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Fragmentation Processes Following Core Excitation in Acetylene and Ethylene by Partial Ion Yield Spectroscopy

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Fragmentation processes following core excitation in acetylene and ethylene by partial ion yield spectroscopy

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Partial ion yield spectroscopy provides a very detailed picture of fragmentation processes following core excitation in isolated molecules. We exploit this potential in the analysis of decay processes following $C1s \rightarrow \pi$ and $C1s \rightarrow$ Rydberg excitations in ethylene and acetylene. We show that the relative intensity of spectral features related to the excitation to empty molecular orbitals or to Rydberg states is a function of the time variation of the fragmentation process. Namely, we see an intensity increase in the Rydberg states compared to the molecular orbitals as the fragmentation process becomes more extensive, a result attributable to the diffuse nature of the Rydberg virtual orbitals, which makes spectator decay more likely than participator decay. Therefore, the number of dissociative final states that can be reached from Rydberg excitation is higher than for excitation to empty molecular orbitals. In acetylene, we obtain the first direct evidence of the presence of a σ^* excitation embedded in the Rydberg series. The formation of the fragment H_2^+ in ethylene occurs following a recombination process, while in acetylene it is related to excess vibrational energy stored in the intermediate state. Furthermore, we can use the enhancement in channels corresponding to doubly charged species as an indication for the presence of shape resonances.

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INTRODUCTION

When a core hole is induced in a molecule, dissociation is very likely to occur following or even during electronic relaxation. The main pathway to molecular fragmentation is the decay of the species with a core hole to molecular ions with a single positive charge (mainly below threshold) or to molecular ions with a double positive charge (mainly above threshold), which are metastable and subsequently dissociate by breaking one or more chemical bonds. The observation of the resulting ions (molecular or atomic) is very informative of the nature of the excited or ionized state and of the dynamics of the photofragmentation process. Such experiments are performed using synchrotron radiation as the exciting source by monitoring the ion yield of all ion fragments (total yield mode) or of the single ion channels (partial yield mode) as a function of photon energy. In the present work we investigate the ion yield spectra of two simple representative

hydrocarbons, acetylene and ethylene, in the photon energy region including the C 1s ionization threshold.

The total electron yield or total ion yield spectra for acetylene and ethylene have been obtained by several groups with an instrumental resolution better than the core-hole lifetime broadening.¹⁻⁴ Thus vibrational fine structure and vibronic coupling have already been observed. However, the experimental methods used have been limited to the simultaneous observation of all channels in either electron emission or ion emission. We report here for the first time single-channel measurements, i.e., partial ion yields for all detectable fragments as a function of photon energy around the C 1s threshold in both systems. Furthermore, in these single-channel measurements we achieve vibrational resolution. The relative strength of the various channels and the intensity distribution within each provide information toward understanding the fragmentation dynamics of both species. In particular, below threshold we observe that the relative intensity for spectral features related to core-to-Rydberg excitation increases as the fragmentation process is more extended. In other words, for the smaller fragments, the Rydberg states are much more prominent than for the parent

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molecular ions. This is directly related to spectator decay being much more probably following excitation to the diffuse Rydberg orbitals, and many or most of the final two-hole/one-particle states are dissociative. This experimental finding sheds new light in the level assignment in acetylene, where it is possible now to discriminate between states with main σ^* or main Rydberg character. Furthermore, the detection of doubly charged positive species is enhanced above threshold due to normal Auger decay, and we show that in acetylene this enhancement can be connected to the relatively well-characterized continuum shape resonance. Also in acetylene we observe a reaction leading to H_2^+ , which requires excess energy stored as vibrational energy in the intermediate state, while in ethylene the same species seems to originate mostly from second-step processes.

EXPERIMENT

Our measurements were performed on undulator beamline 8.0.1.3, at the Advanced Light Source, Lawrence Berkeley National Laboratory. The monochromator resolution at 300 eV was approximately 70 meV when using an entrance slit width of 15 μ and an exit slit width of 18 μ . This resolution was chosen to allow a reasonable signal while still allowing us to observe the higher Rydberg states near the carbon K edge. The experimental apparatus used in the present study has been previously described.⁵ Basically, the apparatus consists of a 180° magnetic mass spectrometer, providing a FWHM corresponding to a fraction of uma, which is adequate to distinguish fragments with a sequential number of hydrogen atoms, a lens system to focus the ions created in the interaction region onto the entrance slit of the mass spectrometer, and a gas cell containing an extraction field to move the ions created in the interaction region into the lens system. The target gas enters the open cell via an effusive jet of 2 mm in diameter. A channel electron multiplier is used at the exit slit of the spectrometer to detect the ions. Finally, a differential pumping system was used to isolate the target chamber vacuum (2×10^{-5} Torr) from the beamline vacuum (1×10^{-9} Torr).

RESULTS AND DISCUSSION

Ethylene

We have obtained partial yield curves for the photofragmentation of ethylene as a function of photon energy near the C K edge for the following ionic species: $C_2H_4^+$, $C_2H_3^+$, $C_2H_2^+$, C_2H^+ , C_2^+ , CH_3^+ , CH_2^+ , CH^+ , C^+ , H^+ , and H_2^+ . Since the mass spectrometer has the capability to detect anions as well as cations,⁵ we investigated the presence of H^- and C^- , but those species were found to be below our detection limit. We attribute this experimental finding to the low polarity of the C–H bonds, in contrast to CO, where it was possible to detect a considerably amount of O^- .⁶

In Figs. 1 and 2 we show the partial yield curves below the $C1s$ threshold for two series of ionic fragments. The lowest-lying intense spectral structure corresponds to the $C1s \rightarrow \pi^*$ transition, with some resolved vibrational structure, while the following series of sharper peaks correspond to the Rydberg series. The absorption spectrum of ethylene

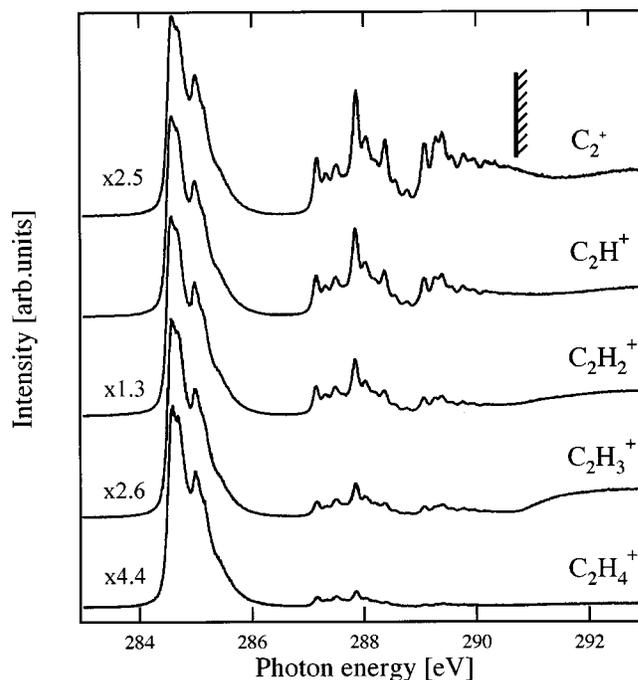


FIG. 1. Partial ion yield curves in ethylene below the $C1s$ ionization threshold [marked at 290.75 eV (Ref. 1)] for the fragments $C_2H_4^+$, $C_2H_3^+$, $C_2H_2^+$, C_2H^+ , C_2^+ . For comparison, the curves are normalized on the intensity of the main peak centered at 285 eV (Refs. 1 and 2). The scaling factors with respect to the most intense fragment are shown.

has been previously measured several times with lower resolution (see, e.g., Refs. 1, 2, and 7). Our ion yield spectra reproduce the previous measurements, but with some differences in the Rydberg series in terms of relative intensity of the spectral features, which are most likely due to our increased resolution. The most evident feature in both series is the increase in relative intensity of the Rydberg series with respect to the $C1s \rightarrow \pi^*$ transition as a function of how extended the fragmentation is. This experimental finding can be related to the fact that following excitation to a Rydberg state, spectator decay is more likely than participator decay. We believe this is due to the diffuse nature of the virtual orbital, and therefore the number of dissociative final states that can be reached is higher in this situation than for excitation to an empty molecular orbital. Thus, fragmentation processes are more likely to take place. This general effect is quite evident for ethylene, and in cases where there is some uncertainty in orbital assignment this effect can be exploited to distinguish between Rydberg states and empty molecular orbitals (see the discussion below for acetylene).

The existence of vibronic coupling and dynamic core-hole localization has been reported in the literature.^{2,3} In particular, the excitation of nontotal symmetric vibrational modes has been calculated for the spectral feature related to the $C1s \rightarrow \pi^*$ transition.² Despite the improved experimental conditions, no further evidence of such vibronic coupling can be derived for our spectra. However, the vibrational progressions of the allowed and forbidden vibration energies reported in the literature² are very closely spaced. Spacing is well below the core-hole lifetime broadening (around 110 meV) and therefore not possible to resolve.

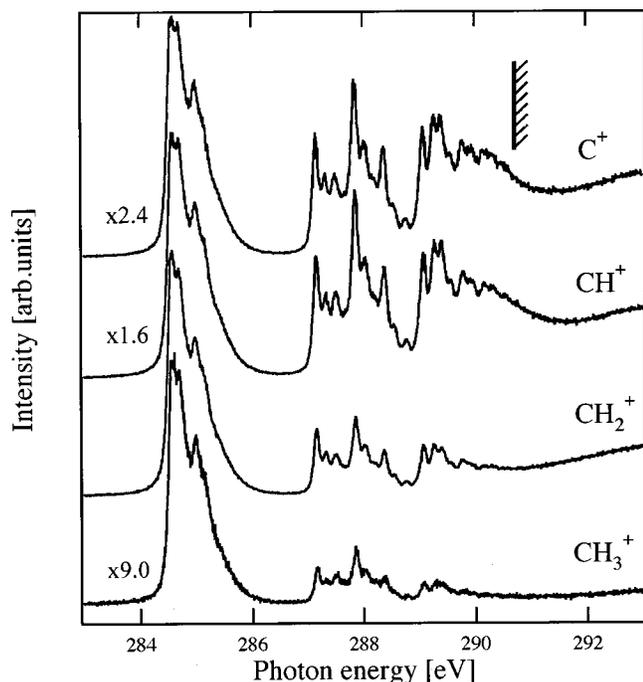


FIG. 2. Partial ion yield curves in ethylene below the C1s ionization threshold [marked at 290.75 eV (Ref. 11)] for the fragments CH₃⁺, CH₂⁺, CH⁺, C⁺. For comparison, the curves are normalized on the intensity of the main peak centered at 285 eV (Refs. 1 and 2). The scaling factors with respect to the most intense fragment are shown.

At variance with this finding, the spectral region of the Rydberg transitions appears to be greatly improved in our dataset with respect to previous measurements.¹ In particular, the region of higher Rydberg transitions (288–291 eV) shows a richer structure, and the C1s→3s transition region consisting of four peaks at 287.15, 287.32, 287.51, and 287.67 eV is better defined. In Fig. 3 we show an enlargement of this prominent region for the C⁺ fragment. We observe that the vibrational progression for this core-excited state cannot correspond to excitation of only one vibrational mode because the peak at 287.51 eV is broader and more intense than the neighboring peak. We also notice a resemblance between this vibrational structure and the peak corre-

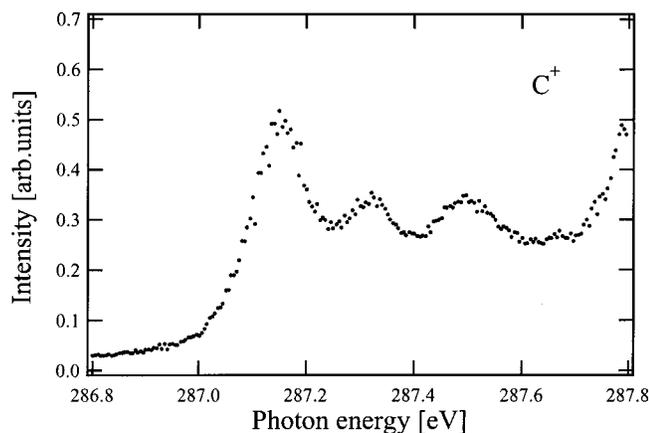


FIG. 3. Rydberg region in the partial ion yield of the C⁺ fragment in ethylene.

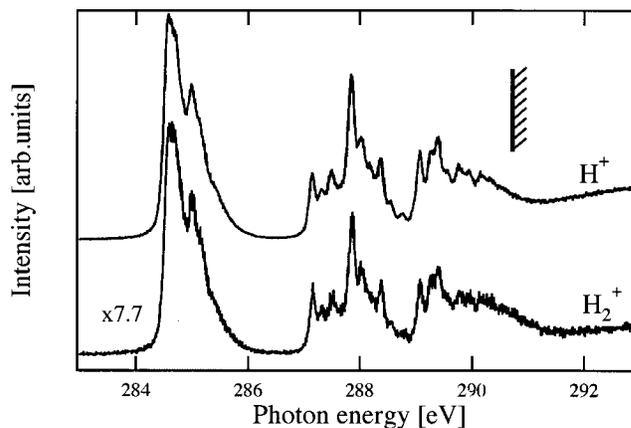


FIG. 4. Partial ion yield curves in ethylene for the fragments H⁺ and H₂⁺. For comparison, the two curves are normalized on the intensity of the main peak centered at 285 eV (Refs. 1 and 2). The scaling factors with respect to the most intense fragment are shown.

sponding to the C1s→π* transition. In the latter case, the literature assignment is based on the excitation of both totally symmetric and nontotally symmetric modes.² The literature assignment for the C 1s→3s state is in terms of C–H modes, without excitation of the C–C stretching mode, and without details on which C–H modes should be active.¹ On the grounds of the above mentioned resemblance, we hypothesize nontotally symmetric C–H modes (such as C–H bending modes) are also excited in the transition to the 3s Rydberg state, contributing to the observed peak at 287.51 eV, which clearly cannot be accounted for completely with only one component.

In Fig. 4 we show the partial ion yields for H⁺ and H₂⁺. These two curves seem to mimic each other over the entire range. In other cases such as H₂O it was demonstrated that the pathway leading to H₂⁺ formation is a high excitation of a specific vibrational mode, the bending mode, which brings the two hydrogen atoms close enough to induce their combination.^{8,9} In ethylene, it appears that the formation of H₂⁺ simply mimics H⁺ formation over the whole energy range. The situation is different for acetylene, where H₂⁺ formation seems to be, similar to water, at least partly connected to higher vibrational excitations (see the discussion below).

In Fig. 5 we show the partial yield curves for some of the fragments above the C1s threshold. All curves show three maxima at about 292, 295.5, and 297.5 eV, followed by a broad structureless continuum. An open question in ethylene is whether there is a continuum shape resonance above the C1s threshold at around 300 eV photon energy. This shape resonance has been identified using NEXAFS data,^{10,11} but cross section measurements for the C1s main line and related satellites^{12,13} have questioned this result. Additionally, an analysis of the vibrational substructure of the C1s photoelectron line has provided contradictory results.^{14,15} In a previous paper, we demonstrated that the detection of anions can help determine the presence of such resonances.⁶ Unfortunately in ethylene, as mentioned above, we were not able to detect negatively charged fragments. Also in CO we noticed that the well-known shape resonance is more evident in the par-

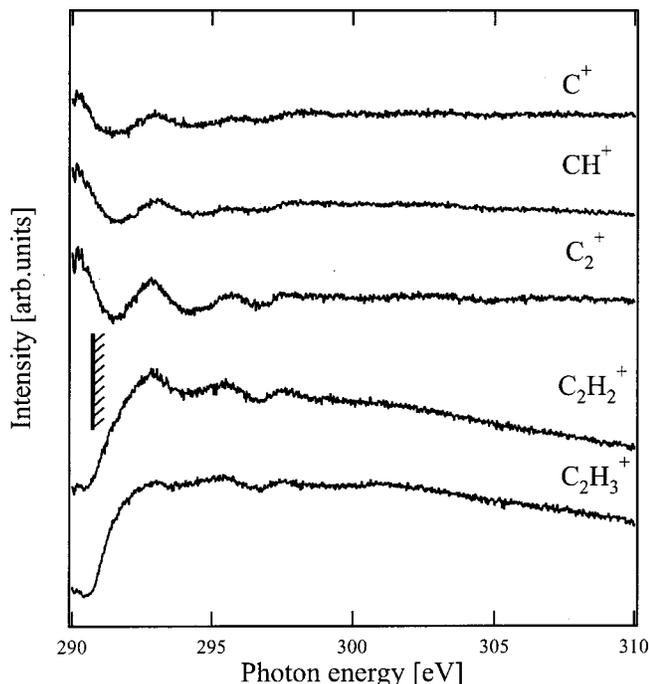


FIG. 5. Partial ion yield curves in ethylene above the $C1s$ ionization threshold (marked at 290.75 eV (Ref. 1)) for the fragments $C_2H_3^+$, $C_2H_2^+$, C_2^+ , CH^+ , C^+ .

tial yield curves of the doubly charged species than in the singly-charged ones. The production of such species should be enhanced when the cross section of the main line and the subsequent normal Auger decay are enhanced by the presence of the shape resonance. In ethylene we detect some molecular doubly charged species, but they are contaminated with singly charged species (e.g., $C_2H_4^{++}$ and CH_2^+ have the same mass-to-charge ratio). If an effect due to the shape resonance is present, it is too weak to be observed under our experimental conditions. The situation is more clear cut for acetylene, where we are able to detect C^{++} , which shows some enhancement that can be connected to the shape resonance (see the discussion below).

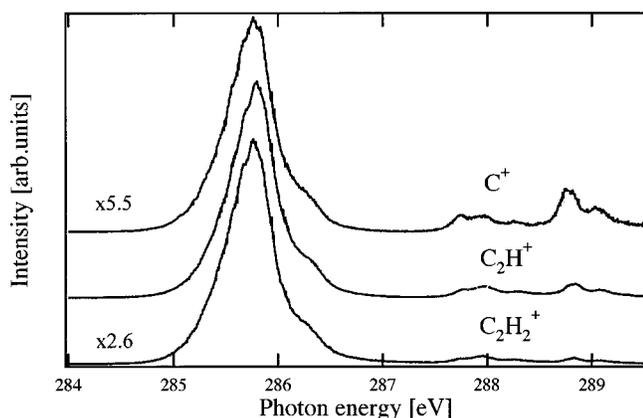


FIG. 6. Partial ion yield curves in acetylene below the $C1s$ ionization threshold [291.1 eV (Ref. 2)] for the fragments $C_2H_2^+$, C_2H^+ , and C_2^+ . For comparison, the curves are normalized on the intensity of the main peak at 285.8 eV (Ref. 3). The scaling factors with respect to the most intense fragment are shown.

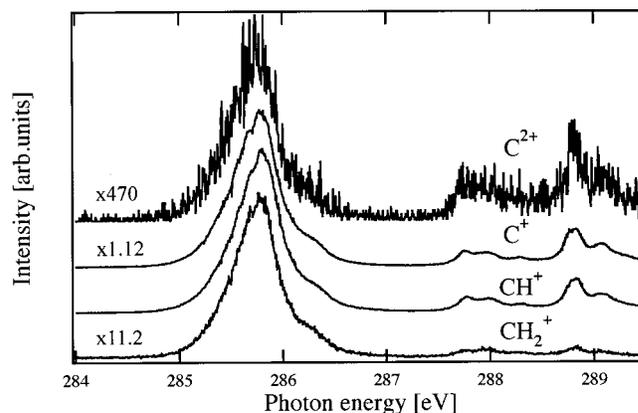


FIG. 7. Partial ion yield curves in acetylene below the $C1s$ ionization threshold [291.1 eV (Ref. 2)] for the fragments CH_2^+ , CH^+ , C^+ , C^{++} . For comparison, the curves are normalized on the intensity of the main peak at 285.8 eV (Ref. 3). The scaling factors with respect to the most intense fragment are shown.

Acetylene

Figures 6 and 7 show the partial yield curves below the $C1s$ threshold for the following ionic fragments: $C_2H_2^+$, C_2H^+ , C_2^+ , CH_2^+ , CH^+ , C^+ , and C^{++} . The first broad peak with some vibrational structure corresponds to the $C1s \rightarrow \pi^*$ transition, while the following spectral structure is due to the Rydberg series. An open question in the spectral assignment for acetylene is the relative position of the $C1s \rightarrow \sigma^*$ transition with respect to the first members of the Rydberg series, and how extended is the valence-Rydberg mixing. A first answer was provided by angle-resolved total-yield measurements, which, combined with theoretical calculations, gave a clear indication of the symmetry of the state,¹⁶ indicating primarily Rydberg character for the lowest-lying feature in the Rydberg region (around 287.74 eV), while the second peak (near 287.94 eV) has a primarily σ^* character. However, the evidence is indirect, being based on calculations and symmetry arguments. We report more direct evidence to confirm the assignment, based on the above-mentioned observation that the relative intensity of spectral features

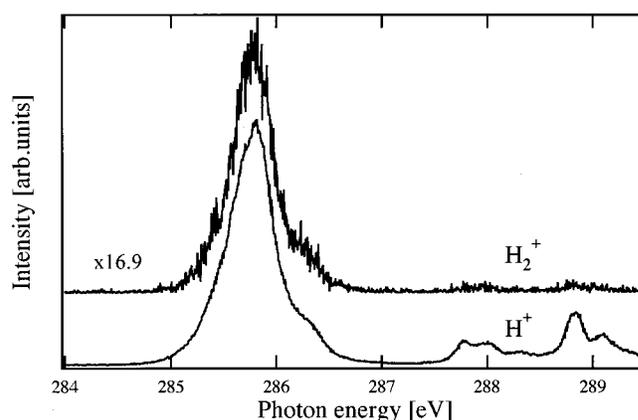


FIG. 8. Partial ion yield curves in acetylene for the fragments H^+ and H_2^+ . The two curves are normalized to each other on the intensity of the main peak at 285.8 eV (Ref. 3) for the sake of comparison. The scaling factors with respect to the most intense fragment are shown.

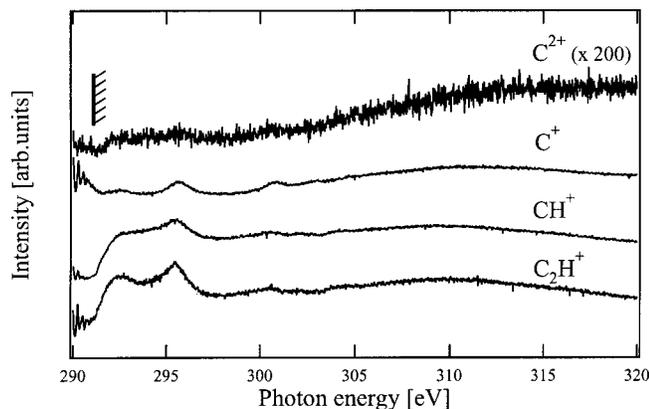


FIG. 9. Partial ion yield curves in acetylene above the $C1s$ ionization threshold [marked at 291.1 eV (Ref. 2)] for the fragments C_2H^+ , CH^+ , C^+ , and C^{++} .

mainly or solely related to Rydberg states shows an increase with respect to features related to transitions to empty molecular orbitals for ionic fragments that originate from a more extended fragmentation.

If we look at the lower-lying Rydberg region (287.5–288.5 eV (in the series of fragments $C_2H_2^+$, C_2H^+ , C_2^+ (Fig. 6) and in the series CH_2^+ , CH^+ , C^+ (Fig. 7), which both correspond to increasing degrees of fragmentation, we notice that the relative intensity of the second peak at 287.94 eV clearly decreases, allowing us to relate it to an intermediate state with main $C1s \rightarrow \sigma^*$ character.

In Fig. 8 we show a direct comparison between the yields for H^+ and H_2^+ . The most interesting finding is that the main feature in the H_2^+ spectrum appears to be narrower on the low photon energy side with respect to the H^+ curve. One explanation for this is storage of significant vibrational energy in the core-excited state is required for the production of the recombination fragment H_2^+ ; the production of this fragment would be ineffective from core-excited electronic states with little vibrational energy.

In Fig. 9 we show above-threshold curves for some of the fragments. We notice that in the yield curve for the C^{++} fragment there is some enhancement in the energy region above 312 eV, where a shape resonance has been observed with other methods.¹⁷ Since the shape resonance implies an enhancement mainly in the cross section of the $C1s^{-1}$ main line, and, consequently, in the corresponding Auger decay, we can assume that such enhancement for a doubly charged species can be related to normal Auger processes, and therefore to the shape resonance appearing in the main line channel and possibly in the related satellite channels at higher photon energy. It is also interesting to notice that, as mentioned above, no such effect is visible in ethylene (see Figs. 5 and 6), where the presence of a shape resonance has never been confirmed.

CONCLUSION

The use of high-resolution partial-ion-yield spectroscopy in the photon-energy region around a core threshold is proven to be very effective in elucidating details of core excitation–deexcitation processes. In both cases examined

here, the excitation of ethylene and acetylene near the $C1s$ ionization threshold, it was shown that the relative intensity of spectral features related to Rydberg states increases as a function of how extended the fragmentation process is. This new experimental finding is explained by molecular fragmentation being more likely following electron decay to spectator states, which are most easily reached from the decay of the spatially extended Rydberg states.

As a consequence, it is now possible to discriminate between some states with main σ^* or main Rydberg character in the acetylene level assignment. Furthermore, we show that in acetylene the enhancement in the yield of doubly charged positive species above threshold due to normal Auger decay can be connected to the relatively well-characterized continuum shape resonance. We also observe a recombination reaction leading to H_2^+ in acetylene, which requires excess energy stored as vibrational energy in the intermediate state, while in ethylene the same species seems to originate mostly from a second-step processes.

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