

## Reappraisal of the Existence of Shape Resonances in the Series $C_2H_2$ , $C_2H_4$ , and $C_2H_6$

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(Received 28 January 1997)

We have measured the main line (single hole) C  $1s$  photoionization cross sections for  $C_2H_2$ ,  $C_2H_4$ , and  $C_2H_6$  in the immediate threshold region. These three molecules occupy a central place in the proposed correlation between shape resonance position and molecular geometry. We find no clearly identifiable shape resonances in the single hole cross sections of  $C_2H_4$  and  $C_2H_6$  and only weak evidence for one in  $C_2H_2$ . [S0031-9007(97)03487-X]

PACS numbers: 33.80.Eh

Following the work of Dehmer and others, e.g., [1–4], various shape resonances have been identified in the photoadsorption spectra of diatomic molecules. These occur in the continuum above the core level absorption threshold and are usually attributed to the resonant trapping of the emitted photoelectron due to the presence of a potential barrier. The latter results from centrifugal, repulsive forces which give rise to a concentric double well potential. An alternative view of this phenomenon [3,4] is to assign the resonances to virtual, antibonding ( $\sigma^*$ ) molecular orbitals (m.o.'s) in the continuum. The two descriptions are essentially equivalent, as has been discussed in several papers, e.g., [5]. Conforming with the notion that the energy of a shape resonance depends on the details of the molecular potential, Stöhr, Sette, Hitchcock, and others have suggested that there is a correlation between shape resonance position and bond length, even in polyatomic molecules [6–10]. Piancastelli *et al.* [11,12] later pointed out that, although such a “bond lengths with a ruler” [8] correlation might be expected (see, e.g., [13]), there were assignment problems in photoabsorption spectra and it was suggested that shape resonances should actually be sought in the corresponding main line, or single hole, cross sections. Such measurements for  $C_2H_4$  and  $C_6H_6$  using synchrotron radiation on a bending magnet beam line did not, however, give an unequivocal answer to this question [14].

The molecules ethyne, ethene, and ethane ( $C_2H_2$ ,  $C_2H_4$ , and  $C_2H_6$ , respectively) occupy a key role in this discussion [7,8,15,16], since there is also a marked variation in C-C bond length with which the apparent position of the shape resonance has been correlated [7,8] (Fig. 1). Moreover, according to the calculations of Farren *et al.* [17] the C-C  $\sigma^*$  resonance is expected to dominate the near-edge region. The C-H resonances, on the other hand, are expected to be weak in the core level excitation spectra. In this Letter we report the measurement of the C  $1s$  main line (single hole) cross sections for the three molecules in the near-threshold region.

Photoelectron spectra of the three molecules were measured on the X1B undulator beam line [18] at the Brookhaven NSLS x-ray storage ring. The kinetic energies of the emitted photoelectrons were determined

with a stationary, angle-resolving magic-angle cylindrical mirror analyzer (CMA), along the axis of which the incident radiation reaches the target region [19]. With this arrangement the total intensity, integrated over all angles around the axis, is independent of the angular distribution of the photoelectrons and the degree of light polarization, enabling partial cross sections to be determined. The angular asymmetry parameter  $\beta$  (not of relevance here) can also be determined by utilizing a specially designed

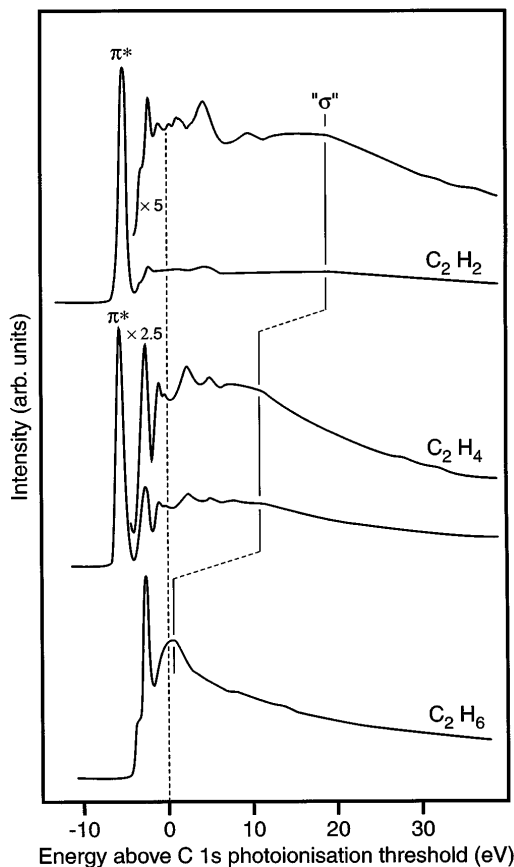


FIG. 1. Carbon  $K$ -edge absorption spectra of ethyne, ethene, and ethane measured with electron energy loss spectroscopy, showing the putative shape resonances and their apparent dependence on C-C bond length. From Hitchcock and Brion [16] and Sette *et al.* [7].

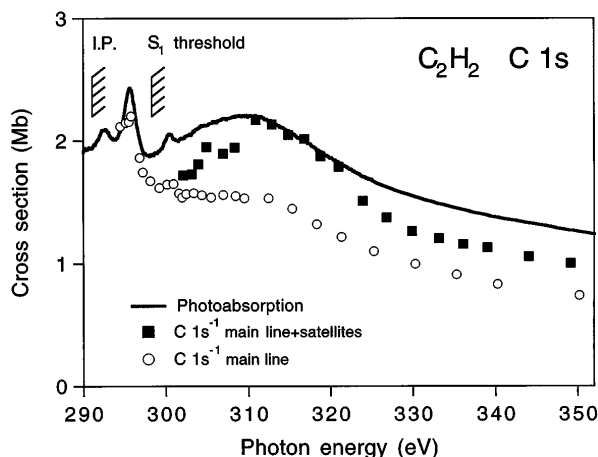


FIG. 2. The absolute photoabsorption cross section of ethyne above the C  $1s$  photoionization threshold as well as the C  $1s$  main line and main line + satellites photoionization cross sections.

eightfold symmetric spatially resolving detector [19]. Core level spectra of  $C_2H_2$ ,  $C_2H_4$ , and  $C_2H_6$  were measured for a range of photon energies above threshold both at high (100–120 meV) and low (200–250 meV) resolution, depending on whether just the C  $1s$  main line or the whole C  $1s$  region, i.e., including shakeup satellites, were included. All spectra were normalized to the intensity of the incident light by alternate measurement of the Ne  $2p$  spectrum at each photon energy [19]. Cross sections were determined by integrating the spectra appropriately and scaling vertically to the photoabsorption cross section. The corresponding photon energy at which the photoionization cross section curve “main line + satellites” coincides with the photoabsorption cross section should be—and is in all three cases—below the expected threshold for shakeoff excitations. (The contribution of valence photoionization to the photoabsorption cross section also has to be extrapolated from the value below the threshold and subtracted.) Absolute photoabsorption cross sections were determined in a separate experiment using an absorption cell, as described previously [20,21]. The possible scaling error in the determination of the absolute photoionization cross sections is estimated to be normally below 7%, but may be as high as 10% in the immediate threshold region.

Figure 2 shows the photoabsorption cross section of  $C_2H_2$  above the C  $K$ -shell excitation threshold. Apart from three relatively sharp peaks below 302 eV, the spectrum is dominated by a broad intense feature centered at  $\sim 310$  eV which has been attributed to a  $\sigma^*(C-C)$  shape resonance [7]. Also shown in the figure are the C  $1s$  main line photoionization cross section (open circles) and the C  $1s$  main line + satellites cross section (filled squares). Note that between the threshold for shakeup excitation and the threshold for shakeoff excitation the main line + satellites cross section corresponds to the C  $1s$  partial photoionization cross section. In the main line, or single hole, cross section the putative  $\sigma^*(C-C)$  feature

is drastically reduced in intensity, and its maximum is shifted by 1–2 eV to higher photon energy.

The three features at 292.4, 295.6, and 300.6 eV in the absorption curve have been assigned to double excitations [22] and the latter two are also clearly visible in the C  $1s$  main line cross section, indicating that decay occurs via autoionization. In such a process one of the excited electrons fills the valence hole while the other is emitted, leaving a C  $1s^{-1}$  state. Subsequently, the core hole is filled in a normal Auger transition. Such double participator transitions have already been observed in CO [23–25],  $CO_2$  [23],  $CH_4$  [26], and  $N_2$  [27]. The difference between the photoabsorption cross section and the two other curves above about 298 eV in Fig. 2 is, however, due to a competing mechanism, namely, resonant Auger transitions that directly fill the  $1s$  hole and do not contribute to the main line cross section. The main effect giving rise to the semblance of an intense shape resonance is a strong, broad feature in the C  $1s$  main line + satellites cross section which is not present in the main line cross section. This is due to the photon energy dependence of the shakeup satellites in the region above their respective thresholds. The total satellite intensity is  $\sim 30\%$  of that of the main line at a photon energy of 310 eV, but decreases to  $\sim 15\%$  at 350 eV: Conjugate enhancement of normal shakeup satellites as well as possible pure conjugate transitions occur in the threshold region [28]. Around 320 eV the C  $1s$  partial cross section deviates again from the absorption cross section, which we attribute to shakeoff processes that give no discrete structure in the photoelectron spectrum. Shigemasa *et al.* [29] have recently measured the angle-resolved ion fragment spectrum of  $C_2H_2$  accompanying C  $1s$  photoionization. Although they find some selection of axes along the direction of the  $\mathbf{E}$  vector around 310 eV, the molecular asymmetry parameter estimated from their curves is around 0.7—smaller than for CO and  $N_2$  [29,30]—with a maximum shifted to 312 eV, thus supporting our observation of a small increase in the energy of the feature in the main line cross section. In summary, the present results indicate that the strong, broad feature in the photoabsorption cross section of  $C_2H_2$  centered at  $\sim 310$  eV is largely due to satellite contributions.

The corresponding curves for  $C_2H_4$  are shown in Fig. 3. Since the structures in the photoabsorption curve are only partly reflected in the main line cross section, there is no built-in check on the correspondence of the photon energy scales in the two experiments. For this reason the Auger spectrum was measured simultaneously with each photoelectron spectrum and integrated to give an Auger yield curve (not shown). The sharp structure just above threshold in this curve was found to correspond exactly to that of the photoabsorption spectrum. Since the satellite spectrum of  $C_2H_4$  is generally weaker than that of  $C_2H_2$ , it is more difficult to obtain an accurate value for the main line + satellites cross section at the threshold of the strongest satellite, which in this case is  $S_0$ . We have thus included the ZEKE data of Medhurst *et al.* [31] which give

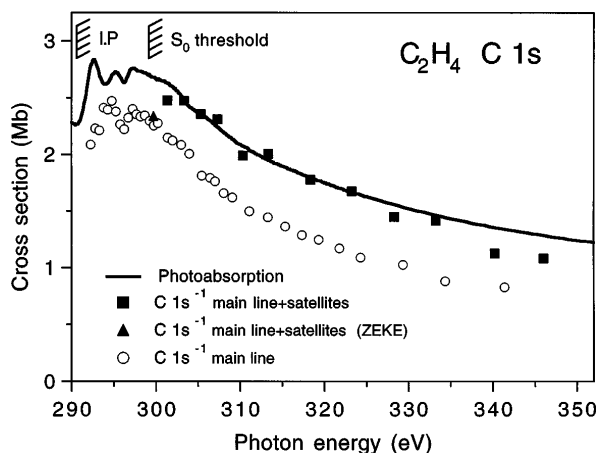


FIG. 3. The absolute photoabsorption cross section of ethene above the C 1s photoionization threshold as well as the C 1s main line and main line + satellites photoionization cross sections.

a combined intensity of 3.7 ( $\pm 0.6$ )% for the  $S_0$  and  $S_1$  satellites relative to the main line at 299.7 eV. This 3.7% has been added to the value of our main line cross section at 299.7 eV to give the filled triangle in Fig. 3. Unlike the situation in  $C_2H_2$  (Fig. 2), and in CO [23,24] and  $N_2$  [27], the first two double excitation resonances just above threshold in the photoabsorption curve are not reflected in the main line cross section (Fig. 3). They thus decay primarily via spectator resonant Auger transitions rather than by valence autoionization. The feature at  $\sim 295$  eV in the main line cross section is clearly an adjacent doubly excited state which is not visible in the photoabsorption curve but decays strongly via autoionization. The third sharp feature above threshold at 297.3 eV can be seen in both the photoabsorption and main line photoionization cross sections. More importantly for the present discussion is that, despite some scatter in the data points, the feature in the photoabsorption spectrum at  $\sim 300$  eV attributed by Stöhr and co-workers to the  $\sigma^*$  shape resonance is not visible in the main line cross section. The origin of this feature is most probably the increase of the intensity of the  $S_0$  satellite with its threshold at 299.2 eV. Whether a shape resonance is present in the immediate threshold region — as proposed by Arvanitis *et al.* [15] and predicted by the calculations of Farren *et al.* [17] — cannot be ascertained from the main line cross section. The calculations would put the shape resonance exactly at the position of the first sharp feature in the absorption spectrum which is not present in the single hole cross section.

Figure 4 shows the corresponding curves for  $C_2H_6$ . Again, an Auger yield curve was used to check the consistency of the two photon energy scales. The photoabsorption curve shows no pronounced features apart from the maximum just above threshold. A sharp feature at  $\sim 294$  eV and a broader one at  $\sim 298$  eV in the main line cross section are just discernible, giving evidence for double excitations decaying via autoionization. This indicates that the maximum just above threshold assigned

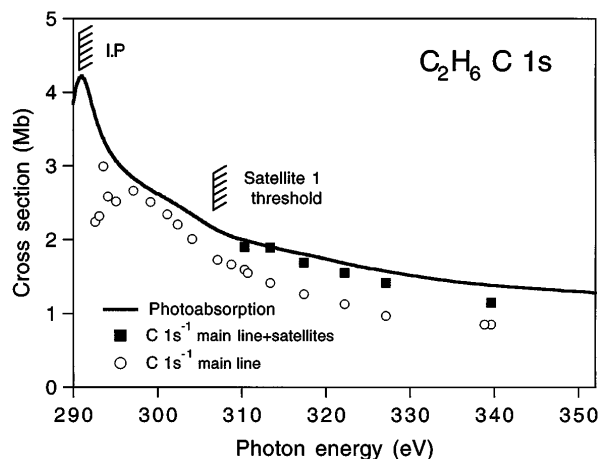


FIG. 4. The absolute photoabsorption cross section of ethane above the C 1s photoionization threshold as well as the C 1s main line and main line + satellites photoionization cross sections.

by Stöhr and co-workers to the  $\sigma^*$  shape resonance may be due to structure produced by doubly excited states decaying mostly via spectator resonant Auger transitions, although this cannot be definitely ascertained: At the point at which the determination of the photoionization cross section is no longer possible, the photoabsorption curve and the latter are divergent. An alternative explanation might be provided by the calculations of Farren *et al.* [17] who place the  $\sigma^*(C-C)$  resonance below threshold, but predict a weak  $\sigma^*(C-H)$  resonance just above.

In the case of CO and  $N_2$  the shape resonances above threshold are strongly reflected in the main line (single hole) cross sections [23,24,27]. Moreover, non-Franck-Condon behavior is observed: The branching ratios of the vibrational fine structure on the main line are markedly perturbed, an effect which is well known in valence level photoemission. In  $CH_4$  [24], on the other hand, a weak feature at  $\sim 303$  eV appearing in both the photoabsorption spectrum and the main line cross section does not influence the vibrational fine structure. Our preliminary analysis of the vibrational fine structures on the C 1s lines of  $C_2H_2$ ,  $C_2H_4$ , and  $C_2H_6$  does not indicate any perturbation of the vibrational lines either. This is particularly relevant for  $C_2H_2$  where the weak feature in the main line cross section may actually be due to a double excitation rather than to a shape resonance, as has been suggested for  $CH_4$  [26]. We should note, however, that Farren *et al.* actually predict a shape resonance, but at a few eV lower energy [17].

In recent years shape resonances have become quite important in surface physics: They have a defined symmetry dictated by the molecular point group and, for an oriented molecule, show a polarization dependence, i.e., the strength of the resonance depends on the angle of the  $\mathbf{E}$  vector of the incident radiation relative to a symmetry element of the molecule. Thus the orientation of the molecule of the surface can be determined [32]; the same is true for the polarization dependence of the corresponding bound resonances below the threshold. Since

photoabsorption features above threshold are frequently assigned to shape resonances, this approach to surface structure determination may also have to be reconsidered if there are problems of identification.

In summary, from measurements of the single hole cross section we are forced to conclude that there are no readily identifiable shape resonances in  $C_2H_4$  and  $C_2H_6$ . The weak, broad feature in the main line cross section of  $C_2H_2$  at  $\sim 312$  eV may be a shape resonance and is predicted as such by theory [17], but there is no conclusive experimental evidence for this. Recent preliminary studies on benzene ( $C_6H_6$ ) also indicate that the two strong features attributed to  $\sigma^*(C-C)$  shape resonances in the photoabsorption spectrum are very weak, if not absent, in the main line cross section [28]. The significance of these results lies in the central role played by hydrocarbon molecules in the bond lengths with a ruler correlation, a concept which at least in its original form [8] appears to be questionable.

We thank J. Feldhaus for very useful discussions and gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft. The National Synchrotron Light Source is supported by the U.S. Department of Energy under Contract No. DE-AC02-78CH00016.

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