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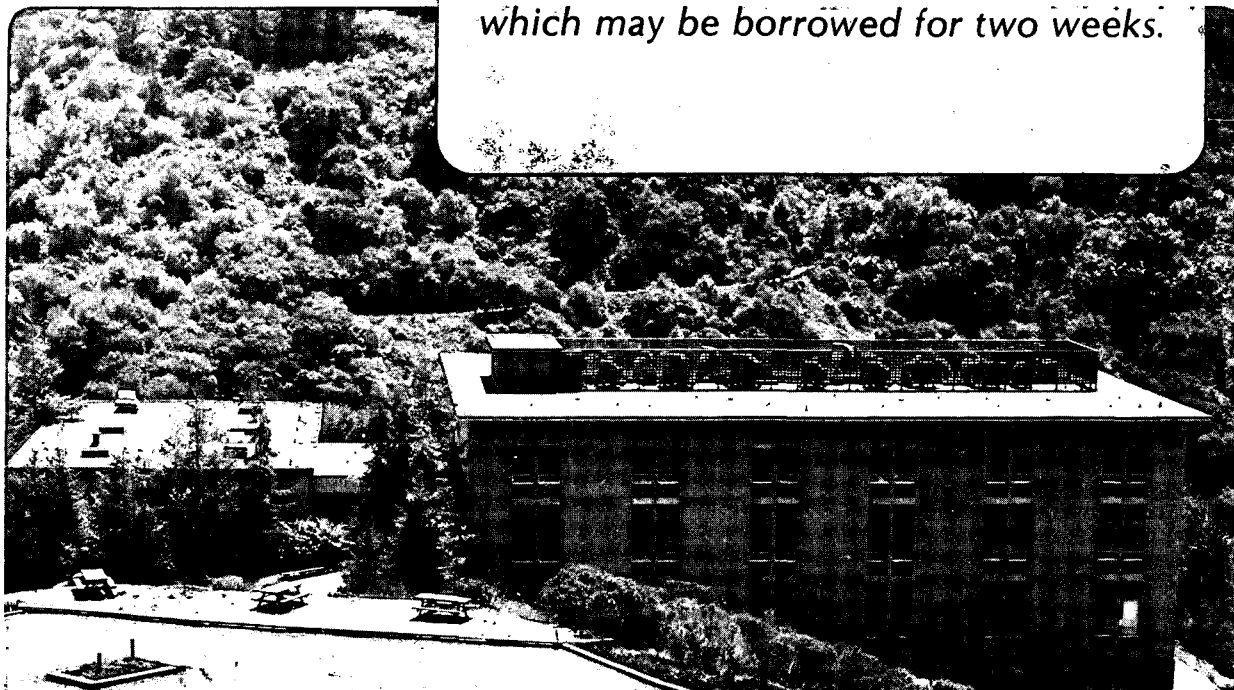## Materials & Chemical Sciences Division

PHOTOELECTRON ASYMMETRY PARAMETER FOR THE S 2p LEVEL OF SO$_2$: A ONE-DIMENSIONAL BARRIER CASE

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Photoelectron Asymmetry Parameter for the S 2p Level of SO$_2$: a One-dimensional Barrier Case

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Abstract

We present a measurement of the asymmetry parameter (β) for S 2p core-level photoionization of SO$_2$ in the vicinity of several continuum resonances. Results are contrasted with β(2p) for the central atoms of the molecules SF$_6$ and SiF$_4$. Atomic calculations for β(S 2p) appear to reproduce qualitatively the molecular curve for SO$_2$ aside from a shift to lower β-values for the molecular case.

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The series of core-level absorption spectra including H_2S, SO_2, SiF_4, and SF_6 have been used to illustrate the wide extent and variety of discrete and continuum resonances in molecular photoemission [1,2]. The SO_2 $L_{2,3}$ photoabsorption spectrum [1], shown in Fig. 1, displays a number of resonances. Features a through d have been ascribed to discrete molecular-orbital excitations and features f and g to Rydberg transitions. High resolution measurements have revealed even more Rydberg structure just below the S 2p edge (175 eV) [3].

In this work, we concentrate on the S 2p continuum, where oscillations over the broad resonances h and i have been related to analogous features in SF_6 (t_{2g}, e_g) and SiF_4 (e, t_2) caused by potential-barrier effects [1,2,4]. A centrifugal barrier on the perimeter of the molecule can be created by the sensitive interplay of attractive (electrostatic) and repulsive (centrifugal) forces. Quasibound states are formed just below the barrier and can be generally associated with excitations to unoccupied molecular orbitals. In the one-electron approximation, the decay of shape resonances leads to an enhancement only in the corresponding main-line continuum channel in the photoelectron spectrum (S 2p for a resonance above the $L_{2,3}$ edge).

These shape resonances are especially pronounced above the S 2p edge of SF_6. The electronegative F atoms in this high symmetry molecule serve to enhance both the magnitude and the spatial extent of the barrier relative to other molecules. In addition, strong

multi-electron effects are exhibited in the decay of the e_g resonance in SF_6 to both the S 2p main line and a S 2p shake-up satellite [5]. In contrast, recent experiments [6,7] on Si 2p photoionization of SiF_4 showed that the fairly intense continuum features in this molecule do conform to the one-electron description [2,8] of quasibound continuum states, with observed decay only to the Si 2p main line.

Despite these differences in the resonant decay characteristics, both SF_6 [5] and SiF_4 [9] exhibit S 2p and Si 2p asymmetry parameters which are nearly identical as a function of kinetic energy. This similarity in $\beta(2p)$ is puzzling, because it seems to imply that the asymmetry parameter, normally sensitive to details of the potential field, is unaffected by the substantial difference between the SiF_4 and SF_6 potential barriers. To explore this question further, we have measured $\beta(S\ 2p)$ for SO_2, where the analogous continuum features are much weaker. The SO_2 molecular potential lies between the atomic and the three-dimensional high-symmetry molecular case. In "one" dimension, along the S-O molecular axis, the barrier should more resemble that in SiF_4 and SF_6. In perpendicular directions the potential is more atomic, and the photoelectron should escape more easily. The object of this study was to ascertain whether $\beta(2p)$ would reflect this intermediate character, or whether it would simply follow the atomic or molecular curves.

Photons emitted from the new 4° "grasshopper" monochromator at

the Stanford Synchrotron Radiation Laboratory (SSRL) ionized an effusive jet of SO_2. The β-parameter was obtained from the ratio of intensities in two time-of-flight electron detectors oriented at $0°$ and $54.7°$ with respect to the photon polarization vector, and using Yang's theorem [10]. The experimental methods have been described in detail elsewhere [11-13]. Calibration of β as a function of kinetic energy was based on the known values of β for Xe(4d) [14,15], Ne(2s), and Ne(2p) [16] photoemission. Systematic errors contribute ±0.10 to the error in β beyond the statistical errors shown in the figure. The photon-energy calibration was obtained to within ±1.0 eV from the time-to-energy converted spectra using known binding and kinetic energies of the following photoemission and Auger peaks: Ne(2s), Ne(2p) [17], Xe(4d) [15], Xe 4d Auger [12,18], and SO_2(S 2p) [3].

In Fig. 2 we show β(S 2p) for SO_2 along with a solid curve to represent the experimental results [5] for β(S 2p) of SF_6. Although not shown in Fig. 2, β(Si 2p) for SiF_4 [9] is nearly identical to the curve for SF_6 as a function of kinetic energy. For SO_2, β(S 2p) increases smoothly from threshold, in contrast to a sharp change in β(S 2p) for SF_6 near 15 eV kinetic energy associated with the e_g shape resonance. In comparison with β(S 2p) for SF_6 and SiF_4, there is no pronounced minimum for SO_2. From Fig. 1 we see that the SO_2 continuum feature i (hν=196 eV) is within the range of our measurement, but no apparent oscillation is present in β(S 2p).

We also compare to Hartree-Slater central field calculations [19] of β(2p) for atomic sulfur (dashed curve, Fig. 2). The atomic β

displays a minimum near threshold caused by the energy–dependent interaction of the ϵs and ϵd photoelectron waves. The $\beta(S\ 2p)$ for SO_2 shows the same qualitative trend as the atomic curve, aside from a shift to a lower absolute value of β. A previous comparison has been made between $\beta(Si\ 2p)$ for SiF_4 and atomic calculations for silicon with a similar result [9]. It was found that variation of the charge on Si to more positive values (relative to the neutral potential) tended to lower the β curves [9]. The atomic curve thus simulates the energy dependence of the molecular β reasonably well for SO_2; the lower value of β in molecules is partly due to effective charge differences on the central atom. There is a somewhat larger deviation from the atomic curve at lower kinetic energies; there is no minimum apparent in $\beta(S\ 2p)$ for SO_2. The minimum might be very close to threshold, as in the S atom, and thus outside the range of our results.

In conclusion, SO_2 demonstrates resonant effects in the $L_{2,3}$ absorption spectrum (Fig. 1), but overall $\beta(S\ 2p)$ behaves much like its atomic sulfur counterpart. We note that photoemission experiments on the valence ionization of SO_2 found no evidence for potential–barrier effects [20]. Another example to study is H_2S, for which there are no detectable continuum resonances above the S 2p threshold.[1] We believe that $\beta(S\ 2p)$ for H_2S should conform even more closely to atomic predictions.

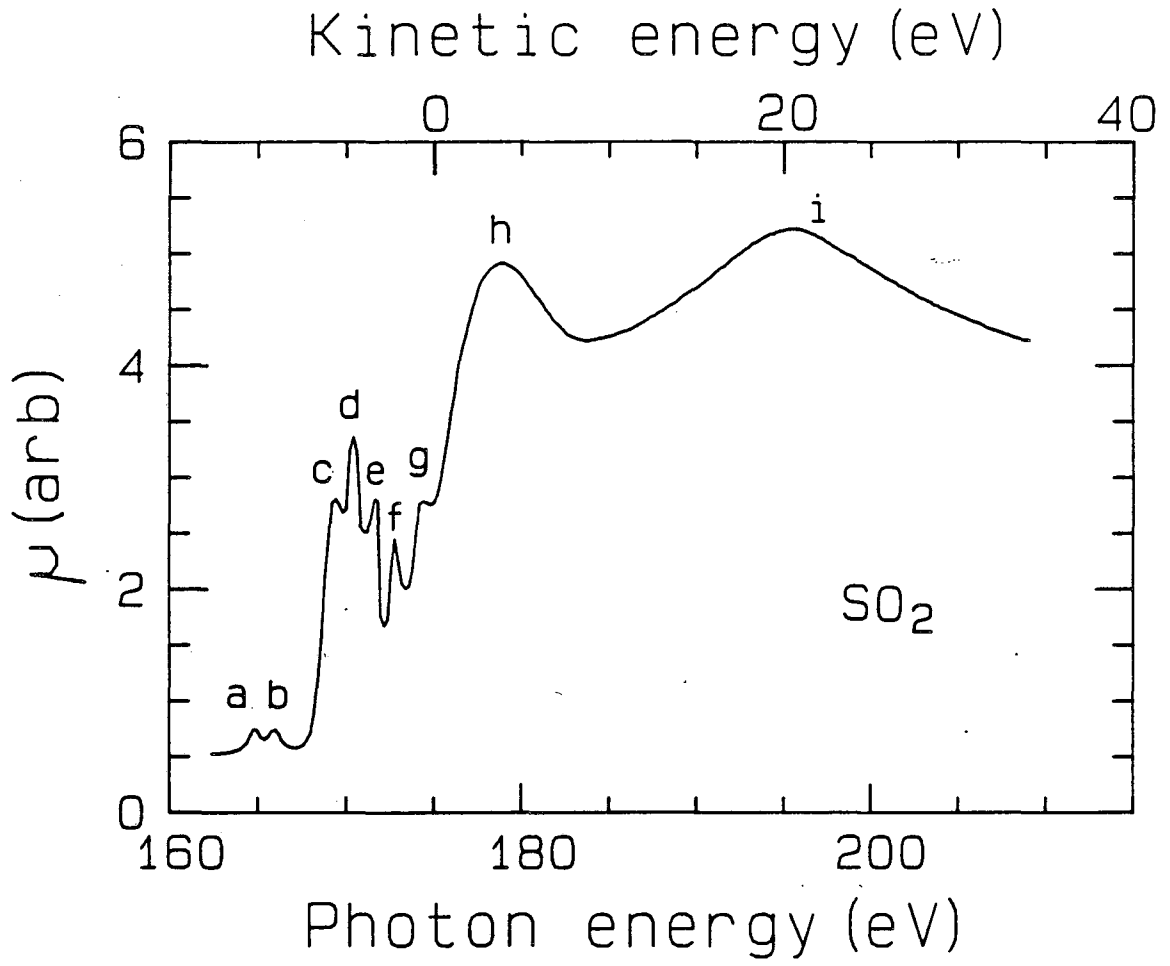## Acknowledgements

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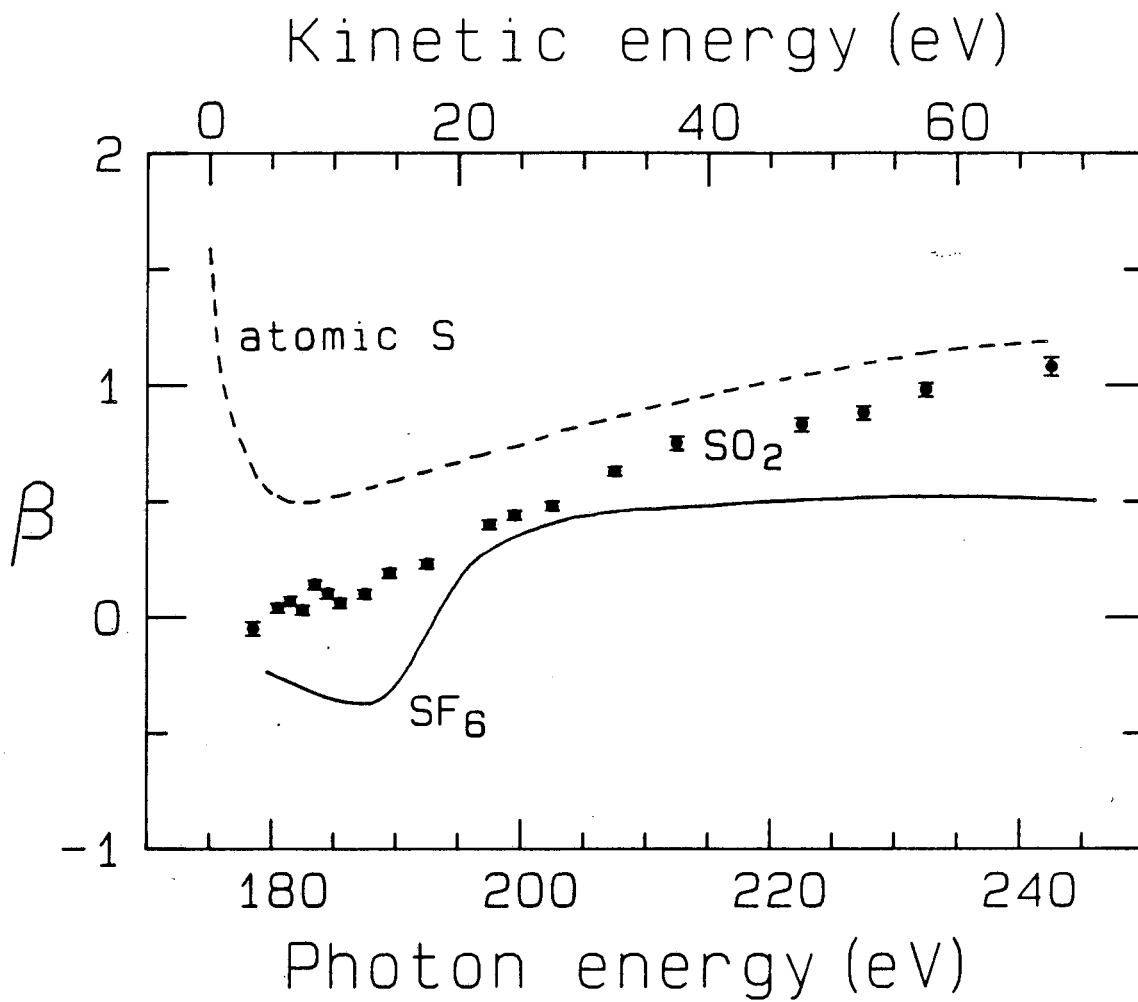
Figure Captions

Fig. 1 The photoabsorption coefficient μ (arbitrary scale) for SO_2 in the vicinity of the $L_{2,3}$ edge. Notation for features a through i is taken from Ref. 1.

Fig. 2 The S 2p asymmetry parameter (β) for SO_2 as a function of photon energy (bottom scale) and kinetic energy (top scale). The solid curve represents experimental data for β(S 2p) of SF_6 [5], plotted as a function of kinetic energy. Hartree-Slater theory curve [19] for the atomic β(2p) of sulfur is also shown (dasned), as a function of kinetic energy.

Figure 1

Figure 2

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