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CONF-830821--3

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PACS:33.50.Eq;33.80.Eh

POLARIZATION OF FLUORESCENCE: A PROBE OF MOLECULAR AUTOIONIZATION*

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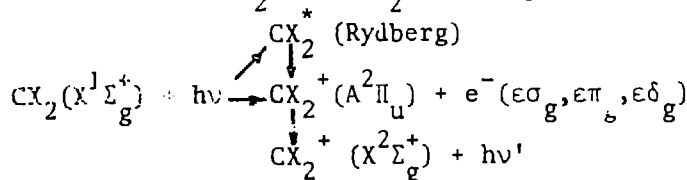
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ABSTRACT

The polarization of fluorescence from excited-state molecular photoions provides a direct probe of the photoionization dynamics and the symmetry signatures of autoionizing resonances. Measurements on CO₂ and CS₂ are presented as examples.

The polarization of fluorescence from excited-state molecular photoions provides a direct measure of their alignment, and thus the relative dipole strength of degenerate excitation channels.^{1,2} Hence fluorescence polarization can be used to characterize the symmetry signatures and dynamical properties of autoionizing resonances.³ We report here the excitation wavelength dependence of the polarization of A²Π_u - X²Π_g fluorescence from CO₂⁺ and CS₂⁺. The processes studied are represented below:



Here CX₂ is either CO₂ or CS₂, and e denotes a continuum electron.

In the experiments, monochromatic VUV radiation (0.8Å bandwidth) from SURF-II (Synchrotron Ultraviolet Radiation Facility at the U.S. National Bureau of Standards) impinged on the gas sample which expanded from an effusive jet. At each excitation wavelength, undispersed fluorescence (hν') at 90° was collected by a planoconvex lens, passed through a polarizer rotated under computer control, and detected by a thermoelectrically cooled photomultiplier. The data were corrected for instrumental effects and the incomplete polarization of the incident radiation. Excitation spectra were obtained with the polarizer removed.

*This work was supported by the U. S. National Science Foundation, the U. S. Department of Energy, the U. S. Office of Naval Research, and the Research Corporation.

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The results for CO_2 are shown in Fig. 1. The excitation spectrum (bottom frame) shows extensive autoionization structure and is in good agreement with previous work.^{4,5} The corrected fluorescence polarization spectrum (P_{fl} , top frame) shows analogous structure, superimposed on a non-resonant background for which $P_{fl} \approx -0.07 \pm 0.01$. Theoretical work^{6,7} indicates that $1\pi_u \rightarrow \epsilon\delta_g$ photoionization is the dominant nonresonant excitation channel near the A-state threshold for CO_2 , and the experimental result is consistent with the polarization calculated² upon that expectation: $P_{fl} = -0.077$. This value arises because the absorption transition dipole is perpendicular to the internuclear axis, whereas the fluorescence transition dipole is parallel to that axis.²

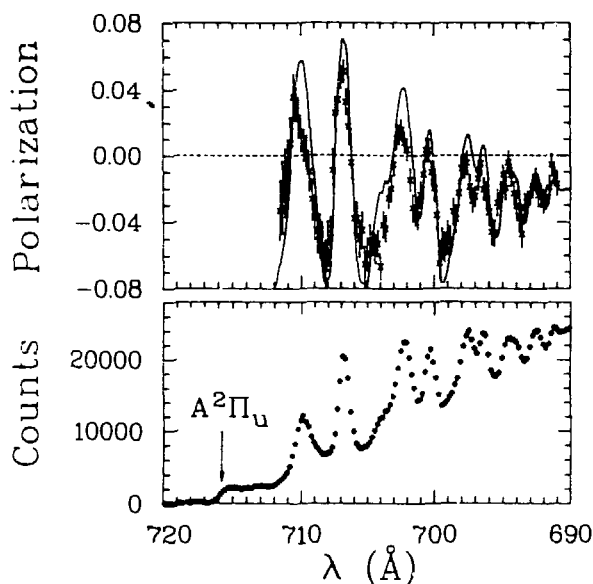


Fig. 1. Excitation spectrum (bottom) and corrected polarization profile (top) for $A \rightarrow X$ fluorescence from CO_2^+ . The solid line is P_{fl} predicted by a simple mixing model.

from the excitation spectrum, based on a simple weighted average of resonant and nonresonant contributions at each wavelength.

For CS_2 , several autoionizing Rydberg series which converge to the B-state of the ion have been identified.^{10,11} A small portion of the fluorescence excitation spectrum (bottom) and the corresponding polarization profile (top) are shown in Fig. 2. The polarization behavior shows clearly that the two resonance features in

The symmetry of the autoionizing Rydberg states will also determine the fluorescence profile in the regions of resonant excitation. There has been some ambiguity regarding the symmetry assignments in this spectral region,^{8,9} but we obtain rather good agreement with the polarization data if we assume that each resonant feature emanates from a $1\Sigma_u^+$ Rydberg state. In this case the transition dipoles are parallel to the intermolecular axis for both absorption and fluorescence, leading to $P_{fl} = +0.143$ for the resonant contributions.² (Rydberg states with $1\Pi_u$ symmetry lead to $P_{fl} = -0.077$, like the nonresonant background.) Hence, these results contradict an earlier assignment⁹ of the 707Å peak as $1\Pi_u$. The solid line in the top frame of Fig. 1 represents the P_{fl} predicted

the excitation spectrum belong to states with *different* symmetry. The stronger peak contributes the positive P_{f1} expected from a Σ state; however, the sharp decrease in P_{f1} at the longer wavelength peak reflects a Rydberg state of Π symmetry. Other members of the latter series are similarly distinguished elsewhere in the polarization spectrum.

These results demonstrate that the alignment of an excited molecular ion in the laboratory frame, which is dependent on the dipole strengths of the competing ionization channels, is reflected in the fluorescence polarization data. Polarization of fluorescence from excited photoions yields spectroscopic and dynamical information about resonant and nonresonant excitation pathways *directly*, thus complementing existing probes of molecular photoionization.

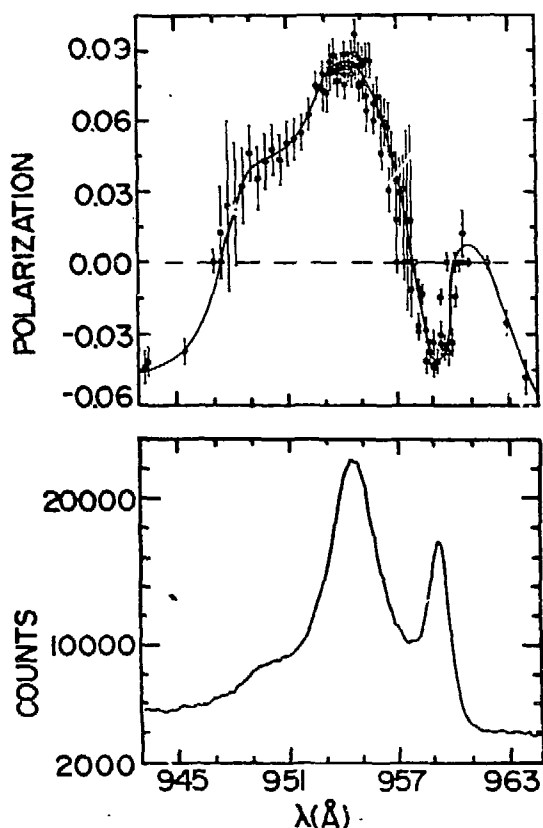


Fig. 2. Portion of the excitation (bottom) and polarization (top) spectra for $A+X$ fluorescence from CS_2^+ [The line through the data points is a guide to the eye, only.]

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