra and used for diagnostics of the samples.

Polyenes served here as a first testing ground for applications of the direct STEX technique on UPS cross sections, and we have shown that cross-section calculations of this kind are indeed feasible. The limiting factor is the representation of the photoelectron function, which is found to require large multicentered basis sets. Due to this limitation the size of the systems reached in UPS cross-section calculations can unfortunately not match the size reached by direct self-consistent field techniques for calculations of bound states. We still believe that in future applications sufficiently large units of polymers and other extended species can be considered to be of practical significance.

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