EXTENDED FINE STRUCTURE IN THE K-SHELL PHOTOIONIZATION SPECTRUM OF Br_2

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The multiple-scattering approach to molecular wavefunctions in the electronic continuum[1] has been used recently to elucidate the structure of the shape resonance just above threshold in the K-shell photoionization spectrum of N_2.[2] A similar calculation for Br_2 has yielded significantly different results, i.e., there is no shape resonance; appearing instead is a single resonance in the discrete spectrum, and the photoionization spectrum is found to oscillate with appreciable amplitude throughout the spectral range investigated, from threshold to 60 Ry.

The calculation was carried out in the same manner as the N_2 calculation reported in Ref. 2. The multiple-scattering potential for the Br_2 ground state was obtained using Johnson's† bound-state multiple-scattering code modified to apply the Latter[4] cutoff condition to the large-r region of the potential. The statistical exchange parameter[5] was set at $\alpha = 1.0$. Convergence of the multiple-scattering expansion of the continuum wavefunction was determined by adjusting the maximum orbital angular momenta ℓ_I and ℓ_{III}, in region I and region III, respectively, until the eigenphase sum for each continuum channel converged to four significant figures. The values determined in this way for each energy range are given in Table 1.

In Figure 1 we plot the spectral variation of the eigenphase sums for the four continuum channels accessible from the K-shell, namely, σ_g, σ_u, π_g, and π_u. The overall rise of the π symmetry phaseshifts is to be contrasted with the overall flat but oscillatory structure of the σ symmetry phaseshifts. Each local enhancement of phase (in all four channels) is due to penetration

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†It is recommended that the reader consult Ref. 3 for a detailed account of the applications of the multiple-scattering method to the electronic structure of the molecules.

TABLE 1. Conditions Required for Numerical Convergence

Energy range, Ry	Maximum ℓ Region I	Region III
0 – 5	7	11
5 – 10	9	15
10 – 20	11	21
20 – 30	13	25
30 – 40	15	29
40 – 50	17	33
50 – 60	19	35

into the molecular core of a particular ℓ component of the continuum wavefunction. Even-ℓ components contribute to the g phaseshifts and odd-ℓ components contribute to the u phaseshifts. As a result, the oscillatory pattern alternates between the σ_g and π_g channels on the one hand and the σ_u and π_u channels on the other hand.

Each local enhancement in phaseshift results in a corresponding enhancement in the integrated cross section. This is seen most clearly in Figure 2 where the resultant cross sections due to even-ℓ and odd-ℓ are plotted separately. In Figure 3 the (observable) sum of these cross sections is plotted, together with twice the atomic K-shell photoionization cross section, computed in the Hartree-Slater model.[6] Near threshold the molecular cross

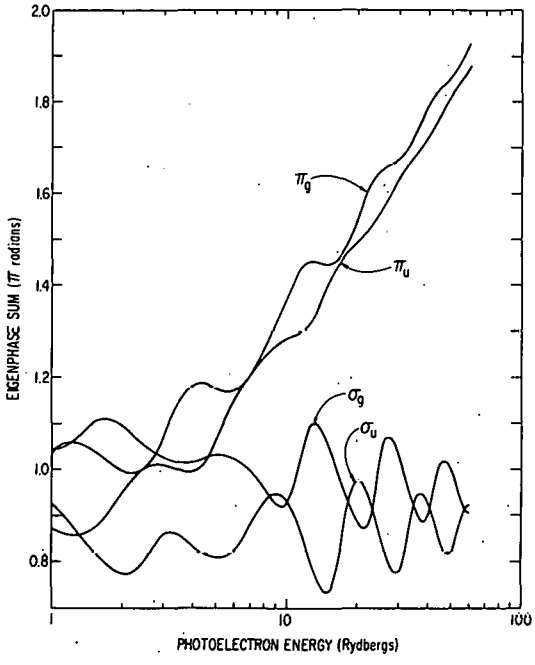

FIG. 1.--Eigenphase sums for the allowed ionization channels in K-shell photoionization of Br_2.

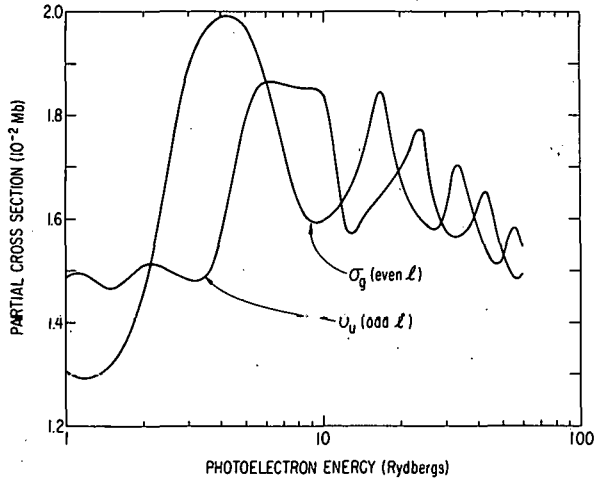

FIG. 2.--Decomposition of the theoretical K-shell photoabsorption cross section for Br_2 into partial cross sections corresponding to even-ℓ and odd-ℓ components of the final state wavefunction.

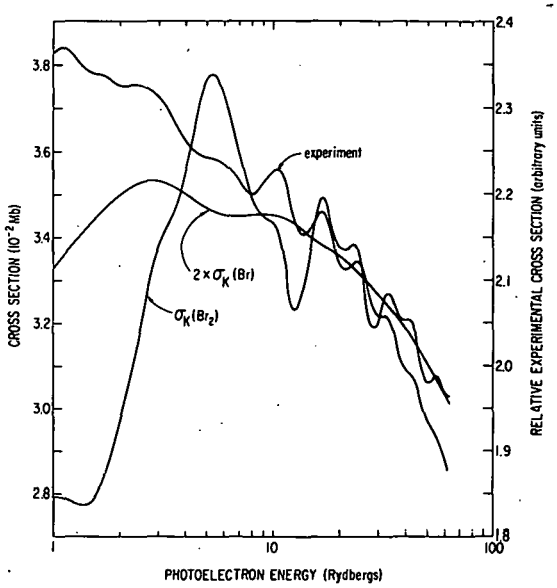

FIG. 3.--Comparison of theoretical K-shell photoabsorption cross sections of Br_2 and Br with experimental results for Br_2 (Ref. 7).

section is depressed relative to the reference atomic cross section. This reflects the concentration of oscillator strength below threshold brought on by the enhanced binding properties of the molecular field.[2] However, the molecular cross section rises rapidly to a broad maximum at 5 Ry, and thereafter it oscillates about the atomic cross section with an amplitude of 2 to 3%.

These oscillations are seen in the recent experimental work of Kincaid and Eisenberger.[7] Their relative cross section results are plotted in Figure 3. This permits a comparison of calculated and observed peak positions, given in Table 2 (the peak numbers are arbitrary). While agreement in peak positions is encouraging, the doublet-like pairing of the calculated peaks is not confirmed by the measurements. This doublet structure is seen in Figures 1 and 2 to trace to an asymmetry in the photoionization intensity according to the parity of the continuum ℓ-component. This asymmetry seems physically unreasonable, especially at the higher energies. It may be due to our neglect of localization of the residual K-shell vacancy on one atom. We are investigating this aspect further.

TABLE 2. Peak Positions for the Extended Fine Structure in Br_2

Peak number	Peak position, Ry		
	Calculated	Observed	% difference
1	5.3	5.8	8.6
2	10.0	10.8	7.4
3	16.8	16.6	1.2
4	23.0	24.0	4.2
5	33.2	32.0	3.8
6	41.5	42.5	2.4
7	55.0	55.0	—

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