

Continuum resonance in ethylene: Evidence from vibrationally resolved core photoionization

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The carbon $1s$ photoelectron spectrum of gas-phase ethylene has been measured with high resolution in order to study changes in vibrational structure arising from core photoionization through a continuum resonance. By evaluating the changes in vibrational intensity distribution we are able to determine that the ionization is non-Franck-Condon for energies close to the maximum of the broad resonance in the ethylene absorption spectrum. From these measurements it is possible to investigate the specific effect on the vibrational intensity distribution arising from the resonance. We find that the intensity of the C-H stretch vibrational mode is constant as the photon energy is scanned through the resonance, while the intensity of vibrations associated with the C-C bond varies with photon energy. This shows the existence of a shape resonance which, according to the scattering model of the shape resonance, must be primarily associated with the C-C bond rather than the C-H bond. [S1050-2947(98)04609-5]

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I. INTRODUCTION

Very recently, the existence of shape resonances near the C $1s$ ionization threshold in C_2H_2 , C_2H_4 , and C_2H_6 was brought into question by Kempgens *et al.* [1]. Putting aside the commonly accepted interpretation of the broad structure above the core ionization threshold in molecules as being a shape resonance, the structures in C_2H_4 and C_2H_6 were identified as arising wholly from double excitations, i.e., two-hole-two-electron ($2h-2e$) core-excited states. This interpretation was based upon the absence of an increase in (single-hole) $1s$ photoionization cross section in the resonance region. Thus the absorption resonance would be composed of a multitude of close-lying $2h-2e$ discrete states. Shape resonances, however, are known to affect photoionization observables in other significant ways. Photoionization via a shape resonance is known to produce distinctly non-Franck-Condon vibrational intensity distributions, and variations in the angular asymmetry parameter are also known to be indicative of shape resonances [2–6].

Broad resonances are found in the absorption spectra of many hydrocarbon molecules; they are generally located within 30 eV of the ionization threshold for both valence and core electronic states [7,8]. These continuum σ -like states are found to influence the photoionization cross section, the distribution of vibrational intensity within a progression [3,4,6,7,9], molecular alignment [10], and photoelectron angular asymmetry [5]. In two studies of near-threshold ionization in ethylene both discrete, multielectron resonances and broad, σ -like continuum resonances were identified above the ionization threshold [11,12].

Another study of chemisorbed ethylene offers an indepen-

dent confirmation of the shape-resonant nature of the broad resonance. It was shown that the C-C internuclear separation varies with substrate for chemisorbed ethylene; subsequent changes in the energy of the continuum resonance were observed, indicating a connection between the C-C bond length and the resonance energy [13]. The angular anisotropy of the resonance was also measured for these adsorbed molecules; the absorption resonance was shown to have σ symmetry [5]. These findings strongly suggest that this resonance is indeed a C-C resonance which is associated with the C-C bond [13]. In addition, multiple-scattering calculations provide evidence supporting the existence of a C-C shape resonance in C $1s$ ionization of gas-phase ethylene [14].

In this study we address the question of the existence of a shape resonance in C_2H_4 by studying individual vibrational modes in the C $1s$ photoelectron spectrum as a function of photon energy. In order to do so we rely upon a relatively simple picture of core photoionization of molecules which has been proven useful in many cases [5,15,16], allowing a complicated vibrational manifold to be described by a few parameters which may be determined independently of one another. With these tools the question of whether ionization takes place within the Franck-Condon region may be approached. In our study we show that there are changes in the vibrational intensity distribution as the photon energy is scanned through the resonance region. These changes are not due to post collision interaction (PCI) effects, but are attributed to the existence of a continuum resonant state through which photoionization takes place. The changes are not as dramatic as those seen in, for example, carbon monoxide, but they are sufficiently large that the concept of a continuum resonance near the C $1s$ ionization edge in ethylene should not be discarded.

II. EXPERIMENT

The experiment was performed on beam line 51 at MAX Lab in Lund, Sweden [17]. The details of this monochro-

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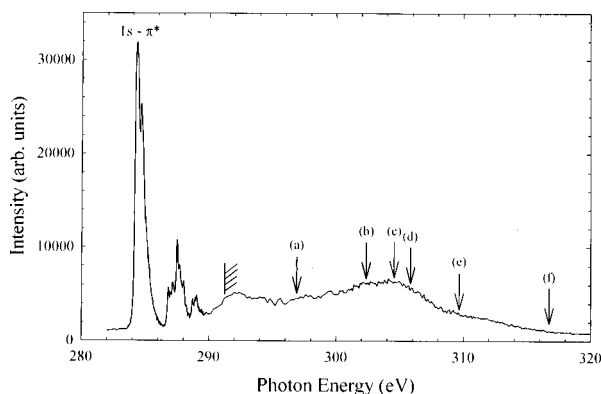


FIG. 1. The ionization spectrum of gas-phase ethylene. The total electron yield spectrum was measured with a photon-energy resolution of 100 meV.

mator have been described elsewhere. The measurements were made using a versatile end station which includes a rotatable hemispherical electron-energy analyzer (SES-200) [18]. The analyzer was mounted at angles of 0° and 54.7° with respect to the polarization plane of the undulator radiation for these measurements. The spectra were measured using analyzer settings which were matched to the monochromator resolution. The broadening from the spectrometer is 75 meV full width at half maximum (FWHM), and the monochromator bandpass was about 80 meV. The total experimental resolution was found to be 115 meV. Doppler broadening is negligible in these spectra. The sample was obtained from L'Air Liquide with a purity of 99.5%. The binding-energy scale was calibrated internally by measuring C_2H_4 together with CO_2 gas.

III. SPECTRA

The ionization spectrum of ethylene is shown in Fig. 1 with a maximum at about 303 eV. Six photon energies in and around the broad resonance were chosen for this study. In Fig. 2 the C $1s$ photoelectron spectra of C_2H_4 measured at the photon energies indicated in Fig. 1 are shown. The spectra shown here are measured at 0° relative to the polarization of the ionizing photons. The intensity of the 0° spectra is better than those measured at the magic angle (54.7°) due to the angular symmetry of the core hole, and any effect from the shape resonance should be more clearly visible at this angle due to the σ symmetry of the resonance. All of the spectra show distinct vibrational structure, but there are some features which stand out. First, the overall shape of the vibrational manifold changes, especially as the photon energy increases from 298.5 to 306.0 eV. The changes are most apparent at about 150–220 meV from the adiabatic peak. Second, the apparent width of the peaks shown in the plots changes with photon energy with the largest width seen in the 298.5-eV spectrum which exhibits a strongly asymmetric line profile. The pronounced asymmetry seen in the low-photon-energy spectra arises from postcollision interaction which is a manifestation of the interaction between the outgoing slow photoelectron and the fast Auger electron [19,20]. The measured value for the adiabatic energy of the C $1s$ state is 290.72(5) eV after calibration of the spectra to the binding energy of CO_2 . This differs slightly from the

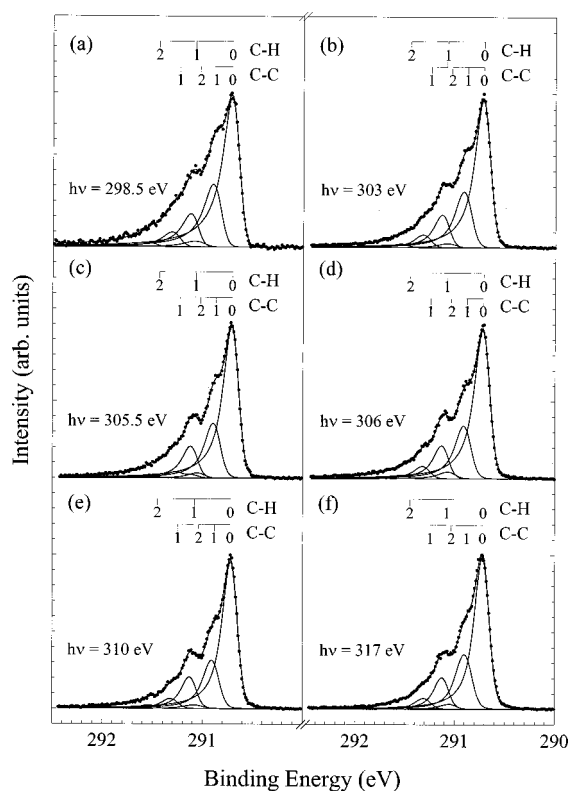


FIG. 2. The C $1s$ photoelectron spectra measured at photon energies (a) 298.5 eV, (b) 303.0 eV, (c) 305.5 eV, (d) 306.0 eV, (e) 310.0 eV, and (f) 317 eV. The vibrational progressions are indicated with bars in the figure. The spectra are background subtracted.

recently published value of 290.75 [15], but is well within the given error.

A. Vibrational structure

Based upon previous work by several other groups [15,22] we first attempt to fit the highest kinetic energy spectrum with two normal vibrational modes. The C-H stretch mode with an energy of about 400 meV and the C-C stretch mode with an energy of 210 meV were used. A systematic lack of intensity was found at about 150 meV from the adiabatic peak. When a third mode, corresponding to the H-C-H in-plane bend with an energy of 165 meV (see Fig. 3), was added the fits became consistent. The lifetime was held constant for all spectra in the series. The intensity of the C-H vibration relative to the adiabatic peak is about 0.22 for all spectra.

Because the two lower-energy modes are separated by an energy which is within the lifetime width of the core level it is difficult, if not impossible, to assign exact intensities to these peaks. Higher-resolution measurements would not increase the accuracy of these intensities appreciably. Thus we restrict ourselves to a discussion of the combined action of these two vibrational modes (C-C stretch and H-C-H bend). Fortunately this grouping of vibrational modes has a physical basis since both of these modes involve both a C-C stretch movement and a bend in the H-C-H angle. These two modes are shown schematically in Fig. 3. It is clear that neither the bending mode nor the C-C mode is a pure bending or stretching vibrational mode. We find the following energies (see

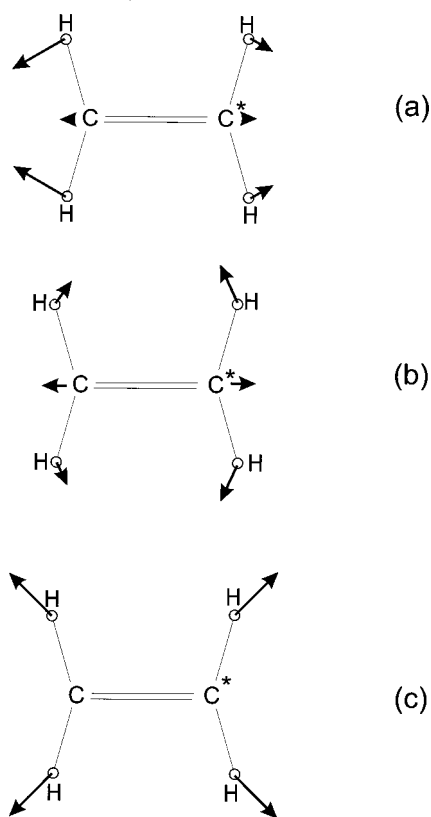


FIG. 3. Schematic representation of the vibrational modes in ethylene. (a) The H-C-H bending mode. (b) The C-C stretch mode. (c) The C-H stretch mode.

below) for these three normal vibrational modes: the C-C stretch vibrational mode 210(10) meV, the C-H stretch vibrational mode 410(5) meV, and the H-C-H bending mode ~ 165 meV. The two low-energy modes are described in detail in Ref. [23]. The vibrational energies in the 317-eV spectrum were confirmed by parallel analysis of the C $1s$ spectrum of deuterated ethylene (C_2D_4) measured at the same photon energy [24].

B. Vibrational analysis

The spectra were fit using a least-squares minimization routine implementing PCI line profiles convoluted with a Gaussian profile ($\Gamma = 115$ meV) to represent the monochromator and electron analyzer broadening.

To obtain reliable values for the vibrational energies we begin with the spectrum measured at 317-eV photon energy. This photon energy is above the resonance region where ionization is well described by the Franck-Condon principle for ionization [24]. We find that in this case the spectrum may be reproduced rather well using a linear-coupling model [25] effectively reducing the number of free parameters necessary for fitting. For each vibrational progression the vibrational separation is held constant and the intensities for the higher vibrational levels are determined from the intensity ratio of the adiabatic peak and the first vibrational peak. The quantity describing the ratio of the first vibrational peak intensity to the intensity of the adiabatic peak is called the S factor. The subsequent peak intensities within a vibrational progression

are determined solely from this parameter. The intensity of a given vibrational mode, r , is expressed as

$$I(0-n_r) = e^{-S_r} \frac{S_r^{n_r}}{n_r!}, \quad (1)$$

where $I(0-n_r)$ is the Franck-Condon factor for a transition from the $\nu=0$ state to the $\nu'=n_r$ state. Here S_r is the S factor for mode r . The S factor is related to the relative change in normal coordinates, δ , by $S_r = \frac{1}{2} \delta$.

In the case of carbon $1s$ ionization the harmonic approximation utilized in this model is well motivated since the bond-length change is relatively small upon ionization, and the number of measurable vibrational excitations is seldom, if ever, large [15,22,26].

If the photoionization process is direct, and within the Franck-Condon region then the only free parameters required in the fitting procedure are the vibrational energy and the S factor for each vibrational mode, the natural lifetime width of the core-hole state, and the PCI asymmetry parameter. The PCI parameter was determined from the low-binding-energy side of the spectrum. In addition, studies of the profile utilized here have been made on spectra measured with this spectrometer. Atomic photoelectron lines were fit for different excess photoelectron energies and the profile was able to reproduce the line shapes satisfactorily. In practice, the PCI asymmetry parameter is correlated with the lifetime width, and to some extent the background level. In order to account for this we have measured spectra with at least 1 eV of background on either side of the spectrum in order to accurately fit a linear, nearly flat background function, which is also well justified by the spectrometer transmission function. In addition, we require that the lifetime width of the core-ionized state be constant for all of these core photoelectron spectra. The PCI asymmetry parameter depends upon the Auger electron kinetic energy, the lifetime of the hole state, and the excess energy of the photoelectron in the model [19,20]. The Auger electron kinetic energy is not accurately known, but it does not vary appreciably from spectrum to spectrum. If the lifetime width and the Auger energy are constant then the PCI asymmetry parameter will be inversely proportional to the square root of the photoelectron excess energy [19]. The results of the fits are shown in Table I.

Systematic application of these constraints allows us to control the lifetime, PCI asymmetry parameter, vibrational spacing, and instrumental broadening parameter in the fits. For the 317-eV spectrum we fit the lifetime, PCI, and intensity parameter together with a background while paying careful attention to the low-binding-energy side of the spectrum. The PCI profile must reproduce the low-energy side of the profile which also changes form as the excess energy changes. The next step is to work on the vibrational structure and extract the two parameters necessary for each vibrational progression. The C-H and C-C normal stretching modes were easily determined from this procedure. The third vibrational mode was found through comparison of the residuals from each fit, and confirmed by comparison with deuterated ethylene. This assignment is also confirmed by independently measured photoelectron spectra [23].

TABLE I. Intensities and vibrational energies extracted from fits to the ethylene C 1s spectra. For each photon energy two values for the intensity of the first peak in each vibrational series are presented. The first (LC) is the S factor obtained within the linear-coupling model and the second is the intensity ratio obtained by fixing the vibrational energies to the values in the table and fitting the intensities of each peak independently.

Energy (eV)	$I_1(\text{H-C-H})$	$\hbar\omega$ (meV)	$I_1(\text{C-H})$	$\hbar\omega$ (meV)	$I_1(\text{C-C})$	$\hbar\omega$ (meV)
317.0(LC)	0.209	165(5)	0.199	402(5)	0.156	0.208(5)
317.0	0.238		0.214		0.121	
310.0(LC)	0.231		0.213		0.131	
310.0	0.196		0.214		0.155	
306.0(LC)	0.199		0.233		0.213	
306.0	0.191		0.222		0.178	
305.0(LC)	0.227		0.216		0.184	
305.0	0.187		0.219		0.184	
303.0(LC)	0.212		0.208		0.204	
303.0	0.169		0.216		0.226	
298.5(LC)	0.326		0.225		0.144	
298.5	0.238		0.219		0.197	

After the vibrational energies are known from this spectrum, we proceed to the rest of the spectra. If the ionization proceeds within the Franck-Condon region, the linear-coupling model should describe the spectra after the PCI asymmetry parameter is allowed to vary as predicted by semiclassical models [19,20] and which has been verified in several studies of atomic Auger lines (e.g., Arcuni, Ref. [21]). In another molecule, ethane, we found that the linear-coupling model was able to reproduce core photoelectron spectra very well at several photon energies between 10 and 28 eV above the 1s ionization threshold. A comparison of two ethane C 1s spectra is shown in Fig. 4. The spectrum measured with 317-eV photons was fit, and the linear-coupling parameters were used to simulate the 303-eV spectrum after the PCI asymmetry parameter was adjusted for the lower excess energy. The agreement is very good, and from this we conclude that the energies used here did not correspond to any resonance states. The changes in the spectra in this case were attributable mainly to the PCI effect, and not to any changes in vibrational branching ratio. From this simulation we conclude that the PCI profile utilized here is valid even as the excess energy decreases, and that in ethane there are no apparent non-Franck-Condon effects in photoionization at 303 eV.

In ethylene, on the other hand, we find changes which are outside of the extent of the linear-coupling model. We made fits employing this model and found that the intensities of the lower-energy modes varied with photon energy. This is verified by simulating a spectrum by using the linear-coupling parameters from the 317-eV spectrum. The results of the simulation are shown in Fig. 5. The agreement between the simulated and the measured 298.5-eV spectrum is not good. This leads us to conclude that the linear-coupling model is not applicable to the spectra measured within the continuum resonance. Since the spectra are not fittable within this model

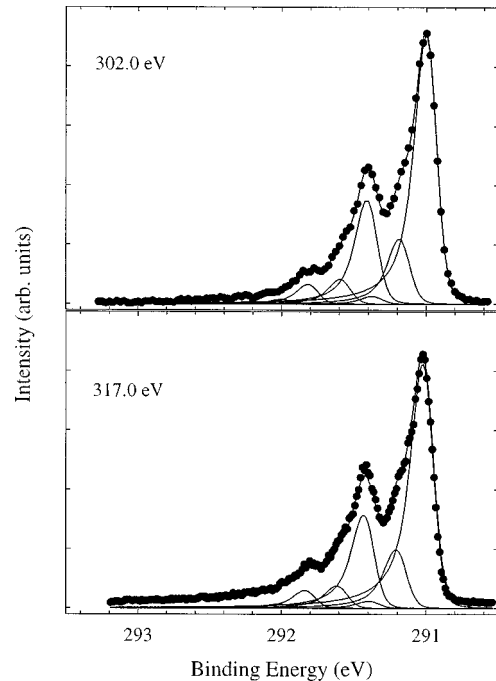


FIG. 4. (a) Fit to the ethane C 1s photoelectron spectrum measured at 317-eV photon energy. The fit was made for two vibrational modes, the C-H and the C-C normal stretch vibrations. (b) The intensity and vibrational-energy parameters from the fit to the 317-eV spectrum were used to simulate the 302-eV spectrum. The PCI asymmetry parameter was varied to account for the change in excess energy, the constant background parameter and the intensity of the adiabatic peak were adjusted. All other parameters are identical.

then we may conclude that ionization is non-Franck-Condon-like for the lower photon energies, especially 298.5 and 303 eV.

IV. DISCUSSION

Vibrationally resolved C 1s spectra have been reported in which the C-H stretch is clearly resolved [15,22]. A recent study based upon measurements at the Advanced Light Source reports measurements of ethylene C 1s spectra of slightly better resolution in which the lower-energy vibrational modes are resolved, and a simulation including three normal vibrational modes is presented [23]. In this study it is shown that the intensity of the H-C-H bending mode is about four times stronger than the C-C stretch modes. The vibrational energies and intensities reported in this work are in accord with the results of the fit to the 317-eV spectrum. Our study separately monitors the intensity variations of different principal normal vibrational modes in the region near threshold.

Because of the uncertainty in the relative intensity distribution between the H-C-H bending mode and the C-C stretch mode we treat these two modes together in the discussion of shape-resonance-induced effects. We combine the branching ratios for these low-energy modes and compare to the branching ratio for the C-H stretch mode. It should be noted that even with better resolution it would be very difficult to distinguish between these two modes, as is also pointed out in the work of Bozek *et al.* [23].

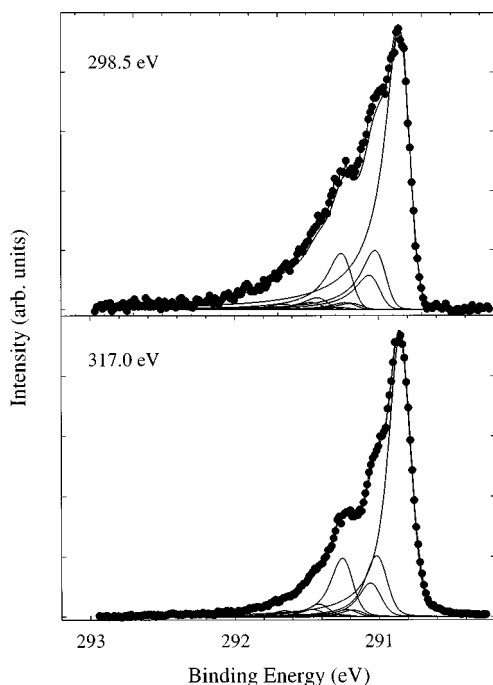


FIG. 5. (a) Fit to the ethylene C 1s photoelectron spectrum measured at 317-eV photon energy. The fit was made using three vibrational modes as discussed in the text. (b) The intensity and vibrational-energy parameters from the fit to the 317-eV spectrum were used to simulate the 298.5-eV spectrum. The PCI asymmetry parameter was varied to account for the change in excess energy. The background constant was altered to account for statistics, and the adiabatic intensity parameter was adjusted. All other parameters are identical.

The vibrational branching ratios, $I(\nu=1)/I(\nu=0)$, for the C-H stretch vibrational mode and the combined C-C and H-C-H normal modes are presented in Fig. 6. It is clear from this figure that the combined branching ratios for the C-C stretch and H-C-H bending vibrational modes are sensitive to the photon energy, while the C-H stretch vibrational branching ratios do not change appreciably [22]. These measurements thus strongly support the presence of a C-C shape resonance in the 300–310 photon-energy range.

Such behavior has been explained in the literature by using a single-particle scattering picture in which the scattering centers' distance and masses determine the effects of the continuum resonance on experimental observables [7,14]. One of the conclusions drawn from this model is that resonances associated with the C-C bond should exert a much greater influence on the corresponding vibrational process compared to those corresponding to other bonds. This arises from the smaller number of electrons on the hydrogen atoms relative to the carbon atoms.

Our study shows changes in the vibrational intensity distribution as a function of photon energy. These changes are not dramatic, but they are large enough that they cannot be accounted for solely by PCI effects by any uncertainties in the analysis model. The changes appear mainly in the low-energy vibrational modes whereas the higher-energy C-H

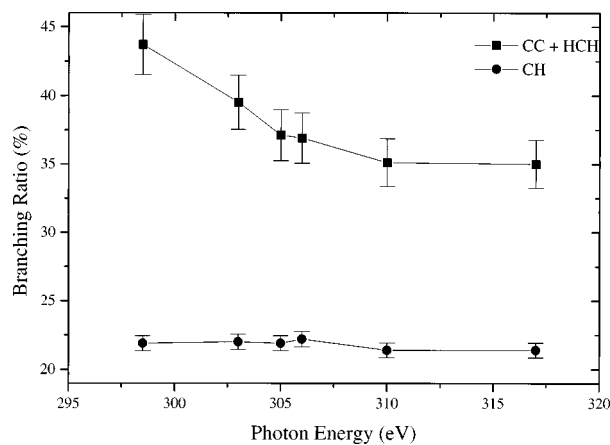


FIG. 6. The branching ratio C-H normal vibrational mode together with the branching ratio of the combined C-C and H-C-H normal vibrational modes in ethylene derived from the fits to photoelectron spectra. The data represent the intensity of the vibrational peak as a fraction of the intensity of the adiabatic peak. The errors in these values are estimated to be 5% from studies made in which the S factors were varied and the χ^2 was evaluated.

stretch vibrational mode is relatively unaffected by the continuum resonance.

V. CONCLUSIONS

High-resolution photoelectron spectroscopy has been applied to gas-phase ethylene using synchrotron radiation to tune the photon energy through the broad absorption resonance above the carbon K -shell ionization threshold. The different normal vibrational modes excited after core-electron ionization are revealed and monitored separately as a function of photon energy. We find that the vibrational manifold is not well reproduced in spectra measured within the resonance region using a linear-coupling model while outside of this region agreement is good. The results show that the C-H vibrational mode is not affected noticeably by the quasibound state while the partial vibrational cross section for modes involving the carbon atoms varies with photon energy. The existence of such changes clearly indicates the presence of a shape resonance. In addition, our results exhibit the weaker effect of a shape resonance on vibrational modes localized on the C-H bond in a polyatomic molecule when compared to the larger effect on C-C localized vibrations. This confirmation of the C-C shape resonance disagrees with the conclusions of Kempgens *et al.* [1], since it strongly supports the more general and widely accepted concept of a C-C related shape resonance in this photon-energy region.

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