Electron Correlation Effects in Photoemission from the $1\pi_u$ Level in Acetylene

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(Received 29 March 1983)

The photoemission cross section for the $1\pi_u$ level in acetylene is calculated including electronic correlations using a time-dependent local-density approximation. Structure in the cross section from 12 to 17 eV is identified as arising from a Fano autoionization resonance ($2\sigma_u \rightarrow 1\pi_g$) and a redistribution of oscillator strength from a bound-to-bound transition ($1\pi_u \rightarrow 1\pi_g$) to the continuum. A minimum in the observed photoemission asymmetry parameter and the optical frequency polarizability are also accounted for with electronic correlations.

PACS numbers: 33.80.Eh, 33.60.Cv

Photoemission from the $1\pi_u$ level of acetylene (C_2H_2) has been a subject of recent interest. A double-peak structure with a deep minimum has been observed in the cross section a few electronvolts above the ionization threshold.[1-3] A minimum has been observed in the asymmetry parameter in the same energy region in experiments with discrete line sources[4] and synchrotron radiation.[5,6] A number of explanations have been suggested for these structures, including various autoionization resonances[1-6] and shape resonances.[4] Calculations to date[1-4,6] do not include dielectric effects arising from screening in the finite system, although their need has been recognized.

In this Letter we apply the time-dependent local-density approximation (TDLDA)[7] to explain the photoemission from the $1\pi_u$ level of the acetylene molecule. The TDLDA is a random-phase approximation (RPA) theory based on a local-density-functional approximation (LDA) to the ground state which includes exchange and additional correlation effects by a linearization of the exchange-correlation function about its ground-state value. The calculation includes both intrachannel and interchannel coupling in a nonperturbative fashion at the level of the RPA. The results reported here are the first application of the TDLDA to molecules (earlier applications were to atoms) and one of the few molecular studies to include dielectriclike electron correlation effects such as an autoionization resonance.[8] Since the theory has been previously presented, we only summarize the key points here; the details of the implementation in the molecular geometry are deferred to a later paper.[9]

The dynamic polarizability, $\alpha(\omega)$, is proportional to the dipole moment of the charge density induced by an external field E_0:

$$\alpha(\omega) = (2e/E_0) \int z\, \delta n(\vec{r}, \omega) d^3r' .$$

Neglect of electron-electron interactions leads to the independent-particle approximation (IPA) for the induced charge density:

$$\delta n(\vec{r}, \omega) = \int \chi_0(\vec{r}, \vec{r}', \omega) \varphi^{\text{ext}}(\vec{r}') d^3r' , \tag{1}$$

where $\chi_0(\vec{r}, \vec{r}', \omega)$ is the independent-particle density-density response function. In the TDLDA version of the RPA the external field in (1) is replaced by the self-consistent field φ^{scf} equal to the sum of the external field, the Coulomb potential produced by the induced charge density $\delta n(\vec{r}, \omega)$, and an induced exchange-correlation potential

$$\delta V_{\text{xc}}(\vec{r}, \omega) = \left(\frac{\partial V_{\text{xc}}}{\partial n}\right)_{n_0(\vec{r})} \delta n(\vec{r}, \omega) .$$

Solution of the self-consistent field equations yields an approximation of the dynamic polarizability $\alpha(\omega)$. The total cross section is proportional to the imaginary part of $\alpha(\omega)$ while partial cross sections are given by Fermi's "golden rule" formula with the replacement of the external potential by the self-consistent potential.

Following Zangwill and Soven,[7] we find the independent-particle susceptibility using the expression

$$\chi_0(\vec{r}, \vec{r}', \omega) = \sum_i^{\text{occ}} [\varphi_i^*(\vec{r}) \varphi_i(\vec{r}') G(\vec{r}, \vec{r}', \epsilon_i + \hbar\omega) + \varphi_i(\vec{r}) \varphi_i^*(\vec{r}') G^*(\vec{r}, \vec{r}', \epsilon_i - \hbar\omega)],$$

where the use of the Green's function eliminates an infinite sum over all single-particle excited states. We calculate the Green's function and bound-state wave functions using a single-center angular momentum expansion[10] about the molecular center; matrix differential equations are solved numerically. The primary advantages are the conceptual simplicity and convenience in performing the self-consistent-field calculations; the primary disadvantage is that the wave functions are not easily represented near the nuclei which requires the use of many spherical harmonics in the expansions.

To calculate the photoresponse of acetylene, we performed an LDA self-consistent field calculation of the ground state using a Gaussian orbital program.[11] The basis set was a slight extension of that suggested by van Duijneveldt.[12] The potential was found self-consistently in the Gaussian orbital basis, projected into a single-center representation, and used without further modification. New bound-state wave functions were found in the single center; valence eigenvalues differed by about 1 eV from those of the Gaussian expansion, when all relevant harmonics up to $l = 19$ were included.

The predicted optical-frequency polarizability is compared to experiment in Table I. The dielectric screening reduces the independent-particle polarizability by a considerable factor, and brings the result to within 15% of the experimental value.[13] In addition to seeking this agreement for its own sake, the existence of the sum rule[7,14]

$$\int_0^\infty [\sigma(\omega)/\omega^2]\,d\omega = (2\pi^2/c)\,\alpha(0)$$

implies that the photoemission spectrum will have the negative-second moment nearly correct. (The optical-frequency polarizability and the static polarizability do not differ greatly.[13]) The theory also satisfies the f-sum rule.

Our calculated $1\pi_u$ partial cross section is shown in Figs. 1 (IPA) and 2 (TDLDA) along with experimental data.[2,3] All theoretical predictions in Figs. 1–3 have been arbitrarily shifted 1.1 eV to higher photon energy. The IPA cross section is very similar to Langhoff's Hartree-Fock result.[2,3] The calculation gives a good account of the gross background of the spectrum, but interpolates through the prominent structure near threshold. In contrast, the inclusion of dielectric effects gives rise to marked structure in this spectral region, which arises from an autoionization resonance involving the $2\sigma_u \rightarrow 1\pi_g$

TABLE I. Optical-frequency polarizabilities of acetylene at 2.71 eV (in cubic angstroms) are given for light polarization parallel (∥) and perpendicular (⊥) to the molecular axis.

	$\alpha_{\parallel}$	$\alpha_{\perp}$
IPA	27.30	4.24
TDLDA	5.46	3.04
Exp (Ref. 13)	4.86	2.94

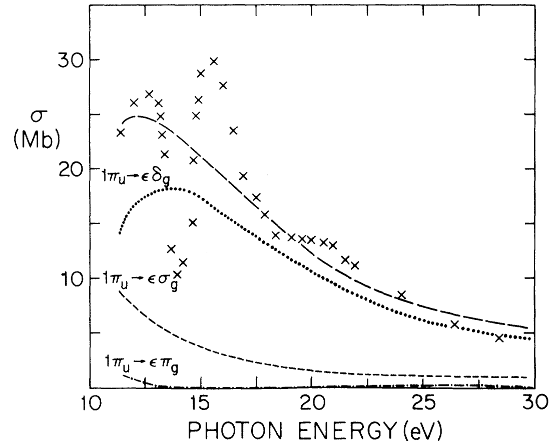

FIG. 1. Photoemission partial cross section for the $1\pi_u$ level of acetylene. Data from Ref. 2. Experimental uncertainty is ± 3 Mb in absolute normalization and ± 3% in relative values for each point. Dashed curve, present IPA results. Other line types and symmetry components as indicated. Theoretical curves are shown from the physical threshold (11.4 eV). Theoretical curves have been shifted 1.1 eV to higher energy. 1 Mb = 10^{-18} cm^2.

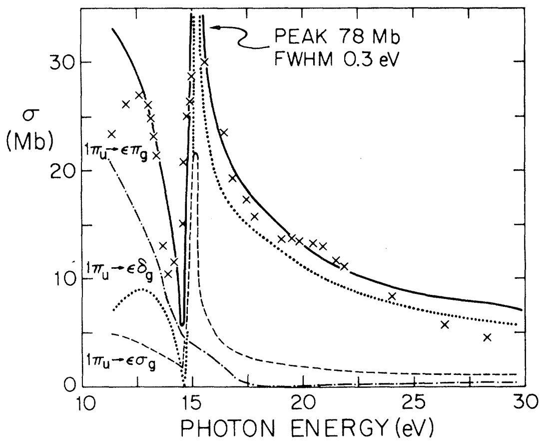

FIG. 2. Same as Fig. 1, except solid curve is TDLDA result.

bound-to-bound transition. This resonance accounts for the peak at 15.5 eV as well as approximately half of the peak at 12.5 eV. The autoionization resonance occurs exclusively for the light polarization perpendicular to the molecular axis. Thus, we support the interpretation that the $2\sigma_u \rightarrow 1\pi_g$ autoionization resonance is crucial in this spectral region.[2,3,5] The calculation yields the asymmetric line shape characteristic of the Fano theory of autoionization resonances.[8] We attribute no special significance to the need to shift the peak position by about 1 eV; this primarily reflects a lack of convergence in the single-center expansion. Increasing the number of partial waves would shift the resonance to somewhat higher energies (perhaps 0.7 eV), judging from the Gaussian basis set results. The very narrow high peak that our calculation predicts is not seen, probably because of vibrational broadening and instrumental resolution, both of which are comparable to the calculated full width at half maximum. A convolution of the theoretical calculation and these broadening mechanisms recovers the experimental line shape.

We propose a different mechanism to account for the rest of the strength in the 12.5-eV peak. In the IPA, nearly all of the oscillator strength for parallel light is associated with the $1\pi_u \rightarrow 1\pi_g$ transition. The inclusion of interactions within an RPA-type theory redistributes oscillator strength to higher frequencies, some of which appears above the physical threshold as part of the 12.5-eV peak. This general process has been proposed before.[15] A TDLDA calculation of atomic barium demonstrates that this mechanism may be sufficiently important to alter completely the photoemission spectrum predicted by the independent-particle approximation and provide agreement with experiment.[16] In contrast to the suggestions of other authors,[2-4,6] we see no support in our calculation for the existence of a second autoionization resonance.

In Fig. 3, the theoretical and experimental asymmetry parameters β are shown. A 1.1-eV shift is included for consistency, but has no qualitative effect. The experimental value is averaged over the vibrational states to recover the "electronic part," since the calculation was performed with the nuclei fixed in space. While the IPA is sufficient to account for the general behavior of β, dielectric effects are needed to account for the single dip. The data of Ref. 6 are similar to, but not in strict agreement with, the data of Ref. 5 shown in Fig. 3. The vibrational branching ratios are not given in Ref. 6, so that the "electronic part" of the asymmetry-parameter spectrum could not be recovered. Earlier muffin-tin calculations[4,6] are in general agreement with the IPA results and do not account for the observed minimum in the asymmetry parameter.

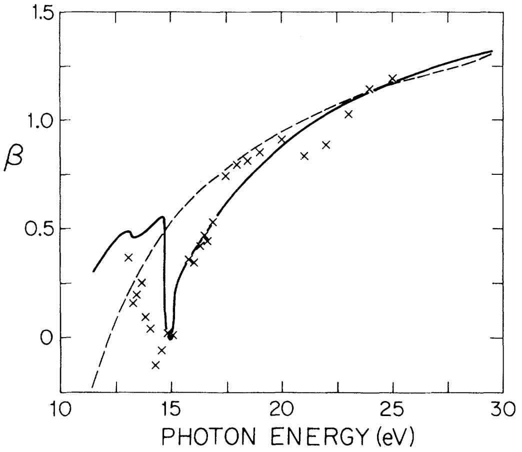

FIG. 3. Asymmetry parameter β for the $1\pi_u$ level of acetylene. Data from Ref. 5 have been averaged over vibrationally resolved levels with experimental branching ratios. Experimental uncertainty is typically ± 0.07 β units. Dashed curve, IPA calculation; solid curve, TDLDA calculation.

We wish to thank R. P. Messmer for allowing us to use the Gaussian orbital program. We are grateful to A. Zangwill for many useful discussions. This work was supported by the Gas Research Institute and by the National Science Foundation Materials Research Laboratory program under grant No. DMR 7923647.

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