Shape Resonances in K-Shell Photoionization of Diatomic Molecules[*]

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We show that K-shell photoionization spectra of diatomic molecules can exhibit strong shape resonances near threshold. The molecular field is decisive in this phenomenon. It induces the resonant contraction of high-l components of the ionization channels, and it couples these components with low-l components produced in the atomic cores by K-shell photoionization. We demonstrate the effect for N_2 by using the multiple-scattering model. Clear evidence for this phenomenon exists for N_2, CO, and NO.

Recent x-ray[1] and "pseudo photon"[2-4] absorption spectra exhibit nondydrogenic behavior within a few rydbergs above the K-shell edges of first row diatomic molecules. The novel feature of these spectra is a general enhancement of the background continuum by several factors over a band of 5 to 10 eV. Not only is this enhancement nonhydrogenic, but it has no counterpart in either the spectra of the constituent atoms or the spectra of the united atom. Here we show that strong shape resonances can be expected within 10 eV or so above the K-shell photoionization threshold for these molecules, and that it is this one-electron phenomenon which causes the broad enhancement of photoelectric current in the near continuum of these spectra.

The essence of the effect can be described in mechanistic terms by use of our prototype study of the K-shell photoionization of N_2. The electric dipole interaction, localized within the atomic K shell, produces a photoelectron with angular momentum $l=1$. As this p-wave electron escapes to infinity the anisotropic molecular field can scatter it into the entire range of angular momentum states contributing to the allowed σ and π ionization channels ($\Delta\lambda = 0, \pm 1$). In addition, the spatial extent of the molecular field of the two atoms, separated by 1.1 Å, enables the $l=3$ component of the σ continuum wave function to penetrate the molecular core region at a kinetic energy of ~ 1 Ry. This penetration is rapid, a phase shift of $\sim\pi$ occurring over a range of about 0.4 Ry. These two effects combine to produce a dramatic enhancement of photoelectric current at ~1-Ry kinetic energy, with predominantly f-wave character.

The specifically molecular character of this phenomenon is emphasized by comparison with K-shell photoionization in atomic nitrogen and in the united-atom case, silicon. In contrast to N_2, there is no mechanism for the essential p-f coupling, and neither atomic field is strong enough to support resonant penetration of high-l components through its centrifugal barrier.

The calculation was performed by use of the multiple-scattering formulation of inner-shell molecular photoionization reported recently.[5] The input potential was obtained from a multiple-scattering, $X\alpha$, self-consistent-field calculation[6,7] of the N_2 ground state with use of a code supplied by Johnson,[6] which we modified to apply the Latter cutoff condition[8] to the large-r region of the potential. The coefficient of the Slater exchange potential[9] was set at $\alpha=1$. (The calculation was also carried out with $\alpha=\frac{2}{3}$, with only minor changes in the results.) Convergence to one part in a thousand for all quantities considered here was obtained with partial-wave expansions extended to $l=3$ and $l=5$ about the atomic sites and the molecular center of mass, respectively.

In Fig. 1 we show the eigenphase sums for the σ and π ionization channels, separated into even-l (g) and odd-l (u) components. The eigenphase sum is a fingerprint in multichannel scattering processes, which indicates the presence of rapid changes in phase of a major component. It is defined (modulo 1) by

$$\mu_{\text{sum}} = \pi^{-1}\delta_{\text{sum}} = \pi^{-1}\textstyle\sum_i \tan^{-1}(U^\dagger K U)_{ii},$$

where U is the unitary matrix that diagonalizes the real, symmetric K matrix. The curves have been shifted to lie in the interval $\mu_{\text{sum}}=0$ to $\mu_{\text{sum}}=1$.

In Fig. 1 we can see clearly the large increase in the eigenphase sum for the σ_u channel at ~0.8 Ry. By inspection of the K matrix, this is seen to be caused by the $l=3$ component. This step is superimposed on a general decline due primarily to the $l=1$ component. The $l=5, 7, \ldots$ components do not contribute significantly at this low kinetic energy. The sharp increase in the σ_u μ_{sum} is accompanied by a band of enhanced amplitude in the molecular core and the accessibility of this amplitude by electric dipole ionization, through the p-f coupling by the molecular field, causes a pronounced enhancement of absorption. Note that the μ_{sum} for the π_u channel also rises, but does not show resonant behavior. This indicates that the molecular field can support a quasibound f wave oriented along the molecular axis, but not one oriented perpendicular to it.

The g channels exhibit a monotonic decline. In particular, there is no $l=2$ resonance. Rather, this resonance, responsible for the strong shape resonance seen at 2.3 eV in e-N_2 scattering,[10] has been drawn below threshold. In fact, we expect that the dominant peak at 401 eV in the N_2 photoabsorption spectrum (and analogous peaks in the spectra[3,4] of CO, NO, and O_2) corresponds to a transition to a discrete state with predominantly $l=2$ character. We plan to investigate this aspect of the discrete spectrum by using the multiple-scattering method.

The photoelectric current can be characterized by the integrated cross section

$$\sigma_{tot} = \sigma_g + \sigma_u,$$

and by the asymmetry parameter

$$\beta_{tot} = (\sigma_g\beta_g + \sigma_u\beta_u)/\sigma_{tot},$$

which together determine the differential cross section for photoionization from isolated, randomly oriented molecules,[11]

$$d\sigma/d\Omega = (\sigma_{tot}/4\pi)[1 + \beta_{tot}P_2(\cos\theta)];$$

θ is measured relative to the electric vector of the light.

The photoionization cross sections are shown in Fig. 2. The resonant σ_u component dominates σ_{tot}, with the σ_g component contributing negligibly. Also shown for comparison is 2 times the K-shell photoionization cross section for atomic nitrogen based on the Hartree-Slater model.[12] The resonance has a half-width of ~4.5 eV and a peak-to-background ratio of ~3.8. This width is close to that of the gross shape of the broad peak observed above the K-shell edges in N_2, CO, and NO (cf. Refs. 3 and 4). The peak-to-background ratios are more difficult to discern because of superimposed discretelike structures, which we attribute to multiple-electron excitations.

The asymmetry parameters are shown in Fig. 3. The dominance of the $l=3$ component in β_u yields a distribution which oscillates through the resonance region and deviates markedly from the atomic result, i.e., a pure $\cos^2\theta$ distribution ($\beta = 2$) characteristic of $1s \to \epsilon p$ ionization. On the other hand, β_g varies in much the same way as that for the corresponding united-atom process $2p \to \epsilon p, \epsilon d$.[13] In the region of the resonance, the overall asymmetry parameter β_{tot} reflects sub-

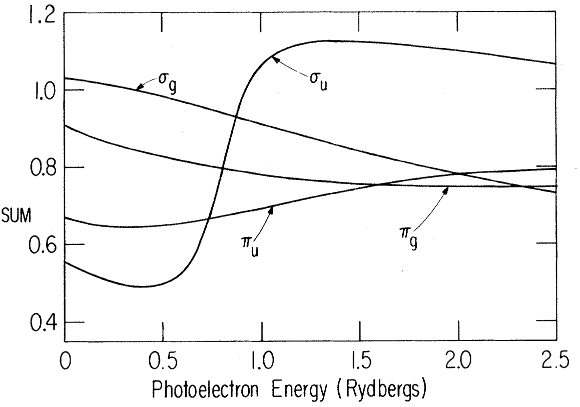

FIG. 1. The eigenphase sum μ_{sum} for the even-l and odd-l components of the σ and π ionization channels of N_2.

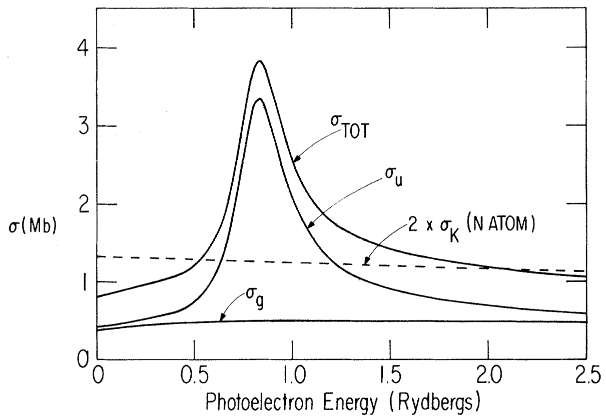

FIG. 2. K-shell photoionization cross section for N_2, showing breakdown into g and u components of the ionization channels. 2 times the K-shell photoionization cross section for atomic nitrogen is given by the dashed line for comparison.

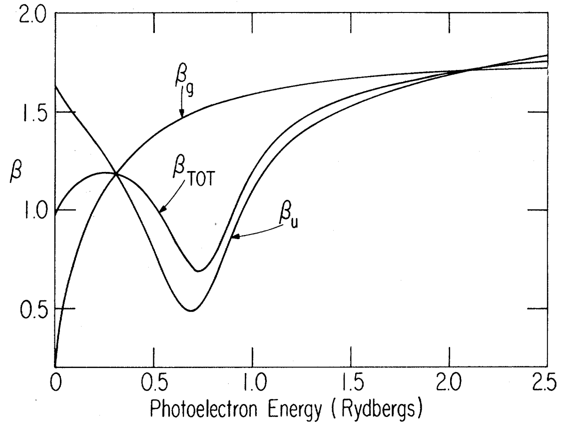

FIG. 3. Asymmetry parameter, β_{tot}, for K-shell photoionization in N_2. Asymmetry parameters for ionization into g and u components of the total ionization channels are shown. The dashed line indicates the corresponding value for K-shell ionization in atomic nitrogen.

stantially the variations in β_u. These variations will be analyzed in detail elsewhere. We present the final results here to encourage experimental verification of the structure of β_{tot}.

Finally, we wish to emphasize the generality of the molecular effects described in this Letter. First, although we used K-shell photoionization as an example, the molecular field can equally well couple high-l components of ionization channels with a photoelectron ejected from a core L shell, M shell, etc. Moreover, these cases could exhibit resonances in ionization channels not accessible in K-shell photoionization, i.e., with $|\lambda| > 1$. Second, molecules with other than diatomic structure are known[14] to exhibit spectral features which are very similar in appearance to those discussed above. Of course, the position, width, and high-l character in these various circumstances depend on the details of each individual case. Therefore, a comprehensive picture of these resonances in various materials will require detailed analyses of several examples. It does appear, however, that this elementary approach based on the multiple-scattering model is well suited for realistic mapping of the gross features of this effect.

We are grateful to K. Johnson for generously making his multiple-scattering, $X\alpha$, self-consistent-field program available to us.

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[6] It is recommended that the reader consult the recent review by K. H. Johnson, in *Advances in Quantum Chemistry*, edited by P. O. Löwdin (Academic, New York, 1973), Vol. 7, p. 143, for a detailed account of applications of the multiple-scattering method to the electronic structure of molecules.

[7] The approximations made in this choice of model potential are described in Refs. 5 and 6. In the present calculation, we make an additional approximation, namely, the neglect of hole localization [P. S. Bagus and H. F. Schaefer, J. Chem. Phys. 56, 224 (1972)]. This approximation is not expected to change the gross features emphasized in this Letter. The degree to which it affects details of the calculation will be determined when we extend our work to systems with $C_{\infty v}$ symmetry. We are grateful to U. Fano for bringing this aspect of the problem to our attention.

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