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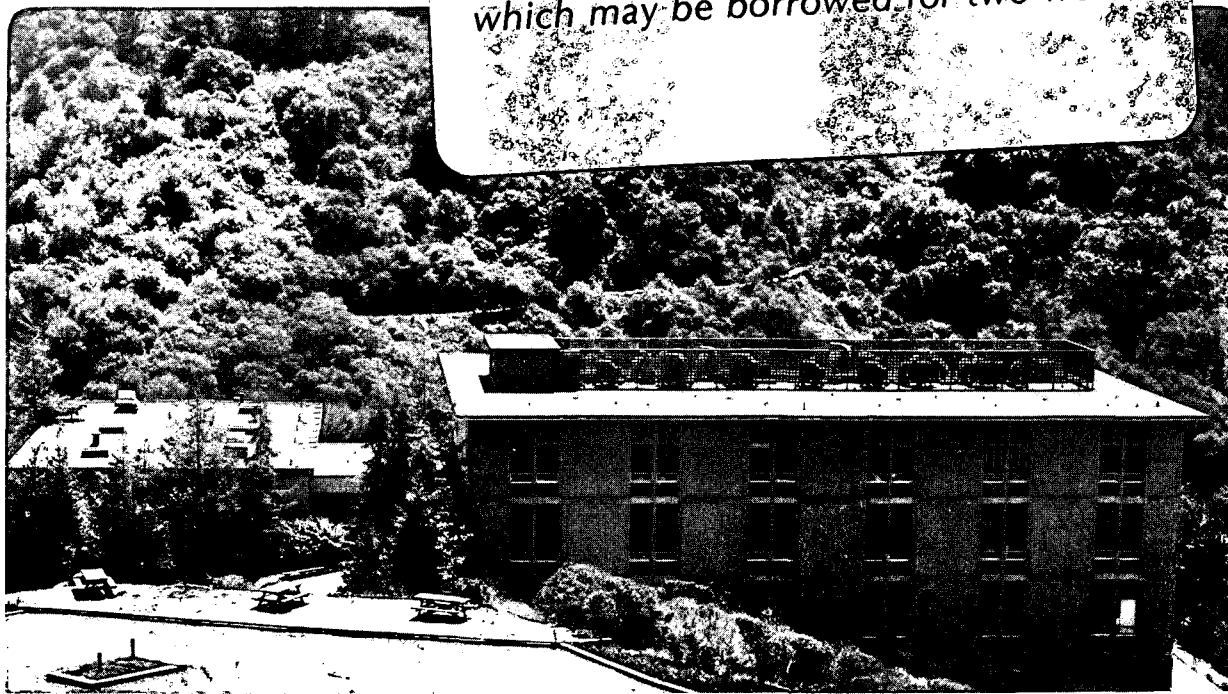
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Reply to Comment on

"The Relationship Between Shape Resonances and Bond Lengths"

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Hitchcock and Stöhr¹ concur with Piancastelli et al.² on three principles relating to the identification of core-level shape resonances: (1) study of the decay channel(s) is of great value; (2) other processes can contribute to the spectral response; and (3) theory is an excellent means of supporting spectral assignments. As a result, the two viewpoints differ only on the rigor with which these principles need be applied. We will return to this point at the end of our Response.

It is well-known that shape-resonance energies and bond lengths are related within a given molecule. Dehmer et al.³ identified a trend for N₂, and Swanson et al.⁴ did so for CO₂. Further, for the isostructural series CCl₄, SiCl₄, GeCl₄, a trend was observed in the apparent shape-resonance energy.⁵ Given these specific successes, it would be very valuable to identify and quantify more general trends over a wider range of molecules. In particular, if quantitative relationships were established between shape-resonance energy δ and bond length R, and if these relationships were still valid when the molecular environment was changed (e.g., by adsorption), then measurement of δ clearly would constitute a convenient measure of R.

Indeed, we are predisposed to expect at least qualitative success along this line because of the impressive and growing evidence that; (1) near-edge x-ray absorption fine structure (NEXAFS) can provide a characteristic "fingerprint" of a molecule's structure, and (2) at least some features of a molecule's NEXAFS spectrum are relatively insensitive to its environment. These two characteristics, plus its orientational sensitivity, establish NEXAFS as a very powerful spectroscopic technique for studying adsorbate (and free) molecules, irrespective of the δ -R relationship.

To establish a general quantitative δ -R relation requires that values of δ be compiled for some candidate group of molecules and compared with known values of R. This first step can be carried out with or without a detailed theoretical understanding of the δ -R relationship. Both groups of investigators have attempted this comparison, reaching quite different conclusions, as discussed below.

While some of the shape-resonance assignments presented by Stöhr, Hitchcock, and co-workers in attempting to establish δ -R relationships are convincing, we believe that many are not. In most cases, loss-spectrum features assigned⁶ as " σ shape resonances" are weak and/or broad and/or possibly due to other processes.⁷ No objective criteria are provided for selecting these features. For example, the above comments apply to the "C-C bond" in C_2H_4 and C_2H_6 (ref. 6, Fig. 2), to the C-H, N-H, and O-H bonds (Ref. 6, Fig. 5), and to the "C=C" bonds in C_n olefins (Ref. 8, Fig. 3), as well as many of the other molecules used in the δ -R correlations of Ref. 6 (see Ref. 2 for details).

At a more basic level, excited and quasibound states of a molecule are expected to possess symmetry corresponding to that of the molecule.

Hitchcock, Stöhr, and co-workers appear to assume that, even in polyatomics, bonds localized between just two atoms are responsible for shape resonances, and that their excitation energies are dependent only on the length of that individual bond. In our opinion this picture is incorrect by symmetry arguments alone. The burden of proof falls on the model's advocates to show that a quantitative δ -R relationship should somehow nevertheless be present.⁹

Reliance on the empirical parameter $Z = Z_A + Z_B$ to obtain satisfactory δ -R correlations for the hypothesized A-B shape resonance is essential, as Hitchcock and Stöhr emphasize; but is it justified to parameterize the effect of the molecular potential with this particular single parameter? Furthermore, Hitchcock and Stöhr incorrectly state that we ignore the ion-core potential. In fact, we clearly noted the importance of the effect of the different ionic potentials resulting from K-shell ionization of different-Z atoms in a single molecule. Even in the prototypical case of CO, the shape-resonance energy at the C K-edge is shifted relative to the resonance energy at the O K-edge.^{2,10} This is a typical result for molecules containing different-Z atoms (see Table I, Ref. 6).

Another especially troublesome feature of the proposed correlation is its failure within small groups of closely related compounds. In Ref. 6, Fig. 6, the "C=O bond" δ values for H_2CO , CH_3HCO , and $(\text{CH}_3)_2\text{CO}$ defy the proposed $Z=14$ trend by exhibiting a 40% range of δ values for essentially the same bond length R . In addition, the fluoromethanes, which have different bond lengths (1.32 - 1.38 Å), show a more-or-less constant (and negative value of) δ for the series. Difficulties such as these need to be understood before significant progress in δ - R correlations can be made.

Hitchcock and Stöhr¹ emphasize the need to exclude molecules such as CO_2 , which they describe as "anomalous," to improve the δ - R correlation. We concur that this additional qualification is necessary within their framework, but we disagree that it is justified since no clear objective criteria are provided for identifying anomalous molecules. In fact, CO_2 is one of only a few cases that appears to be understood, and without good justification should not be excluded at this time.

Hitchcock and Stöhr¹ also emphasize the need to include below-threshold resonances to arrive at useful δ - R correlations. While it is certainly true^{1,2} that discrete resonances may be associated with shape-resonance phenomena, it is not clear^{2,7} that below-threshold resonances are suitable for ascertaining a δ - R relationship (e.g., the fluoromethanes). In retrospect, we may find that inclusion of discrete excitations may be warranted, but much further experimental and theoretical work is required to justify a relationship between bound-state energies and bond lengths.

Before concluding, we return to the three points listed at the beginning of this Response upon which both groups concur. These points, if applied cautiously, could indeed lead us to a stringently tested shape-resonance energy-bond length relationship. Unfortunately, for most of the molecules included in the analysis of Ref. 6, these points have not been considered. While it is true, as Hitchcock and Stöhr assert,¹ that this restrictive framework requires difficult experiments and calculations, we believe it is essential for the development of an accurate δ -R correlation.

In summary, we believe that the δ -R correlation is potentially very valuable. To realize this potential and become generally accepted, the hypothesis must be refined through criticism and response. This process is underway. Clearly we disagree with Hitchcock and Stöhr on several issues, but there are also areas of agreement. To emphasize these, we finish by restating their characterization of our position:

- (1) We do not argue that there is no experimental evidence for the claimed correlation, just that available evidence is not yet totally convincing.
- (2) The "basic theoretical and physical objections" apply only to an oversimplified model, as discussed thoroughly in Ref. 2. In any case, the burden of proof of a controversial hypothesis lies with its advocates.

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