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CORRELATION BETWEEN SHAPE RESONANCE ENERGIES AND C-C BOND LENGTH
IN CARBON-CONTAINING MOLECULES: ELASTIC ELECTRON SCATTERING AND
CARBON K-SHELL EXCITATION BY PHOTONS

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ABSTRACT

We document the correlation of shape resonance energies resulting from (i) elastic electron scattering and (ii) carbon K-shell excitation with π bond order (C-C bond length) for C_2H_2 , C_2H_4 , C_2H_6 , C_3H_8 , C_4H_{10} , and C_6H_6 . A relationship between K-shell σ resonances and bond length was experimentally pointed out previously. These correlations are qualitatively interpreted to indicate that as molecular size increases (or as bond length increases), the configuration space available for valence electrons increases, reducing energy levels rather uniformly and allowing these correlations to emerge. The similarity of shape resonances in electron scattering and photoexcitation occurs because major events in the resonances take place slightly outside the molecular field and receive little influence from the inner structure of the molecule.

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Similarities in shape resonances observed in molecular photoionization and electron-molecule scattering were first pointed out by Dehmer and Dill [1,2], who studied these relations thoroughly for some molecules. These authors also noted the sensitive dependence of shape resonance on internuclear separation. Experimental attempts to quantify these similarities used electron transmission spectroscopy and inner shell electron energy loss spectroscopy or X-ray absorption spectroscopy [3,4]. Sette *et al.* [5] systematically studied K-shell excitation for a variety of molecules and empirically derived a linear relationship between the energy of the K-shell shape resonances and the bond length.

In this report, we present a theoretical result illustrating that shape resonances arising from (i) momentum transfer by electron scattering and (ii) carbon K-shell excitation by X-ray absorption are indeed similarly correlated, directly with the π -bond order and inversely with the C-C bond length. The π bond order (or bond length) is a rough measure of charge distribution between a-b bonding and reflects specific characteristics of each molecule.

In a previous study [6], we showed a clear correlation between the carbon X-ray emission rate in carbon-containing molecules and their π -bond order (the inverse of C-C bond length) for C_2H_2 , C_2H_4 , and C_2H_6 (i.e., a chemical effect). This correlation was interpreted to represent the effective overlap between a carbon 1s hole state and π valence orbitals. This overlap decreases as the π bond order increases (or as the C-C bond length decreases), causing the X-ray emission rate to decrease nearly linearly. On the other hand, the Auger rate has a close relation with valence electron density because two-electron correlation is an essential part of the process, as Larkins showed [7,8]. Since neither theory [1,2] nor experiment [5] addresses the correlations, specifically those mentioned above, we extended the study to search for similar correlations for other physical quantities for these carbon-containing molecules and to provide a theoretical interpretation and rationale for the measured relationship [5].

Briefly, the theoretical approach used the continuum multiple scattering (CMS) method [9,10] to study electron scattering and the multiple scattering method [11] to obtain

molecular wavefunctions and hence to evaluate the coupling matrix element within the dipole approximation. Nuclear motions were approximated as if the nuclei were clumped at equilibrium positions. The present approaches for calculating molecular structure do not offer high precision for absolute energies, but they provide sufficient precision to obtain relative values for the present discussion.

Calculated positions of shape resonances found in electron scattering and X-ray absorption are plotted in Figs. 1 and 2, respectively. For electron scattering, the resonances depicted are those found at the lowest energies; resonances shown for X-ray absorption are σ resonances. The resonance positions in both cases clearly show a correlation with C-C bond length (or π bond order). The shape resonances in the momentum transfer cross sections for C_3H_8 and C_4H_{10} are nearly zero and are not included. Perhaps because the range of C-C distances varies by only 22% and is very narrow, the relation appears to be linear. We can offer no theoretical explanation for the linearity. As Dehmer and Dill pointed out [1,2], these two types of shape resonances have no connection at first glance. However, since a short-range force is dominant in both processes, the shape resonances thus observed are localized within the molecular space and thus preserve their characteristics from one system to another, producing the similarities. We will discuss the underlying physics of these resonances separately.

Electron Scattering

If a molecule has an energetically accessible, unoccupied orbital associated with its centrifugal potential, then an incident electron with matching orbital symmetry can be temporarily trapped in this vacant orbital. Such an orbital normally lies near the ionization threshold.

For C_2H_2 and C_2H_4 , the lowest unoccupied molecular orbital (LUMO) has π^* character, while that of C_2H_6 has σ^* character, with the major charge distribution lying near the two carbon nuclei. These features suggest that a relatively strong shape resonance

through the π^* LUMO, which has little influence from the nuclei, can be expected for C_2H_2 and C_2H_4 . A weaker shape resonance through the σ^* LUMO, which is more localized than its π^* counterpart, can be expected for C_2H_6 . As the number of π electrons increases, the π bond order increases, and the C-C bond length decreases (or, in other words, the molecular size decreases), pushing the π orbitals toward higher energy. The same arguments hold for C_3H_8 and C_4H_{10} ; the energy levels become lower as the bond length decreases. C_6H_6 has a slightly smaller value than C_2H_4 for the π bond order, and the position of the resonance is close to that for C_2H_4 . These energies are in good agreement with measurements and other theoretical results [12].

K-Shell Photoexcitation

An electron, originally occupying the 1s core orbital in one of the carbon atoms, absorbs a photon and is excited to an empty σ molecular orbital embedded in the continuum, giving rise to the σ shape resonance. As the π bond order decreases or the C-C bond length increases (as the molecular size increases), the charge distribution is more concentrated in σ orbitals near the nuclei, reducing the σ energy levels. This feature, similar to electron scattering, gives rise to a trend of decreasing resonance energy as the bond length increases, as is seen in Fig. 2. The carbon 1s orbital energies in these molecules are nearly the same for all of the molecules studied (within 290.5 ± 0.5 eV). These energies are slightly larger than that of the pure C atom (283.8 eV). These energy levels, reveal no sizable molecular effect in the core orbital. However, as the C-C distance in the present calculation increases from C_2H_2 to C_2H_4 and C_2H_6 , resonance energies decrease from 303 eV (or 11.9 eV from the ionization potential) to 297 eV (or 6.2 eV) and 291 eV (or 0.3 eV). (All of these values are slightly smaller than those observed by Sette *et al.* [5].)

This decrease in the resonance energy is a manifestation of a molecular effect and is a characteristic signature for each molecule. As the bond length increases (or the molecular size increases), the valence orbital energy levels shift toward lower energies rather

systematically. Because these resonances in electron scattering and photoexcitation have similar dynamics, a trend observed in one process is likely to be seen in another process.

In the present study, the ratios of the shape resonance positions for C_2H_2/C_2H_4 are 1.6 and 1.8 for photoabsorption and electron scattering, respectively, and those for C_2H_4/C_2H_6 are 20 and 18 for photoabsorption and electron scattering, respectively. These two sets of the ratio agree surprisingly well. This observation clearly suggests that both resonances are well localized outside the space of the molecular field and reasonably far from the central core and most of the valence electron distribution. A resonance electron in this configuration receives little influence from the inner structure of the molecule and, hence, from the scattering potential, contributing to the similarity of the ratios for shape resonance positions. Thus, as the molecular size (or bond length) increases, overall orbital energy levels decrease, reducing resonance energies and increasing the correlation between the shape resonance positions and the molecular size (bond length). In contrast, an event that involves a good part of the inner structure of a molecule is more complex and may not be describable with the kind of simple relation seen here.

The two correlations discussed here manifest themselves as a chemical effect. They are important for providing sound guidelines for further assignments of the near-edge structures observed experimentally.

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Figure Captions

Fig. 1. Resonance positions in momentum transfer cross sections versus C-C bond length.

Fig. 2. Resonance positions in K-shell excitation (measured from the ionization threshold) versus C-C bond length.

Fig. 1

Fig. 2

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