C 1s ionization in C_2H_2 studied by asymmetric $(e,2e)$ experiments

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The dynamics of core ionization by electron impact is investigated through the measurement of the triply differential cross section of the C $\sigma 1s$ orbital in the molecule C_2H_2. The $(e,2e)$ experiments have been performed under asymmetric conditions and at small scattering angles, with a scattered electron energy of 1500 eV and low energies of the ejected electrons (9.6 and 41.0 eV). The measured angular distributions are characterized by large-size recoil lobes, breaking of the symmetry around the momentum-transfer direction, and unusual deviations of the maxima of the recoil peaks towards smaller deflection angles. In the $(e,2e)$ energy spectrum a shift is observed in the position of the C $\sigma 1s$ peak with respect to the expected value as measured by x-ray photoelectron spectroscopy. The amplitude of the shift amounts to 0.46 ± 0.23 eV at 9.6 eV excess energy, and it is too large to be explained only in terms of postcollision interactions.

I. INTRODUCTION

Electron-electron coincidence experiments have been shown to be a very sensitive tool with which to investigate details of the dynamics of electron-induced ionization and to study the electronic structure of atoms and molecules. These experiments, usually termed $(e,2e)$, measure the triply differential cross section (TDCS), in as much as they consist of measuring the energy E_0 of the incident electron, the energies E_a and E_b of the two escaping electrons, and the probability that these coincidence pairs are emitted into solid angles around the directions (θ_a,Φ_a) and (θ_b,Φ_b).

The theoretical models and approximations used for the description of the ionization process can be tested by varying the kinematics of the experiment. In particular, direct spectroscopic informations are obtained from the TDCS, whenever the analysis can be performed within the framework of the impulse approximation, otherwise dynamical aspects of the ionization process are investigated.[1,2]

The interest in using the $(e,2e)$ experiments for inner-shell studies is manifold. The TDCS is expected to produce detailed informations on the many-body response of an atomic or molecular system to the change of the potential as the ionized system relaxes.[3] Moreover, the subject is of fundamental importance in order to develop models for those spectroscopies which are based upon core ionization. The smallness of the cross section and the limitations imposed by the "unavoidable" accidental coincidences (see Ref. 4 for an extensive discussion of the problem) have hampered the extensive application of $(e,2e)$ to inner-shell studies. The few works reported in the literature concern solid-state targets at high incident energy (8 keV and higher).[5,6] Lately, the use of asymmetric kinematics, characterized by TDCS values larger than in the symmetric case, has allowed the extension of the $(e,2e)$ technique to inner shell investigations in gaseous targets. Works have been published on the ionization of Ar 2p by 8-keV electrons.[7,8] This paper reports on the first $(e,2e)$ experiment performed at intermediate incident energy and asymmetric kinematics on the deepest orbital of a molecule, namely, the C 1s orbital in C_2H_2.

II. EXPERIMENTAL PROCEDURES

In the asymmetric $(e,2e)$ measurements the excess energy, $E=E_0-\varepsilon$, where ε is the transition energy of the ionization process, is unevenly shared between the scattered and ejected electrons. In this work the scattered electron energy E_a is kept fixed at 1500 eV, while two different values are selected for the ejected electron, $E_b=9.6$ and 41.0 eV. In measuring the separation energy spectrum, the incident energy E_0 is varied, according to the relation $E_0=E_a+E_b+\varepsilon$ over the region of ionization energies of interest. The coplanar angular distribution for a selected transition is measured by scanning over a wide range the ejected electron angle θ_b, while the scattering electron angle θ_a is held fixed. A complete description of the crossed-beam scattering apparatus has been reported elsewhere.[9,10] In the present experiment the electron gun was operated so as to obtain an electron beam of continuously tunable energy from 1500 eV up to 1900 eV and of few μA. Scattered and ejected electrons are collected by two electrostatic analyzers, each one consisting of a three-element zoom lens followed by an electrostatic hemispherical dispersive element. Collimators in the zoom lens define an angular acceptance of $\pm0.5°$ for the fast electron and $\pm4°$ for the slow ejected one. The full width at half maximum (FWHM) energy resolutions of the two analyzers, operated at constant pass energy, are $\Delta E_a=2.1$ eV and $\Delta E_b=0.5$ eV, giving an overall

energy resolution, $\Delta E = 2.3$ eV. A PDP11/03 microcomputer is devoted to controlling the experiment and collecting data.

To test the reliability of the experimental setup the following measurements on He were done.

(i) The doubly differential cross section (DDCS) for the slow electron, $d^2\sigma/d\Omega_b dE_b$, was measured at the same incident, E_0, and ejected, E_b, electron energies of the $(e,2e)$ experiment. Good agreement was found with the DDCS "recommended" by Kim[11] and with previous experiments[10] in the whole range of angles θ_b investigated.

For the fast electron it was determined that the DDCS, $d^2\sigma/dE_a d\Omega_a$, was symmetric around the direction of the incident electron beam.

(ii) The TDCS $d^3\sigma/dE\, d\Omega_a d\Omega_b$ for the ionization of the He 1s orbital, was measured at the energies E_a and E_b of the C_2H_2 inner-shell experiment. The scattering angle θ_a (5° and 8° at $E_b = 9.6$ and 41.0 eV, respectively) was chosen so as to select kinematics belonging to the Bethe ridge.[12] Upon these kinematics the ionization is known to be well described by binary collisions and the TDCS is expected to be axially symmetric around the direction of the momentum transfer $\mathbf{K} = \mathbf{K}_0 - \mathbf{K}_a$.[13] These measurements are reported in Fig. 1 together with the predictions of a first Born model.[14] The symmetry requirement is satisfied and the first Born model reproduces the shape of the angular distribution, which peaks in two opposite directions: the binary lobe in the **K** direction and the recoil lobe in the opposite one.

The above tests rule out the presence of major systematic distortions in measuring coincidence angular distributions. In particular, the invariance of the coincidence collection efficiency upon variation of the ejected electron angle is ensured.

In order to minimize the momentum transfer the $(e,2e)$ measurements relative to the ionization of $C\ \sigma 1s$ in C_2H_2 have been performed at the smallest scattering angle experimentally accessible, namely 4°. These kinematics were chosen because the majority of ionization processes proceed with small to medium momentum transfer. For high-impact energy and vanishing K the TDCS becomes proportional to the optical oscillator strength and this is the background for most of the electron scattering spectroscopies currently used.

Typical count rates for the inner peak (true coincidences) varied from 0.4 to 0.08 coincidences/s, two orders of magnitude lower than for the outermost valence peak. Integration times from 3 to 12 h were needed for a single experimental point to achieve 25–30% statistical uncertainty.

III. RESULTS AND DISCUSSION

The angular distributions of the TDCS measured for the core C $\sigma 1s$ orbital are reported in Fig. 2. The main feature of these results is the presence of an intense recoil lobe, which at $E_b = 9.6$ eV is even larger than the binary one. A similar behavior has been observed also in the Ar 2p ionization,[7,8] while in the $(e,2e)$ asymmetric experiments on outer shells, at high and intermediate incident energies, the recoil lobe intensity never exceeded the binary one.[9] A large recoil size can be qualitatively explained with a strong elastic scattering from the nucleus.[15] Due to the localization of the core orbital in a region of small r, in inner-shell ionization the probability of final-state interactions of the ejected electron with the massive nucleus is enhanced. As a further consequence of the localization it may follow that collisional regimes close to the photoionization limit are easily achieved for inner orbitals upon asymmetric kinematics. In that case the ejected electron distribution would approach the limit of fully dipolar regime (momentum transfer $K \to 0$), where two opposite lobes of equal intensity, both symmetric around the **K** direction, are expected.[15] In the present kinematics the momentum transfer is not vanishing ($K = 1.26$ a.u. and $K = 1.46$ a.u. in Figs. 2(a) and 2(b) respectively), nevertheless the product $|\langle \mathbf{K}\cdot\mathbf{r} \rangle|^2$ is much

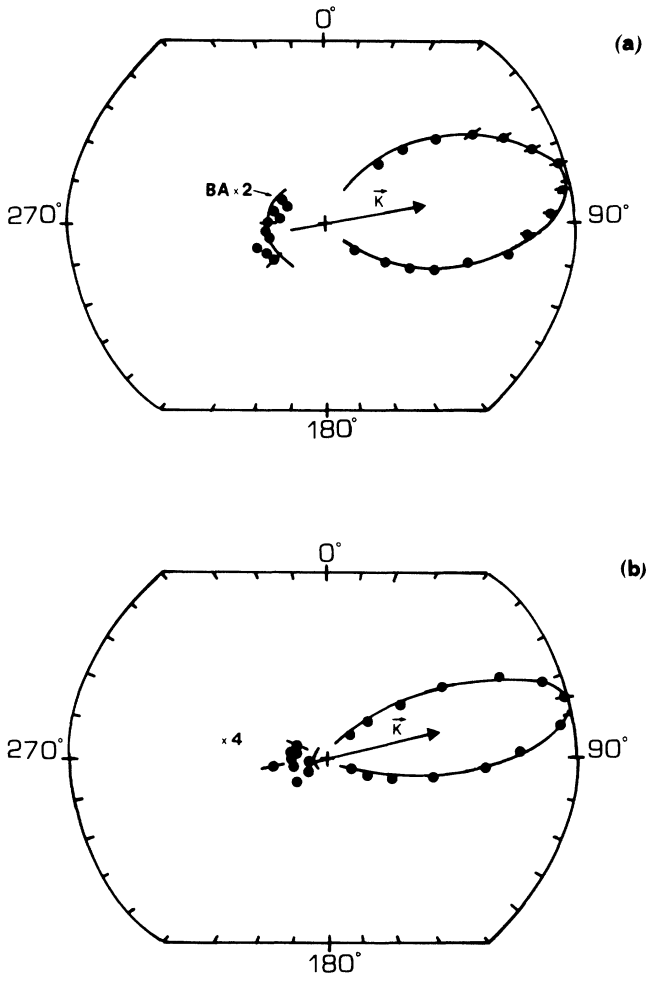

FIG. 1. $(e,2e)$ angular distributions for the ionization of He 1s. Kinematical conditions: (a) $E_0 = 1534.1$ eV, $E_b = 9.6$ eV, and $\theta_a = 5°$, (b) $E_0 = 1565.5$ eV, $E_b = 41.0$ eV, and $\theta_a = 8°$. The energy E_b is 1500.0 eV in both the figures. The solid lines are the predictions of a first Born model [formula (3) from Ref. 14]. In (a) the theoretical calculation for the recoil lobe ($\theta_b > 180°$) has been scaled up by a factor of 2, while in (b) both theory and experimental data of the recoil lobe are scaled up by a factor of 4.

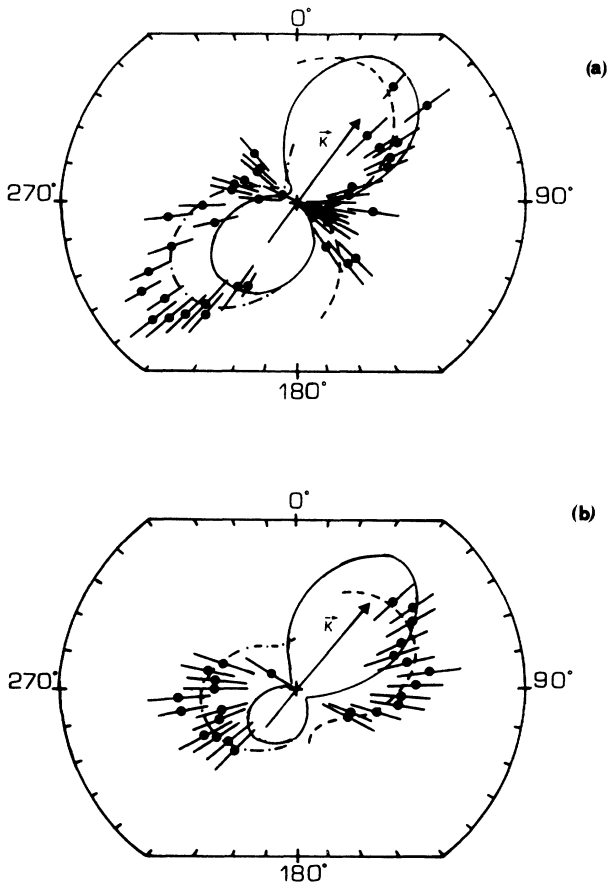

FIG. 2. $(e,2e)$ angular distributions for the ionization of C $\sigma 1s$ in C_2H_2. Kinematical conditions: (a) $E_0=1801.2$ eV, $E_b=9.6$ eV, $\theta_a=4°$, and $K=1.26$ a.u.; (b) $E_0=1832.4$ eV, $E_b=41.0$ eV, $\theta_a=5°$, and $K=1.46$ a.u. The energy E_b is 1500.0 eV in both the figures. The dashed ($\theta_b<180$) and dot-dashed ($\theta_b>180$) curves are separate best fits to the experimental data with the function $W(\theta_b)$ of the text. The solid lines are the predictions of a first Born model [formula (3) from Ref. 14].

smaller than unity (typically 0.09 for C $\sigma 1s$, from 3 to 5 times lower than for the measurement on He). This value might be small enough to justify the truncation of the Coulomb operator expansion to the first order (dipolar approximation) and to cause the high intensity measured in the recoil lobes. According to the dipolar model the angular distribution of the ejected electrons is given by the relationship:[16]

$$W(\theta_b)\propto 1+\frac{\beta}{2}[3\cos^2(\theta_b-\Phi)-1] \quad (1)$$

where Φ is the angle between **K** and the incident beam direction and β is the asymmetry parameter, that is expected to coincide with the photoionization one. $W(\theta_b)$ has been used as a trial function in fitting the experimental data with β and Φ as free parameters. From the Fig. 2 it is evident that the experimental distributions are not symmetric around **K** and that a common symmetry axis in the two opposite half-planes is absent. The function $w(\theta_b)$ was then separately fitted to the individual lobes and the results are represented in the figure by the dashed lines. The best values for the parameters β and Φ, obtained from a least χ^2 minimization, are collected in Table I. No experimental determinations of the photoionization β values for the C $\sigma 1s$ orbital in C_2H_2 are known to the authors, while existing theoretical predictions[17] are reported in the table. In spite of the large experimental uncertainties in the β and Φ values, a sharp disagreement between these results and the dipolar model can be assessed. In addition, it is to be noted that the deviation of the recoil peak maximum from the **K** symmetry is towards smaller deflection angles, in contrast with the deviations usually observed in the previous experiments on outer shells. This disagreement limits the generality of the equivalence between small angle fast electron inelastic scattering and photoabsorption experiments.[18] Such equivalence has been stated from quite recent electron energy loss works on gases,[19–21] i.e., in experiments where the fast electron DDCS is measured. The experiments on CF_4 (Ref. 20) and CO_2 (Ref. 21) performed at energies and scattering angles similar to the present ones, have produced energy loss spectra in the region of the K-shell ionization equivalent to the photoabsorption spectra. Particularly the analysis of the extended fine structure (EXELFS) has given the distances C-F (Ref. 20) and O-O (Ref. 21) and the phases of the backscattered waves in complete agreement with the results of photoabsorption experiments. It is evident that the TDCS enhances most of the effects that the DDCS, integrated over the ejection angle, hides.

TABLE I. Best-fit parameters of the formula (1) to the $(e,2e)$ angular distributions of the C $\sigma 1s$ orbital (see text for details) compared with the direction of the momentum transfer (Φ_K) and the theoretical photoionization asymmetry parameter β_{theor} (Ref. 17).

E_b		$(e,2e)$		Theory	
(eV)	θ_b	Φ	β	Φ_K	β_{theor}
9.6	$<180°$	$20°\pm4°$	1.1 ± 0.2	35.4°	0.7
	$>180°$	$52°\pm5°$	1.3 ± 0.4		
41.0	$<180°$	$56°\pm16°$	0.8 ± 0.7	38.7°	1.2
	$>180°$	$72°\pm15°$	0.5 ± 0.5		

The high sensitivity of the TDCS to the dynamics of ionization is further proven when the first Born model, which was quite good for the He reference measurements of Fig. 1, is applied to the C $\sigma 1s$ data. Its predictions, represented by the solid curves in Fig. 2, reproduce neither the widths, nor the binary to recoil ratios, nor the symmetry of the distributions. In this case, the kinematics that do not belong to the Bethe ridge and the ratio E_0/ε, that is one order of magnitude lower than in the case of the He experiment, make high-energy models truncated at first order of interaction less appropriate to calculate the TDCS.

Beyond these considerations that apply to any shell, a suitable model for inner-shell ionization should take into account that the creation of a core hole is always followed by a rearrangement of the residual ion, which for light atoms ends up in the emission of Auger electrons.

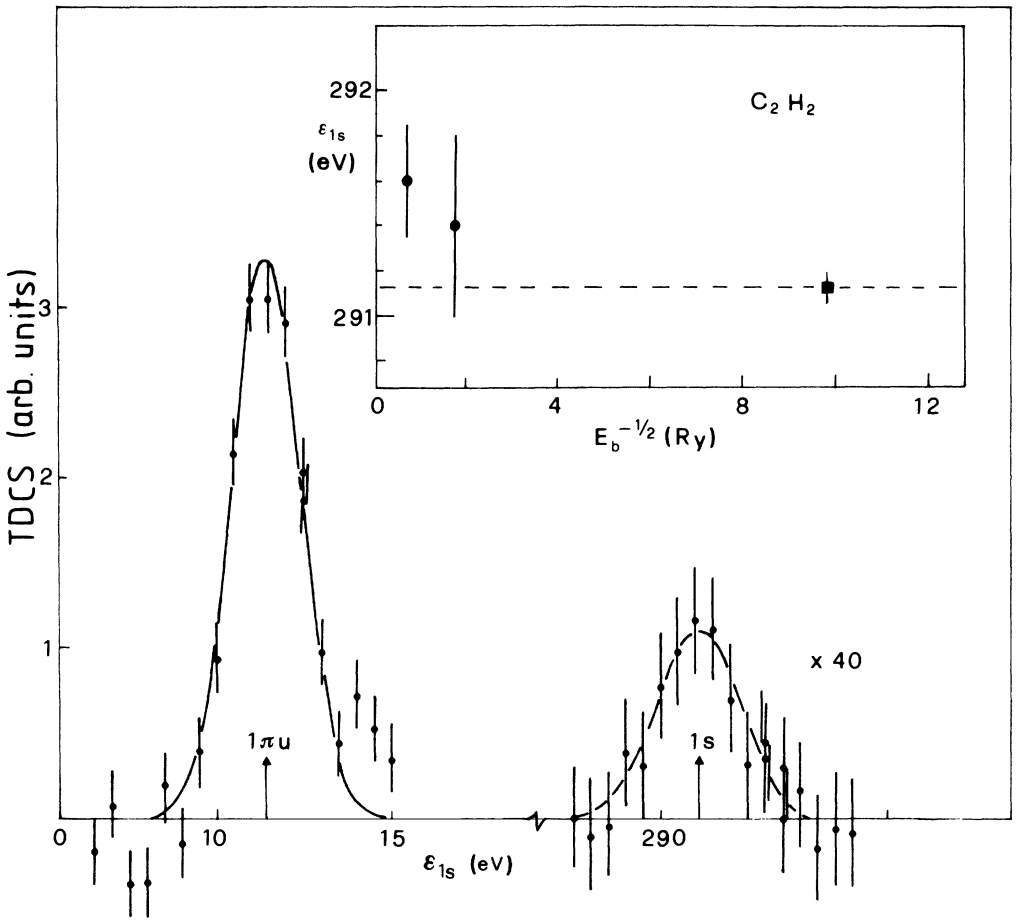

FIG. 3. $(e,2e)$ energy-separation spectrum. The kinematical conditions are the same of Fig. 2(a) and the ejected electron angle is fixed at 60°. In the insert the $(e,2e)$ centroids of the $\sigma 1s$ peak (●) are reported versus $E_b^{-1/2}$ together with the C $\sigma 1s$ binding energy (■) measured by XPS (Ref. 26).

At high energy the two processes can be regarded as independent (two-step model). When the primary ionization event is close to threshold, the ejected electron, slowly receding in the ion field, and the fast Auger electron can exchange energy and momentum.[22] As a consequence of this postcollision interaction (PCI), distortion of the angular distribution and shift of the Auger peaks towards higher energies have been observed in experiments where the scattered and the Auger electron were detected in coincidence.[8] In addition to these effects, in the molecular case and for particular values of the kinetic energy of the emitted electron, the e^--ion interaction can have a resonant character. It is due to final-state effects in which the slow ejected electron is temporarily trapped in quasibound molecular states, supported by the positive wings of the potential.[23] When the electron eventually tunnels into the continuum its angular distribution is perturbed.

To disentangle the different mechanisms that could explain the angular dependence of the measured TDCS (interactions beyond first order, postcollision interaction, and resonant effects) is a severe task. The presence of the above-mentioned PCI mechanisms should result in a shift of the C $\sigma 1s$ peak in the $(e,2e)$ energy separation spectrum with respect to the value measured in high-energy x-ray photoelectron spectroscopy (XPS). Therefore the energy position of the peak has been carefully determined. In Fig. 3 the portion of an $(e,2e)$ energy spectrum, relative to the outermost $1\pi_u$ and innermost C $\sigma 1s$ orbital of C_2H_2 is reported. On the abscissa the kinetic energy balance $E_0-(E_a+E_b)=\varepsilon$ is reported. This quantity is actually measured by the experiment by scanning E_0, while E_a and E_b are held fixed. If the slow ejected electron has lost energy in favor of the Auger electron, the balance must appear to increase. The centroids E_0' and E_0'' of the outermost $1\pi_u$ and of the C $\sigma 1s$ peak, respectively, have been located on a relative scale, by fitting a model function to the energy spectrum. The difference $(E_0''-E_0')$ is expected to coincide with the difference $(\varepsilon_{\sigma 1s}-\varepsilon_{1\pi_u})$ in the separation energies. The calibration of the E_0 scale is done in the energy-loss spectrum versus two sharp structures which fall close to E_0' and E_0'', respectively, i.e., the elastic peak position E_{el} and the C $\sigma 1s\rightarrow\pi^*$ resonance position, E_{π^*}, which lies 5.33 eV (Ref. 24) below the C $\sigma 1s$ threshold. The intervals $\Delta E'=E_0'-E_{el}$ and $\Delta E''=E_0''-E_{\pi^*}$ are measured with good accuracy and are not affected by systematic errors on the absolute calibration of the scale. With this procedure "apparent" separation energies of the C $\sigma 1s$ peak

are obtained following the relationship $\varepsilon_{1s}=\varepsilon_{1\pi}+\varepsilon_{\pi^*}+(\Delta E''-\Delta E')$. The values $\varepsilon_{1\pi}$ and ε_{π^*} are obtained, respectively, from data of photoelectron spectroscopy[25] (PES) and of high-resolution electron-energy-loss spectroscopy[24] (EELS). The vibrational structure of the transitions have been convoluted with the energy response function of the spectrometer. The values ε_{1s} obtained by this procedure at 9.6 and 41.0 eV above threshold are reported in the insert of Fig. 3 together with the XPS value of 291.14 eV.[26] Each of them is the mean of different determinations and, in spite of the uncertainty, a shift towards higher values with respect to the XPS determination is observed. In the atomic case a semiclassical PCI model predicts for the energy exchange between the Auger and the ejected electron $\Delta E \approx \Gamma_k (8E_b)^{-1/2}$ (atomic units have to be used).[27] This expression was found to be in good agreement with the measured Auger shifts in many cases.[28] Γ_k, the natural width of the core level, has been estimated to be 0.15 ± 0.04 eV for C $\sigma 1s$ in C_2H_2 by Tronc *et al.*[24] As a consequence, at $E_b=9.6$ eV a value $\Delta E=95$ meV is calculated. At this energy, however, the experimental shift amounts to 460 ± 230 meV and can not be simply interpreted on the grounds of such a PCI mechanism. It is suggested in the following that the extra contribution may come from vibrational excitation.

The vibrational excitation accompanying core-level ionization in molecules is due to the spatial redistribution of the outer electronic charge in presence of the core hole and, indeed, vibrational structure of XPS peaks has been reported in the literature whenever the energy resolution was high enough to observe it. The vibrational structure of the $(e,2e)$ peak is unresolved in the present experiment, but once convoluted with the experimental energy response function it determines the centroid of the peak. The XPS peak, towards which the shift has been calculated, was also vibrationally unresolved. However, a Frank-Condon distribution must be assumed for it, because the photon energy was high enough to assure the sudden approximation to be valid. In the present $(e,2e)$ spectrum, instead, it is possible that the vibrational structure comes from a non Franck-Condon distribution. This possibility is based on the following observations: (i) the C $\sigma 1s$ ionization, at the energies above threshold of our experiment, proceeds through resonant $\sigma_g 1s \rightarrow K_b \sigma_u$ channels that are expected to take into account up to 30% of the total intensity;[17] (ii) strong non-Franck-Condon effects have been already observed in the photoionization of the valence $1\pi_u$ orbital whenever a resonant channel becomes dominant in the ionization process.[23] The vibrational modes that can be excited with the removal of the C $\sigma 1s$ electron are both the C—H and C—C mode. Tronc *et al.*[24] have suggested that asymmetric C—H stretching ν_3 mode, which has a value of 407 meV in the ground state of C_2H_2, is excited when the core electron is promoted to the empty π_g orbital. Furthermore, an XPS investigation of the CH_4 (Ref. 29) molecule has resolved a vibrational structure, with nearly Poisson distribution of the branching ratios, for the C $1s$ ionization peak. The value of the C—H stretching mode was 391 meV in this latter case. It is therefore plausible to assume that in the $(e,2e)$ spectrum of C_2H_2 the vibrational structure of the C $\sigma 1s$ peak includes the C—H stretching mode. Because of the large value of the spacing associated, a slight change of the vibrational branching ratios could be responsible for the observed energy shift of the $(e,2e)$ peak. It is sufficient, for instance, to assume that the vibrational branching ratios in the high-energy limit are identical to those of CH_4 and that in our $(e,2e)$ experiment they still obey a Poisson distribution but with a reduced intensity of the $v=0\rightarrow v'=0$ transition (from 63% to 25% at $E_b=9.6$ eV).

If the resonant ionization channel is responsible for the energy shift, it would also affect the angular distribution. It was indeed observed that the β parameter in the photoionization of the C_2H_2 $1\pi_u$ orbital undergoes a sharp change in correspondence with the photon energies associated with non-Frank-Condon vibrational ratios.[23]

IV. SUMMARY

The ionization dynamics of the innermost orbital of the C_2H_2 molecule were investigated by asymmetric $(e,2e)$ experiments. In particular the $(e,2e)$ technique was applied for the first time to the ionization of an inner orbital upon kinematics where resonant channels are expected to be relevant with respect to the direct ionization.

Several dynamical effects were observed. The TDCS shows a large recoil lobe and severe deviation of the symmetry axis of both recoil and binary peak maxima from the momentum transfer direction. The disagreement with first Born predictions is more pronounced than for the outer-shell ionization performed in similar kinematic conditions. In particular, the recoil intensity is shifted to form smaller angles with the incident beam direction. This is in contrast with what is usually observed. The transition energy of the $(e,2e)$ peak is found to be shifted, for the first time, with respect to the correspondent XPS transition.

The angular distribution of the TDCS is not accounted by a dipolar approximation which, instead, would account for the equal intensity of the two opposite lobes and which was found to be adequate in describing the DDCS for similar molecules upon similar kinematics. On the basis of the results of the extensive theoretical work done for the outer-shell ionization, it is argued that, because of the localization of the core orbital, the description of the ejected electron wave function in the region of small r is crucial to the description of the process.

A semiclassical PCI model is insufficient to account for the "apparent" energy shift of the $(e,2e)$ peak in the energy separation spectrum. A tentative explanation for the observed shift requires a non-Frank-Condon unresolved vibrational structure of the C $\sigma 1s$ peak. This effect could be due to above-threshold resonant channels which were relevant in the present experiments. The presence of such channels would also contribute to the distortion observed in the TDCS angular distributions.

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