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THE RELATIONSHIP BETWEEN SHAPE RESONANCES AND
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The Relationship Between Shape Resonances and Bond Lengths

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A discussion is presented on the general nature of shape resonances in small molecules and how they may relate to molecular bond lengths. Criteria for assigning photoabsorption features as shape resonances are described, and the usefulness of photoemission experiments to such assignments is highlighted. Based on these criteria, all unambiguously identified K-shell shape-resonance features in molecules containing B, C, N, O, and F are examined in an attempt to identify empirically a shape-resonance energy/bond length relationship. Although the available data are insufficient to establish a quantitative correlation, they indicate the influence of other variables besides the bond length to the energy position of a shape resonance.

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I. INTRODUCTION

Molecular shape resonances are relatively common one-electron phenomena in small molecules containing low-Z elements, where they are usually observed as broad continuum resonances in the photoabsorption or photoionization cross section within a few eV of the ionization threshold.[1-4] This resonant enhancement has been ascribed[1-3] to the trapping of the outgoing photoelectron by a potential barrier, through which the electron eventually tunnels and emerges in the continuum. In this qualitative picture, emphasis is placed on the molecular potential and the attractive (mostly Coulombic) and repulsive (centrifugal, electron screening) forces whose interplay determines the details of the potential.[2,3] A second model,[4] which highlights the chemical aspects of shape resonances, relates them to (virtual) unoccupied valence molecular orbitals. Both of these qualitative pictures account adequately for shape-resonance phenomena, and their essential similarities have been noted.[5] In the discussion which follows, we will use primarily the potential-barrier description, because it is better suited for discussing the shape resonance/bond length relationship.

In the particular case of molecular K-shell shape resonances, in which the initial state is well-localized, shape-resonant effects have been described as probes of the details of the molecular electrostatic potential.[2,6] It is also interesting to ask what other molecular properties might be determinable using K-shell shape resonances as a "fingerprint" of the molecule. For example, one important and highly successful application of shape-resonance studies has yielded

information about the orientation of adsorbate molecules on crystal surfaces by measuring the polarization dependence of shape-resonance excitations.[7]

Another important candidate molecular property about which shape-resonance studies may yield information is bond length.[8-11] If a quantitative relationship between shape-resonance energies and bond lengths could be determined, a powerful analytical tool would be at our disposal. Such a relationship could be applied to molecules in different environments[12] (such as surface adsorbates) or to systems with unknown bond lengths. Furthermore, because of the resonant nature (i.e. higher cross section) of the process, bond-length determination in this manner probably would be competitive with other techniques such as extended X-ray absorption fine structure (EXAFS). Because of the obvious desirability of a quantitative shape-resonance energy/bond length relationship, and because K-shell shape resonances have recently received increased experimental and theoretical attention, this work addresses the aspects involved in an empirical determination of such a relationship. Because most of the previous work on shape resonances has dealt with small molecules containing B, C, N, O, and F, we will focus on these K shells.

As a step toward determining a shape-resonance energy/bond length correlation, the purpose of this paper is to suggest necessary and sufficient criteria for interpreting observed spectral features in photoabsorption and photoemission as shape resonances, and to apply these newly established criteria to available data. Based on our analysis, we find insufficient evidence to establish quantitative trends

between shape-resonance energies and bond lengths among widely different molecules. Although a qualitative link between shape-resonance energies and bond lengths has been established in a few well-defined cases,[13-15] the quantitative connection is complicated because the resonance energies depend on many parameters, and most generally on the complex molecular potential.[2-4,6]

We begin in Sec. II with a description of the nature of shape resonances, including a discussion of an atomic-scattering picture[16] of shape resonances (similar to EXAFS) that theoretically yields a direct quantitative relationship between shape-resonance energies and bond lengths. A presentation of criteria for assigning shape resonances to spectroscopic features is given in Sec. III. Section IV contains a discussion of the relationship between shape-resonance energies and bond distances and an examination of the data which meet the criteria established in Sec. III. Conclusions are presented in Sec. V.

II. DESCRIPTION OF SHAPE RESONANCES

A shape resonance can be described as a one-electron continuum-state phenomenon in which the photoelectron is resonantly trapped by a potential barrier through which it eventually tunnels.[1-3] The barrier is presumed to arise from the sensitive interaction of the Coulomb, screening, and centrifugal forces acting on the ionized electron in the vicinity of the molecule.[2] Furthermore, the forces combine to produce shape-resonance effects (i.e. a potential barrier) only under special circumstances of a particular symmetry and angular momentum for the continuum channel. If a barrier does occur, it resides on the perimeter of the molecule,[2] because that is where the attractive and repulsive forces are most nearly equal. The result is a relatively weak anisotropic barrier, guaranteeing that shape resonances will occur only at low energy near threshold and will depend sensitively on the details of the molecular potential throughout the molecule.

According to the above description, the photoelectron kinetic energy at which shape resonances occur clearly will depend to a large extent on the shape, height, and width of the potential barrier, as seen in even the simplest case of a square-barrier potential.[17] In fact, the details of the potential should reflect even subtle changes in electronic configuration, molecular geometry, chemical environment, etc. Therefore, a complete description of shape-resonance energies in terms of molecular bond distances must account for the complicated molecular potential.

Unfortunately, a simple quantitative description of shape
resonances in terms of molecular structure in not available for several
reasons.[18] This has several important implications for our search for a
shape-resonance energy/bond length correlation. To begin with, the
kinetic energy at which the photoelectron experiences a shape resonance
is quite small (~30 eV or less), allowing the molecular valence
electrons to interact strongly with the continuum electron, because both
have approximately the same energy. One result of this interaction is
that the photoelectron is generally sensitive to the details of the
molecular potential, because these details reflect the presence of
screening and other effects due to the valence electrons.[2,3] Such
effects have been observed even within simple Hartree-Slater
calculations for atoms.[19] Secondly, while the kinetic energy of a shape
resonance depends strongly on the shape of the potential, the dependence
of the potential-barrier parameters on bond length is not well-
understood. For example, the width of the barrier is not described
easily in terms of a bond distance, but is expected to play an important
role in the resonant process (e.g. the case of a square-barrier
potential[17]). Thirdly, the shape of the potential must also depend on
other molecular parameters besides bond length, such as the chemical
environment (e.g. molecular symmetry, electronegativity of the atoms in
the molecule, etc.), and the core-hole depth (i.e. which K shell is
ionized). Finally, the molecular potential has a 3-dimensional
character that is clearly anisotropic. Thus, for example in a diatomic,
although the potential may be closely dependent on the bond length in
the dimension along the bond axis, in _any_ other direction the importance

of bond distance to the molecular potential is much less clear. These examples serve to illustrate some of the difficulties in parameterizing the multi-dimensional molecular potential (and thus shape-resonance energies) in terms of a single variable (the bond length). They also highlight the strong influence of the details of the molecular potential on the quantification of shape-resonance phenomena.

Nevertheless, if one neglects many of the details of the molecular potential and reduces the shape-resonance problem to one dimension (i.e. along a bond axis), a dramatic simplification can be obtained by considering shape resonances as arising from atomic scattering within the molecule. In fact, a model of shape resonances based on a muffin-tin potential has been proposed[16] which ignores the complications mentioned above, and which describes shape resonances in a manner similar to EXAFS phenomena. For want of a better term, we will refer to this picture as "EXAFS-like". The result is a direct and simple correlation between shape-resonance energies and bond lengths. Taking this picture one step further, recent work[8-11] has used the rationale of this simple model to support a search for an empirical correlation between shape-resonance energies and bond lengths in a wide variety of small molecules containing the atoms B, C, N, O, and F. With the advent of these first attempts to determine a quantitative correlation, it seems appropriate to review what approximations are entailed in describing shape resonances by a model similar to that used for EXAFS, so that we can determine what restrictions or cautions need to be applied both to the interpretation of experimental data and to the

empirical comparisons themselves. The remainder of this paper is devoted to discussing these topics.

A first step in discussing the validity of an atomic-scattering EXAFS-like approach to shape-resonance phenomena is to compare the molecular potential appropriate for "pure" EXAFS phenomena to what we know about the potential-barrier interaction which produces shape resonances. In EXAFS, the important interaction for the ionized core electron is with an adjacent atomic-core potential in the molecule. The subsequent backscattering from this core and scattering off the original atomic core from which the electron was ionized produces the interference effect commonly referred to as EXAFS.[20] Because EXAFS is observed at relatively high kinetic energies (~100 eV or more), the interplay between attractive and repulsive forces which produce the low-energy details of the molecular potential (and possibly a barrier) generally has a negligible effect on the "high-energy" photoelectron. Thus, it suffices to ignore details of the molecular potential between the atomic cores and to treat the problem in a single-dimensional picture along the bond axis. The important question is whether this type of description, which involves the bond length in a staightforward way, can be applied to lower kinetic energies, where the complex potential barrier can be expected to play a more important role.

For shape resonances, the spatially extended nature of the photoelectron interaction with the electron cloud rather than just with adjacent atomic cores is demonstrated by considering that:

1) atomic shape resonances are well-known and relatively well-understood,[21] and of course in these cases there are no adjacent atoms from which to backscatter.

2) molecular shape resonances are exhibited not only in ionization from core levels localized on a single atomic core, but also in ionization from diffuse valence orbitals which are delocalized throughout the molecule.[15,22-25]

3) even in diatomic molecules, the electron probability density for the shape-resonance continuum state need not be localized solely <u>between</u> the two atoms, but rather inside a more spatially extensive 3-dimensional region around the molecule [see for example the MSM-Xα calculations for the σ_μ $\ell=3$ continuum channel in the K shell of N_2 (Ref. 2)].

Consideration of the above points hints at some of the complications inherent to shape resonances that do not apply to higher-energy EXAFS phenomena. Finally, these complications suggest that the most important intramolecular distance for shape resonances might be the distance from the point of ionization to the potential barrier, rather than the bond length. If this is true, and because the potential barrier resides at the perimeter of the molecule,[2] difficulties will be encountered in relating bond lengths and shape-resonance energies, except in the somewhat restricted cases of very similar molecules or the same molecule in different environments.

Other important differences between an atomic-scattering EXAFS model and shape-resonance phenomena exist which are relevant in trying to elucidate the applicability of an "EXAFS-like" approach to shape resonances. First, there is not in general a one-to-one correspondence

between shape resonances and the type or number of chemical bonds in a given molecule, as is the case for EXAFS. For example, CF_4,[24] CCl_4,[15] CS_2,[23] and SiF_4,[26] all of which have only one type of chemical bond, seem to show more than one shape resonance, while other molecules such as F_2 (Ref. 27) show no continuum resonances at all. Other aspects of the distinction between shape-resonance and EXAFS processes, related to the resonant-versus-extended nature of the effects in energy and to the differing angular-momentum character, have been detailed previously.[28] Additional complications of the shape-resonance energy/bond length correlation will be presented in Sec. IV.

One final issue concerns the inclusion of below-threshold resonances in a search for a shape-resonance energy/bond length relation.[11] Discrete resonances are not describable in terms of core scattering from adjacent atoms because they do not have a continuum electron in the final state to be scattered. This problem can be solved if one considers shape resonances as due to a barrier in the molecular potential (or as unoccupied molecular orbitals), because the character of both the continuum and discrete wavefunctions can be modified by interaction with the barrier. The intensity of discrete below-threshold excitations can be enhanced, and continuum shape resonances can be produced.[2-4]

Even within this unified picture, however, some distinction from continuum resonances should be maintained because the decay characteristics of the discrete states are quite different from those observed for continuum shape resonances: above-threshold features that are related to shape resonances generally decay by a one-electron

intrachannel effect, whereas the below-threshold resonances decay by
autoionization (a multielectron, interchannel process) into many
channels.[29] It is known[30] that interchannel coupling of a discrete
autoionizing state to many continua perturbs the energy of the
resonance. Therefore, it is unclear whether discrete resonances are as
suitable as continuum shape resonances for ascertaining the relationship
between resonance energies and bond distances. In fact, a previous
attempt to examine the relationship between discrete resonance energies
and bond lengths demonstrated that the $1s \rightarrow \pi^*$ discrete resonance
energies in the series C_2H_2, C_2H_4, and C_2H_6 show very little if any
dependence on the carbon-carbon bond distances.[11] This concern also may
apply to resonances above a K-shell threshold if a doubly excited
autoionizing state is wholly or partly responsible for the resonance
intensity. The one-electron nature of continuum shape resonances
suggests that they will be most useful in the search for a quantitative
correlation.

In related work, recent experimental and theoretical studies on
valence photoionization of SF_6 (Ref. 31) and N_2 (Ref. 32) have indicated
that the shape resonances in these molecules probably exhibit
significant multi-electron character. Although these findings are still
to be completely understood, cases such as these in which the one-
electron description of shape resonances breaks down will involve
similar complications as those discussed above for discrete
autoionization resonances. Additional caution with respect to the
shape-resonance energy/bond length relationship is warranted for any
system in which multi-electron effects play an important role.

In conclusion, both the importance of establishing a correlation between shape-resonance energies and bond distances and some of the complications involved in attempting to do so are clear. If the determination of such a correlation is to be tractable, then it must be so despite the complexity of the molecular potential experienced by a low-kinetic-energy continuum electron. We have discussed several reasons why this complexity could pose difficulties to finding a simple relationship. However, because of the potential usefulness of a shape-resonance energy/bond length correlation, we are encouraged to search the available data for an empirical relationship. There are recognized complications inherent in the incompletely understood phenomenon of shape resonances; thus we choose to be cautious in our selection of usable results for K-shell shape resonances. This caution is reflected in the next section in the criteria established for assigning spectral features in absorption as shape resonances. The results of our search and comparison to previous work along these lines are presented in Sec. IV.

III. ASSIGNMENT OF SHAPE RESONANCES

Molecular shape-resonance phenomena constitute a relatively new area of study, and no consensus has been established as to what evidence is required to confirm the assignment of a shape resonance to a spectroscopic feature. Although more experimental and theoretical work is needed to understand thoroughly the phenomena, at this time we propose the following requirements in order to assign unambiguously a feature in absorption as a shape resonance:

1) a gas-phase partial-cross-section measurement as a function of photon energy, demonstrating that only the main-line intensity is enhanced at the resonance (intrachannel decay). Angular-distribution measurements are desirable also, because they are likely to show an effect in the vicinity of the resonance, and can be useful in comparison with theory.

2) theoretical support, illustrating at least the qualitative existence and symmetry, and ideally the angular-momentum character of the shape-resonance continuum state. Reasonable quantitative agreement with experiment is desired as well, especially when experimental interpretation is complicated.

The adoption of these rather strict criteria is desirable for several reasons. First, the requirement that partial cross sections be measured is essential because there exist above-threshold features related to other phenomena, such as satellite onsets and excitations to doubly-excited states, which may not be distinguishable from shape-resonance features by a photoabsorption or an electron energy-loss

(EELS) experiment alone. A dramatic example of this problem is illustrated at the carbon K edge of CO, where the EELS measurement[33] indicates a maximum in the absorption cross section at 304 eV. The maximum at this energy has been assigned as the σ^* shape resonance in CO.[11] However, C 1s photoemission results[34] find the maximum (and hence the shape resonance energy) to be about 2 eV higher in energy. This discrepancy recently has been determined to be due to a strong contribution of a C 1s satellite in CO (Ref. 35) whose binding energy is about 304 eV,[34] and whose threshold intensity is approximately 20% of the C 1s main-line intensity at this energy.[37] Although the presence of the satellite intensity is not easily identifiable in the absorption measurement, it clearly shifts the energy at which the total cross section peaks relative to the peak in the C 1s partial cross section. Another example concerns the weak maxima in the absorption coefficients of CH_4, NH_3, and H_2O (C, N, and O 1s, respectively), which have been assigned as shape resonances,[11] but very likely could be doubly excited states leading to satellite thresholds. This possibility can be deduced by comparing the absorption results to X-ray photoelectron-spectroscopy measurements of the 1s main lines and related satellites for these molecules.[38,39] Furthermore, hydride molecules with one central atom bonded soley to hydrogen atoms are unlikely to exhibit a shape resonance because the hydrogens tend to be a very weak perturbation on the potential of the central atom.[2] A final example is provided by perfluoro-2-butene,[9] for which a complicated EELS spectrum has been interpreted without consideration of these other possible processes.[40]

The added requirement that only the main-line cross section be enhanced ensures that other decay channels, which would indicate autoionization character (i.e. multi-electron discrete-resonance character), are not participating in the resonant process. A striking example is provided by S 1s photoionization in SF_6, in which an above-threshold resonance in absorption previously assigned as a shape resonance[1] recently has been interpreted as a doubly excited discrete state which autoionizes to several different continuum channels.[41]

Secondly, theoretical calculations should provide confirmation that the resonance observed in a partial cross section is indeed of shape-resonance character, especially in cases where more than one continuum resonance exists.[15,22,23,26] Although the experimental partial cross-section evidence may be overwhelming for interpretation as shape resonances, we stress the need for theoretical understanding, especially if comparison is to be made among different molecules. For example, the angular-momentum character of the shape-resonance continuum state may be different for different molecules.[2,6] Although it is not completely understood what quantitative effect this difference may have on the resonance kinetic energies from one molecule to another, it does illustrate a general lack of knowledge about shape-resonant trends among different molecular species. Finally, using theoretical calculations alone to assign shape resonances can be misleading because a theoretical resonance energy can easily be several eV off from the experimental value, even in well established cases.[24,34]

IV. SHAPE RESONANCES AND BOND LENGTHS

It is clear that shape-resonance energies and bond lengths are, in general, related, and in fact qualitative trends have been identified in a few special cases. For example, calculations have shown that varying just the bond distance in a given molecule [N_2 (Ref. 13), CO_2 (Ref. 14)] leads to monotonic variations in the valence-shell shape-resonance energies. This correlation, restricted to a single molecule, may have implications for studying bond-length changes as a function of molecular environment (e.g., gas-phase vs. adsorbate).[12] However, caution must be exercised even in such well-defined cases, because the molecular vibrations, which have a significant effect on the resonance energy,[13] also will be modified under any circumstances in which the bond length changes.

A second example of an observed shape-resonance energy/bond length relationship pertains to the series of isostructural molecules CCl_4, $SiCl_4$, and $GeCl_4$. In this series, angular-distribution parameters have been measured [and theory exists for CCl_4 (Ref. 42)] for valence orbitals of the same symmetry ($1e$ and $2t_2$) for all three molecules.[15] If the minima in the angular-distribution results are related to shape-resonance phenomena (which has been confirmed for $SiCl_4$ by partial-cross-section measurements[43]), then the resonance positions appear to shift toward the ionization threshold on going from CCl_4 to $SiCl_4$ to $GeCl_4$. In this special case of very similar molecules, the resonance energy shift can be related to the change in the central atom and the concomitant bond-length change, or more generally to the change in the

overall molecular potential. However, for less similar series of molecules, more than one parameter (e.g. bond length, oxidation state, type of chemical bonds, core level ionized, etc.) may be changing simultaneously. Thus, in series such as C_2H_2, C_2H_4, C_6H_6, and C_2H_6,[11] or CO, HCOOH, and CH_3OH,[8] trends identified for resonant features present in absorption (whether they are shape resonances or not) may be due to many factors.

We have noted the occurrence of shape-resonance energy/bond length relationships in cases where the bond length changes in a single molecule or in a closely related series of molecules. To be of more widespread use, however, a correlation among a variety of molecules is desirable. To investigate this possibility quantitatively for core-level shape resonances, we show in the top panel of Fig. 1 the resonance kinetic energies (i.e. the energy above the ionization threshold) for all molecules in which a K-shell (B, C, N, O, or F) continuum shape resonance can be identified unambiguously using the criteria established in Sec. III, without regard to the symmetry[44] or angular momentum of the resonant continuum state. We plot the shape-resonance energy positions relative to the K edge (δ) as a function of bond length for comparison to Fig. 6 of Ref. 11, and to ascertain the possible existence of an empirical relationship between shape-resonance energies and bond distances. Many candidate molecules[11] have been omitted because they do not satisfy at least one of the criteria presented here. We have, however, included along with the molecules in the top panel of Fig. 1 those cases (discussed below) for which some incomplete evidence exists (bottom panel, Fig. 1). One can see from Fig. 1 that no empirical

relationship between shape-resonance energies and bond lengths is yet

apparent in the available data.

A previous investigation[11] of the relationship between shape-

resonance energies and bond distances obtained results at odds with the

present work. Specifically, these workers empirically found a linear

relationship between δ and bond length for a wide variety of molecules.

These molecules were broken into several series distinguished by the

parameter Z, the sum of atomic numbers of the "absorber and the

scatterer" atoms[11] from which the "atomic-scattering" resonance is

considered to arise. Using this idea, features in photoabsorption were

related to individual bond lengths in the molecules, even for those

molecules containing more than two atoms of B, C, N, O, or F. Finally,

the empirically determined linear correlations have been used

preliminarily as an analytical tool to estimate unknown bond lengths to

$\pm0.03-0.05$A.[8-11]

The differences in the present and previous findings can be traced

primarily to the stricter criteria applied here for assigning shape

resonances to spectroscopic features. None of the molecules excluded in

the present analysis have been studied in a K-shell gas-phase

photoemission experiment, and only a few have been treated

theoretically; all of the excluded molecules fail on at least one

criterion from Sec. III. However, because of the dramatic difference

between the previous work and our findings, it is fitting to provide

more details concerning the assignments of shape resonances in both

studies. Therefore, we briefly discuss some of the specific reasons we

used to exclude from Fig. 1 most of the molecules for which K-shell

photoabsorption or EELS spectra are available. In doing so, we will highlight some difficulties in assigning shape resonances based on absorption data alone, and we will discuss a few "borderline" cases that partially fulfill our criteria.

To begin with, we have chosen not to include molecules with discrete resonances below the K edge that may be associated with shape-resonance phenomena. The reasons for this were presented in Sec. II, and are related to the generally complicated multi-electron nature of below-threshold resonances. Examples of molecules excluded on these grounds are O_2,[33] CH_3OH, CH_3NH_2,[45] CH_xF_{4-x},[46] and NF_3.[47] In addition, for most of these molecules,[35,45,46] previous assignments of discrete resonance features have invoked Rydberg orbitals rather than σ^* shape-resonance phenomena to explain the below-threshold features. Without further experimental and theoretical work to distinguish Rydberg and shape resonances and to understand the multi-electron effects of discrete resonances, none of these molecules can be included in our analysis with confidence.

A second set of molecules is not included in Fig. 1 because of ambiguities in the assignments of the continuum features in the photoabsorption spectra. For example, one ambiguity arises in the case of ethane, where a cross-section feature slightly above the C K-edge has been interpreted as a σ^* shape resonance.[11] The uncertainty in this assignment is demonstrated by the lack of mention of any resonant feature at all above the K edge in the original report of the ethane spectrum.[48,49] A second example is CF_4, for which theory[50] and experiment[34] for C K-shell photoionization disagree. Also

excluded are molecules for which previous assignments based on the atomic-scattering picture (see Sec. II) made a one-to-one correspondence between individual bonds (e.g. C-O double or C-C single bonds) and particular features in absorption. Examples are CH_3CHO (Ref.8) and C_2N_2.[11] While this is appropriate within an atomic-scattering picture of shape-resonance phenomena as "the first EXAFS wiggle",[8] the complexity of the molecular potential at low continuum-electron energy renders such a straightforward correlation uncertain. The molecule OCS, for which a carbon K-shell photoemission measurement has been made,[34] also is omitted on these grounds.

The difficulty with a one-to-one correspondence can be understood by recourse to the picture of shape-resonance phenomena as corresponding to unoccupied molecular orbitals.[4] In general, unoccupied molecular orbitals are spread throughout the molecule, especially for larger, more complicated systems. Likewise, the resonant continuum state accessed at a shape resonance is delocalized in the molecule, rather than being concentrated along one bond between a pair of atoms. This picture of shape resonances works well despite the fact that the resonance is in the continuum, because the part of the continuum wavefunction in the interior of the molecule looks very much like a discrete molecular orbital.[2,4] Going one step further, it is this interior part of the continuum wavefunction that primarily determines the enhanced transition amplitude from the initial core level to the continuum resonant state, which we recognize as a shape resonance.[2-4] Thus, both accepted qualitative pictures[2-4] of shape-resonance phenomena indicate that association of a shape resonance with a _particular_ bond in a polyatomic

molecule is an unproven simplification. This point can be emphasized by considering highly symmetric molecules with only one bond length or type of bond, such as SF_6 and SiF_4. For these molecules, more than one continuum resonance has been observed,[1,26,41] and clearly they cannot be associated with different bonds in these molecules. However, treating these multiple continuum resonances as potential-barrier effects or equivalently as being related to unoccupied molecular orbitals naturally allows for the possibility of more than one resonance for these symmetric molecules.

To continue, we have not considered molecules for which the observed resonances in absorption are very weak. In these cases, it is very possible that the weak structure is associated with multi-electron satellite processes (double excitation and shake-up). Examples are C_2H_4,[48] CH_4, NH_3, and H_2O.[45] The latter three molecules also are problematic because their proposed shape resonances must be due to scattering by hydrogen atoms. More intense features also may be associated with double-excitation or shake-up processes. In fact, the continuum features chosen as shape resonances[11] in C_6H_6 and HCN also have been discussed as being the result of satellite transitions in these molecules.[48,51]

Finally, there are a few molecules that have suggestive evidence for a K-shell shape resonance, but for one reason or another do not satisfy the set of criteria used in this work (these are included in the bottom panel of Fig. 1). Probably the leading candidate of this group is C_2H_2,[52] for which theory predicts a K-shell shape resonance.[53] Only a photoemission experiment is needed to confirm the assignment. There

also exists theoretical work for the carbon K edge in C_6H_6,[54] but more than one continuum resonance exists in experiment and theory for this highly symmetric molecule. For BF_3 (Ref. 24) and HCN,[25] shape resonances have been observed experimentally and theoretically in valence subshells, indicating that shape resonances could be present in the K shells as well. Finally, the continuum resonance in H_2CO (Ref. 55) is intense enough that it very likely is a shape resonance similar to the one already identified in CO,[34] but no photoemission or theoretical results are available at the carbon K edge of formaldehyde.

After application of the criteria in Sec. III, and consideration of the points listed above, we are left with the molecules CO, CO_2,[34] N_2, and NO[29] as the only ones exhibiting unambiguously identified K-shell shape resonances (top panel, Fig. 1). Those molecules for which incomplete evidence exists as discussed in the preceding paragraph are shown also (bottom panel, Fig. 1). Clearly, either sample size is insufficient to ascertain a quantitative relationship between shape-resonance energies and bond lengths. In addition, the comparisons in Fig. 1 are not necessarily appropriate, because the shape resonances are not in the same K shell, nor are they all of the same symmetry or angular-momentum character. Much more experimental and theoretical work is required to fill in Fig. 1 and test for a correlation.

A final comment is appropriate about the data presented in Fig. 1. Because core-relaxation energies for different atoms can affect the shape-resonance energy positions, even for a single molecule a shape resonance observed at different K edges may not occur at the same kinetic energy (e.g., CO and CO_2). Moreover, for two molecules with the

same Z but with a different atomic pair (e.g. CO and N_2), the shape-resonance energies will be shifted to different extents by the relaxation of the continuum state in the presence of the different 1s holes (among other effects). Such shifts can be several eV for core levels, as seen for CO_2 in Fig. 1, for which the difference in the energy positions for the shape-resonance continuum states observed at the C 1s and O 1s thresholds is about 5 eV.[34] This discussion itself is oversimplified, and other factors (i.e. hole localization, molecular environment, etc.) also need to be considered.[56]

V. CONCLUSION

An analysis of the available experimental data and theory for well-documented K-shell shape resonances in molecules containing B, C, N, O, and F does not indicate an empirical relationship between bond lengths and resonance energies. Although in special cases (i.e. vibrational-induced changes in molecular bond lengths, and changes in the central atom in isostructural molecules) a trend has been identified, there is no conclusive evidence at this time that this relationship is applicable to a wide variety of molecules. Although evidence has been reported for empirical correlations between bond lengths and the energies of certain K-shell features in molecular absorption spectra, the features have not been shown to be shape resonances. Until a plausible explanation exists for these empirical findings, their usefulness remains to be determined. Finally, we look forward to further progress in the experimental and theoretical understanding of shape resonances, and to the eventual determination of the quantitative connection between shape resonances and bond lengths.

ACKNOWLEDGEMENTS

REFERENCES

1. J.L. Dehmer, J. Chem. Phys. $\underline{56}$, 4496 (1972).

2. J.L. Dehmer in Resonances in Electron-Molecule Scattering, van der Waals Complexes, and Reactive Chemical Dynamics, edited by D.G. Truhlar (American Chemical Society, Washington, D.C. 1984); J.L. Dehmer, D. Dill, and A.C. Parr in Photophysics and Photochemistry in the Vacuum Ultraviolet, edited by S.P. McGlynn, G. Findley, and R. Huebner (Reidel, Dordrecht, Holland, 1985); J.L. Dehmer, A.C. Parr, and S.H. Southworth in Handbook on Synchrotron Radiation, Vol II, edited by G.V. Marr (North-Holland, Amsterdam, 1986).

3. V. McKoy, T.A. Carlson, and R.R. Lucchese, J. Phys. Chem. $\underline{88}$, 3188 (1984); D.L. Lynch, V. McKoy, and R.R. Lucchese in Resonances in Electron-Molecule Scattering, van der Waals Complexes, and Reactive Chemical Dynamics, edited by D.G. Truhlar (American Chemical Society, Washington, D.C. 1984).

4. P.W. Langhoff in Resonances in Electron-Molecule Scattering, van der Waals Complexes, and Reactive Chemical Dynamics, edited by D.G. Truhlar (American Chemical Society, Washington, D.C. 1984).

5. A.P.Hitchcock, C.E. Brion, and W.J. Van der Wiel, J. Phys. B 11, 3245 (1978).

6. J.L. Dehmer and D. Dill, Phys. Rev. Lett. $\underline{35}$, 213 (1975).

7. J. Stöhr, K. Baberschke, R. Jaeger, R. Treichler, and S. Brennan, Phys. Rev. Lett. $\underline{47}$, 381 (1981); J. Stöhr and R. Jaeger, Phys. Rev. B $\underline{26}$, 4111 (1982).

8. J. Stöhr, J.L. Gland, W. Eberhardt, D. Outka, R.J. Madix, F. Sette, R.J. Koestner and U. Doebler, Phys. Rev. Lett. $\underline{51}$, 2414 (1983).

9. A.P. Hitchcock, S. Beaulieu, T. Steel, J. Stöhr, and F. Sette, J. Chem. Phys. $\underline{80}$, 3927 (1984).

10. J. Stöhr, F. Sette, and A.L. Johnson, Phys. Rev. Lett. $\underline{53}$, 1684 (1984).

11. F. Sette, J. Stöhr, and A.P. Hitchcock, J. Chem. Phys. $\underline{81}$, 4906 (1984); Chem. Phys. Lett. $\underline{110}$, 517 (1984).

12. F. Sette, J. Stöhr, E.B. Kollin, D.J. Dwyer, J.L. Gland, J.L. Robbins, and A.L. Johnson, Phys. Rev. Lett. $\underline{54}$, 935 (1985).

13. J.L. Dehmer, D. Dill, and S. Wallace, Phys. Rev. Lett. $\underline{43}$, 1005 (1979).

14. J.R. Swanson, D. Dill, and J.L. Dehmer, J. Phys. B $\underline{14}$, L207 (1981).

15. M.N. Piancastelli, P.R. Keller, J.W. Taylor, F.A. Grimm, T.A. Carlson, M.O. Krause, and D. Lichtenberger, J. Electron Spectrosc. $\underline{34}$, 205 (1984).

16. C.R. Natoli in EXAFS and Near Edge Structure, edited by A. Bianconi, L. Incoccia, and S. Stipcich (Springer, Berlin, 1983).

17. A. Messiah, Quantum Mechanics, Vol. I (North-Holland, Amsterdam, 1961), p. 96.

18. While the virtual molecular orbital picture[4] and the potential-barrier picture[3] have met with success in quantifying the effects in individual molecules, these successes have not included detailed results on bond-length dependence in a wide variety of molecules.

19. S.T. Manson and J.W. Cooper, Phys. Rev. $\underline{165}$, 126 (1968).

20. P.A. Lee, P.H. Citrin, P. Eisenberger, and B.M. Kincaid, Rev. Mod. Phys. $\underline{53}$, 769 (1981).

21. The best-studied case is Xe, which is discussed in the following: D.L. Ederer, Phys. Rev. Lett. $\underline{13}$, 760 (1964); J.W. Cooper, Phys.

Rev. Lett. 13, 762 (1964); S.T. Manson and J.W. Cooper, Phys. Rev. 165, 126 (1968); J.B. West, P.R. Woodruff, K. Codling, and R.G. Houlgate, J. Phys. B 9, 407 (1976); S.P. Shannon, K. Codling, and J.B. West, J. Phys. B 10, 825 (1977); S.H. Southworth, P.H. Kobrin, C.M. Truesdale, D.W. Lindle, S. Owaki, and D.A. Shirley, Phys. Rev. A 24, 2257 (1981) and references therein.

22. T.A. Carlson, A. Fahlman, W.A. Svensson, M.O. Krause, T.A. Whitley, F.A. Grimm, M.N. Piancastelli, and J.W. Taylor, J. Chem. Phys. 81, 3828 (1984).

23. T.A. Carlson, M.O. Krause, F.A. Grimm, J.D. Allen Jr., D. Mehaffy, P.R. Keller, and J.W. Taylor, J. Chem. Phys. 75, 3288 (1981).

24. J.L. Dehmer, A.C. Paar, S.H. Southworth, and D.M.P. Holland, Phys. Rev. A 30, 1783 (1984) and references therein.

25. D.M.P. Holland, A.C. Parr, D.L. Ederer, J.B. West, and J.L. Dehmer, Int. J. Mass Spectrom. Ion Phys. 52, 195 (1983).

26. T.M. Zimkina and A.S. Vinogradov, J. Phys. (Paris) 32, C4-3 (1971); H. Friedrich, B. Pittel, P. Rabe, W.H.E. Schwarz, and B. Sonntag, J. Phys. B 13, 25 (1980); G.M. Bancroft, S. Aksela, H. Aksela, K.H. Tan, B.W. Yates, L.L. Coatsworth, and J.S. Tse, J. Chem. Phys. 84, 5 (1986).

27. A.P. Hitchcock and C.E. Brion, J. Phys. B 14, 4399 (1981).

28. J.L. Dehmer and D. Dill, J. Chem. Phys. 65, 5327 (1976).

29. For N_2, the different decay characteristics can be seen in H.W. Haak, G.A. Sawatzky, L. Ungier, J.L. Gimzewski, and T.D. Thomas, Rev. Sci. Instrum. 55, 696 (1984); and D.W. Lindle, C.M. Truesdale, P.H. Kobrin, T.A. Ferrett, P.A. Heimann, U. Becker, H.G. Kerkhoff, and D.A. Shirley, J. Chem. Phys. 81, 5375 (1984).

30. U. Fano, Phys. Rev. 124, 1866 (1961); U. Fano and J.W. Cooper, Phys. Rev. 137, 1364 (1963); Rev. Mod. Phys. 40, 441 (1968).

31. J.L. Dehmer, A.C. Parr, S. Wallace, and D. Dill, Phys. Rev. A 26, 3283 (1982).

32. G.V. Marr, J.M. Morton, R.M. Holmes, and D.G. McKoy, J. Phys. B 12, 43 (1979); J.A. Stephens and D. Dill, Phys. Rev. A 31 1968 (1985); S. Southworth, A.C. Parr, J.E. Hardis, and J.L. Dehmer, Phys. Rev. A 33, 1020 (1986).

33. G.R. Wright and C.E. Brion, J. Electron Spectrosc. Relat. Phenom. 4, 313 (1974); A.P. Hitchcock and C.E. Brion, J. Electron Spectrosc. 18, 1 (1980).

34. C.M. Truesdale, D.W. Lindle, P.H. Kobrin, U.E. Becker, H.G. Kerkhoff, P.A. Heimann, T.A. Ferrett, and D.A. Shirley, J. Chem. Phys. 80, 2319 (1984).

35. L. Ungier and T.D. Thomas, Phys. Rev. Lett. 53, 435 (1984).

36. U. Gelius, J. Electron Spectrosc. 5, 985 (1974).

37. L.J. Medhurst, D.W. Lindle, P.A. Heimann, T.A. Ferrett, S.H. Liu, and D.A. Shirley (unpublished results).

38. D.K. Creber, J.S. Tse, and G.M. Bancroft, J. Chem. Phys. 72, 4291 (1980).

39. For CH_4, NH_3, and H_2O, there are features in the absorption spectra located about 12, 14, and 16 eV above the C, N, and O K edges, respectively.[11,38] For each case, the X-ray photoelectron spectrum shows complex satellite structure about 7-8 eV above the absorption maximum, leading one to suspect the absorption features to be a series of doubly excited states leading to the satellite thresholds.

40. Furthermore, perfluoro-2-butene may be a particularly bad example, because of the special role F atoms seem to play in potential-barrier effects in some compounds.[31,41]

41. T.A. Ferrett, D.W. Lindle, P.A. Heimann, H.G. Kerkhoff, U.E. Becker, and D.A. Shirley, Phys. Rev. A (in press).

42. P.R. Keller, J.W. Taylor, T.A. Carlson, and F.A. Grimm, Chem. Phys. 9, 269 (1983).

43. T.A. Carlson, A. Fahlman, M.O. Krause, T.A. Whitley, F.A. Grimm, M.N. Piancastelli, and J.W. Taylor, J. Chem. Phys. 84, 641 (1986).

44. For detailed comparison among different molecules, the molecular symmetry will be important. For nonlinear or nonplanar molecules, the σ and π descriptions generally used for shape resonances are incorrect. A classification scheme based on the molecular point group should be used.

45. G.R. Wright and C.E. Brion, J. Electron Spectrosc. 4, 25 (1974).

46. R.E. LaVilla, J. Chem. Phys. 53, 3841 (1973); G.R. Wright and C.E. Brion, J. Electron Spectrosc. 4, 327 (1974); A.P. Hitchcock and C.E. Brion, J. Electron Spectrosc. 13, 193 (1978); F.C. Brown, R.Z. Bachrach, and A. Bianconi, Chem. Phys. Lett. 54, 425 (1978).

47. A.S. Vinogradov, T.M. Zimkina, V.N. Akimov, and B. Shlarbaum, Bull. Acad. Sci. USSR Phys. Ser. 38, 69 (1974); R.N.S. Sodhi C.E. Brion, and R.G. Cavell, J. Electron Spectrosc. 34, 373 (1984).

48. A.P. Hitchcock and C.E. Brion, J. Electron Spectrosc. 10, 317 (1977).

49. We conjecture that the shape of the cross-section curve just above the carbon K edge for ethane is dominated not by any resonant

processes, but by the natural variation of the cross section modified by very weak multi-electron processes at higher energy.

50. J.A. Stephens, D. Dill, and J.L. Dehmer, J. Chem. Phys. $\underline{84}$, 3638 (1986).

51. A.P. Hitchcock and C.E. Brion, Chem. Phys. $\underline{37}$, 319 (1979).

52. A.P. Hitchcock and C.E. Brion, J. Electron Spectrosc. $\underline{22}$, 283 (1981).

53. L.E. Machado, E.P. Leal, G. Csanak, B.V. McCoy, and P.W. Langhoff, J. Electron Spectrosc. $\underline{25}$, 1 (1982).

54. J.A. Horsley, J. Stöhr, A.P. Hitchcock, D.C. Newbury, A.L. Johnson, and F. Sette, J. Chem. Phys. $\underline{83}$, 6099 (1985).

55. A.P. Hitchcock and C.E. Brion, J. Electron Spectrosc. $\underline{19}$, 231 (1980).

56. D. Dill, S. Wallace, J. Siegel, and J.L. Dehmer, Phys. Rev. Lett. $\underline{11}$, 1230 (1978); $\underline{12}$, 411 (1979).

FIGURE CAPTION

Fig.1.   K-shell shape-resonance energies (Refs. 24, 25, 29, 34, 52-55)

relative to ionization thresholds δ(eV) as a function of bond

length (Å). The top panel includes only those molecules that

strictly conform to the criteria established in Sec. III of the

text. The bottom panel includes molecules which partially

conform to these criteria, as discussed in Sec. IV. For all

molecules, the ionized 1s core level is denoted by the

underlined atom. For CO, CO_2, and H_2CO, two points are shown,

corresponding to different δ values for C 1s and O 1s

ionization. For HCN, one point is shown which corresponds to

the shape-resonance energy for both C and N ionization.
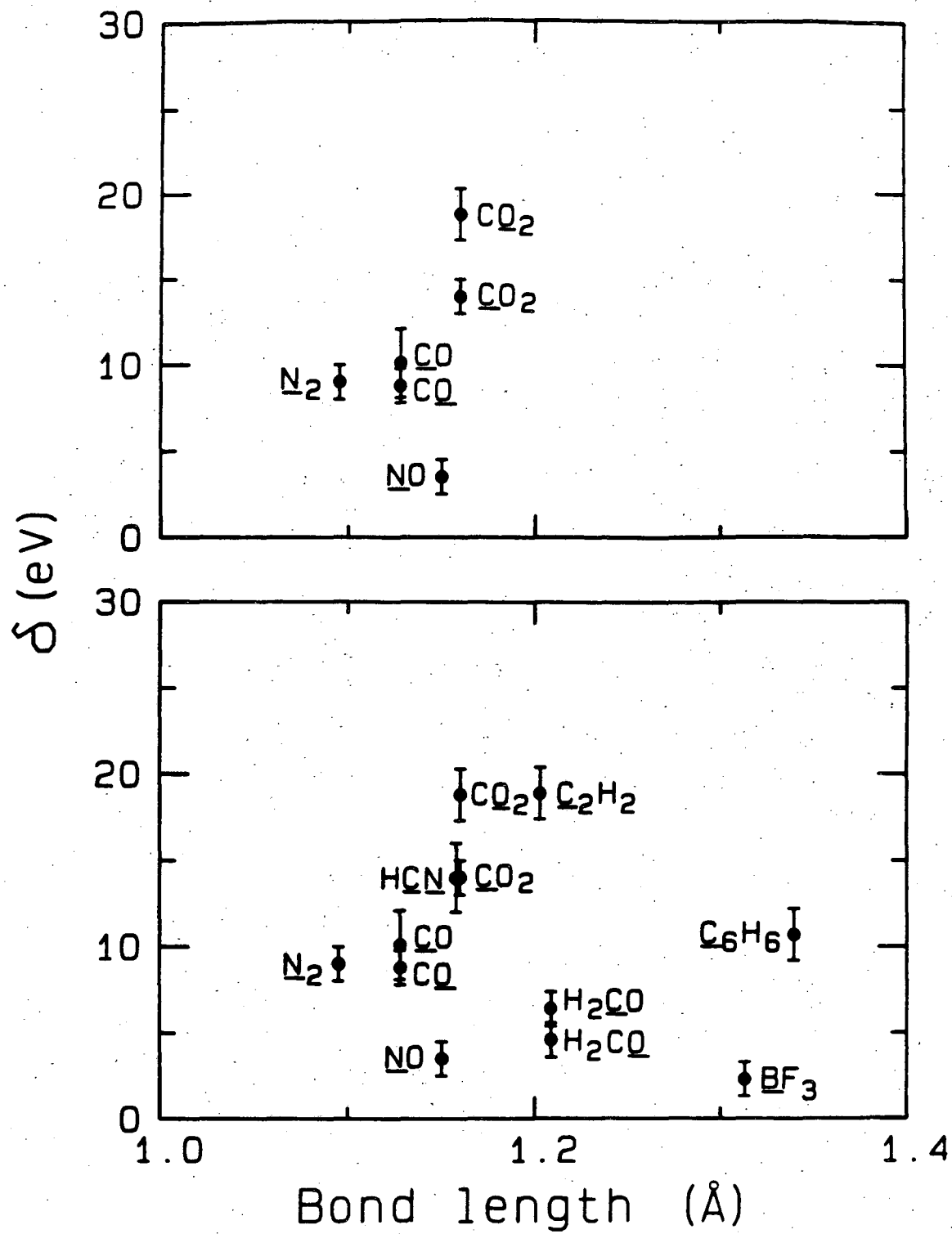
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Figure 1

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