

correlation function" for the resulting stable arrangement of the 1000 sulfur atoms. Its first peak is very narrow and entirely isolated from all remaining pairs. Specifically, no atom pairs whatsoever are found in the interval between 2.36 and 3.03 Å which lies between the first and second peaks. The sharp first peak incorporates precisely and unambiguously 874 covalent bonds. These bonds connect the atoms into a variety of chain, ring, and branched structures ranging in size from S_2 to S_{30} . Figure 2 shows the size distributions for these fragment types in the potential minimum obtained.

The stable low-temperature form of sulfur involves S_8 rings, and that property is reproduced by our model.³ The deepest potential minima therefore would display 1000 covalent bonds. That only 874 exist in the packing created in our test indicates that a rather high-lying relative minimum is involved. We estimate that it is located approximately 0.16 eV/atom above the absolute minimum.

The steepest-descent mapping protocol for identifying molecular species clearly passes the extreme test imposed. Consequently we believe as a general procedure it has wide theoretical applicability beyond the specific case of sulfur. As another example (again with pair and triplet potentials) it should be possible to model dense-phase reactions of I_2 and

Cl_2 to form ICl , the rates and chemical equilibria for which should be accessible through molecular dynamics simulation. At high temperature and pressure it would be unclear from low-order atomic distribution functions how many reactant and product species were present, until steepest-descent reduction to potential minima removed the ambiguity.

Likewise, it would be instructive to apply this method to simulations of ion pairing equilibria in aqueous electrolytes, and of proton transfer reactions (acid-base association, dissociation, and neutralization), provided suitable model potentials for these cases were available. In each of these cases as well, it is unlikely that conventional atomic distribution functions could unambiguously provide the relevant species concentrations.

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COMMENTS

K-shell shape resonances and intramolecular bond lengths. Comments on "The relationship between shape resonances and bond lengths"

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(Received 27 January 1987; accepted 18 May 1987)

The relationship between $1s \rightarrow \sigma^*$ excitation energies and bond lengths to atoms adjacent to the core excited atom has received considerable attention recently.¹⁻⁵ We have demonstrated^{3,4} that features observed both above and below the I.P. in the core spectra of numerous molecules occur at positions consistent with the molecular structure according to a correlation involving bond lengths and atomic numbers. Recently Piancastelli *et al.*⁵ have argued that: (1) there is no experiment evidence to support the claimed correlation and (2) there are basic theoretical and physical objections to the existence of such a correlation. In this letter we comment on their treatment, which in our opinion does not lead to the claimed conclusions.

Many of the general points discussed by Piancastelli *et al.*⁵ are valid and valuable contributions to the developing understanding of core excitation in covalent molecules. In

particular: (1) studies of the decay, as well as the excitation, are of great value in deriving spectral assignments; (2) other processes (two-electron excitations, shakeup continua) can give signal in the same spectral region as $1s \rightarrow \sigma^*$ transitions; and (3) theoretical calculations are an excellent means of supporting spectral assignments. However, the assumptions that Piancastelli *et al.*⁵ use in making their conclusions are such that they are discussing a possible correlation very different from that presented.¹⁻⁴

Firstly, they exclude large sections of the data base either because the features occur below the I.P. or because the features have not been sufficiently well characterized, according to their criteria for a "shape resonance." It is true that shape resonances are generally understood to be continuum phenomena. However, the term is used frequently⁶ to describe features both above and below the I. P. in order to

indicate a common origin of the intensity in terms of localization of a virtual orbital by a potential barrier. There is a close connection between discrete K shell excitation resonances and continuum shape resonances in electron-molecule scattering. Thus we consider $1s \rightarrow \sigma^*$ excitation energies in a similar fashion, regardless of whether they occur above or below the $1s$ ionization threshold. Secondly, they include the data for CO_2 , a molecule whose anomalous character had already been noted.⁴ The fact that anomalous molecules had been recognized already and purposefully excluded was not acknowledged. It is true that within this changed framework the experimental evidence available for the correlation becomes unconvincing. Thirdly, Piancastelli *et al.*⁵ attempt to construct a correlation very different from that presented by us.¹⁻⁴ They ignore, without apparent justification, a factor that was found to be *essential*^{1,4} to obtain a satisfactory correlation, namely the effect of the ion core potential. This has been accounted for^{1,4} by grouping the data into classes defined by the parameter Z , the sum of the atomic numbers of the core excited, and bond-length-connected atoms.

Although valuable, the criteria suggested by Piancastelli *et al.*⁵ for the existence of a σ shape resonance require a variety of difficult measurements and state-of-the-art calculations. In view of the sparsity of such information we chose to search for general trends in the available K -shell excitation data. In our original work²⁻⁴ we examined the spectra of 28 simple molecules and predicted a general correlation linking $1s \rightarrow \sigma^*$ energies to *both* the intramolecular bond length and the sum of atomic numbers of the bonded atoms. In some cases the σ^* resonances were attributed to spectral features that had either been unassigned (e.g., C_2H_6 ³) or differently assigned. Based on our spectral interpretations, the data for all but four molecules closely follow the derived correlation. While Piancastelli *et al.*'s critique⁵ largely hinges on the exceptional case of CO_2 , we draw attention to the remarkable success of our correlation in explaining not only the originally presented data but also a large set of: (i) new gas phase data of simple and complex molecules; (ii) near-edge x-ray absorption fine structure (NEXAFS) data of condensed and chemisorbed molecules; and (iii) energy loss and NEXAFS data of polymers.

Over the past two years systematic studies of the core excitation spectra of over 80 molecules⁷⁻¹⁴ have shown that in the vast majority of cases major features in the near edge region can be interpreted as $1s \rightarrow \sigma^*$ transitions with the aid of the correlation and the molecular geometry. Better characterization of these spectral features by photoemission studies and by calculations is certainly desirable. The level of consistency with the δ - R correlation over such a large data set suggests that it is a very useful empirical device for spectral assignment. The assignments of resonances in gas phase K -shell spectra are confirmed and complemented by studies of condensed and chemisorbed molecules on metal and semiconductor surfaces. Over the last five years approximately 35 different molecules have been investigated by polarization-dependent NEXAFS spectroscopy.¹⁵ The preferential orientation of molecules relative to the surface leads to a pronounced angular dependence as the electric field vector of the polarized x-ray beam is aligned along different direc-

tions of the oriented molecule. Dipole selection rules and the polarization dependence provide symmetry labeling and often allow unambiguous spectral assignments. Studies of the same molecule on different surfaces provide direct evidence that the σ resonance position is a sensitive measure of the intramolecular bond length.^{16,17} Finally, recent NEXAFS studies reveal that the spectra of complex polymers,¹⁸ which consist of a superposition of π and σ resonances characteristic of the various functional groups of the polymer, are consistent with our originally established correlation.²⁻⁴

The exceptions to the correlation give insight into its physical basis and limitations. In general, the identified deviations take the form of multiple $1s \rightarrow \sigma^*$ features in the core spectra of molecules which contain two or more bonds of the same length and type. The simple correlation between $1s \rightarrow \sigma^*$ energy and bond length proposed by us assumes that a given bond gives rise to only one σ^* resonance. This assumption fails for molecules where conjugation or delocalization occur. For example, the K -shell spectrum of benzene, which has been extensively analyzed both experimentally and theoretically,¹⁹ contains more than one σ^* resonance. Other examples include CO_2 ,²⁰ allene, $\text{CH}_2 = \text{C} = \text{CH}_2$,²¹ and other aromatics.^{10,12,19} These spectra exhibit multiple $1s \rightarrow \sigma^*$ transitions where the σ^* levels are delocalized over several bonds.

CO_2 is particularly notable since the σ^* resonances in both the $\text{Cl}1s$ and $\text{O}1s$ spectra²⁰ deviate greatly from the trends established by the spectra of other molecules. Calculations of $\text{O}1s$ ionization,²² low energy electron scattering,²³ and valence photoemission²⁴ indicate that the σ_g^* and σ_u^* levels are separated by ~ 16 eV. Excitations from $\text{O}1s$ to both σ^* levels are observed (the existence of the weak $\text{O}1s \rightarrow \sigma_g^*$ transition is confirmed by calculation,²²) whereas only the $\text{Cl}1s \rightarrow \sigma_u^*$ transition is observed, consistent with the dipole forbidden character of the $\text{Cl}1s \rightarrow \sigma_g^*$ transition. *The average energy of the two $\text{O}1s \rightarrow \sigma^*$ transitions in CO_2 ($\delta_{\text{av}} = 9.2$ eV) is, in fact, in very good agreement with the predicted position ($\delta = 8.4$ eV) based on the CO bond length ($R = 1.16$ Å) and the $Z = 14$ correlation line.*⁴ This splitting into two levels about a mean position in agreement with the correlation is exactly the situation found in benzene¹⁹ and other aromatics.^{10,12,19} Large energy splittings associated with delocalization of the σ^* levels appear to occur to the greatest extent in rigid molecules which contain conjugated or delocalized bonds.²⁴ They do not occur in long chain or branched alkanes¹¹ whose $\text{Cl}1s$ spectra exhibit only one principal feature above the I.P., at a position consistent with the correlation. MO treatments of polyatomic molecules predict delocalized σ^* orbitals and thus there is no obvious reason for a simple relation between σ^* energies and the lengths of individual bonds. However, our experimental observations indicate that the number of cases in which the localized bond length correlation is successful, even for complex molecules, greatly exceeds the cases where delocalization produces a strong modification from that predicted by the bond length correlation. In the latter cases average energies of multiple σ^* resonances match the simple correlation.

In summary, the negative comments of Piancastelli *et al.*⁵ regarding the existence of the correlation only apply

within their very restrictive framework. We emphasize the importance of both R and Z as correlation parameters as well as the continuity of the correlation in describing spectral features observed both above and below the I.P. There is clearly a need for theoretical investigation of the physical basis of the observed strong, systematic relationship between $1s \rightarrow \sigma^*$ energies and bond lengths.

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Reply to the "Comment on 'The relationship between shape resonances and bond lengths' "

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(Received 8 April 1987; accepted 18 May 1987)

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 N_2 and Swanson *et al.*⁴ did so for CO_2 . Further, for the isostructural series CCl_4 , $SiCl_4$, and $GeCl_4$ 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 dif-