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COMMUNICATIONS

Shape resonance effects in the rotationally resolved photoelectron spectra of O₂

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Studies of rotationally resolved photoionization in molecules can provide insight into molecular properties and dynamics, including important details of excited electronic states,^{1,2} as well as the angular momentum composition of³⁻⁵ and the influence of autoionization on⁶⁻⁸ the electronic continuum. Recently, Tonkyn *et al.*⁹ used narrow band VUV laser radiation and a novel pulsed field ionization (PFI) technique to measure the photoelectron spectrum of O₂ with rotational resolution near threshold, where a shape resonance has been well documented in *vibrationally* resolved and other studies.¹⁰⁻²⁰ Analysis of *rotational* branch intensities (and photoelectron angular distributions) should reveal rich and otherwise unavailable information on the partial wave character of shape resonances. In addition, the internuclear distance dependence of the electronic transition moment associated with this shape resonance²¹⁻²⁴ can be expected to lead to a dependence of the rotational branch intensity on the ion vibrational state.

Figure 1 shows results of theoretical and experimental studies of rotationally resolved single-photon photoelectron spectra of O₂ leading to the $v^+ = 0, 1, \text{ and } 2$ levels of the $X^2\Pi_g$ state of O₂⁺ at threshold. These "cold spectra" clarify the analysis of the rotationally warm ($T \sim 200$ K) spectrum reported in Ref. 9, which showed a great deal of spectral congestion. Briefly, a single tunable VUV photon excites ground state O₂ molecules to very high Rydberg states ($n \geq 180$), within a few cm⁻¹ of the ionization threshold. A weak electric field (< 0.5 eV/cm) is used to ionize these Rydberg levels after a time delay. Field ionization of these Rydberg levels just below threshold should provide a measure of the direct near-threshold photoionization cross sections due to the continuity of the oscillator strength across the threshold. As long as the Rydberg levels are field ionized with uniform efficiency, l mixing induced by the external

field will not affect the interpretation of the intensities. The photoelectron spectrometer and VUV laser source have been described in detail elsewhere.^{9,25} The spectrometer has been modified here to incorporate a differentially pumped pulsed molecular beam source for rotational cooling of the target molecules. The rotationally resolved photoelectron spectra are calculated by generalizing the earlier treatment²⁶ to include a complete description of the mixed Hund's case (a)-(b) ionic ground state, the details of which will be given elsewhere.²⁷ The required bound-free amplitudes are obtained with static-exchange photoelectron orbitals^{28,29} and include a full treatment of the internuclear distance dependence of the electronic transition moment caused by the shape resonance.¹⁰

The calculated rotational spectra at 5 K, where only the $K = 1$ rotational level of the ground state is significantly populated, are dominated by low $\Delta K = (K^+ - K)$ branches ($Q-S$ for F₁; $R-T$ for F₂). Analysis of the transition amplitudes shows that these branches are mostly due to $l = 1$ partial waves. The high ΔK branches ($T-V$ for F₁; $U-V$ for F₂), on the other hand, are dominated by $l = 3$ partial waves. The difference in the angular momentum composition of the photoelectron wave function for low ΔK peaks versus high ΔK peaks is especially evident in the photoelectron angular distributions which will be discussed in a future publication.²⁷ Calculated spectra at higher resolution (not shown) which can distinguish between different J levels in the ground state ($J = 0, 1, \text{ and } 2$ for $K = 1$)³⁰ reveal even richer information on the partial wave character of the photoelectron continuum. For example, for certain J -resolved branches, *only* $l = 3$ and higher waves are allowed.²⁷

As the vibrational excitation increases from $v^+ = 0$ to 1 to 2 in the 5° spectra, the ratio of low ΔK peaks to high ΔK peaks increases significantly. This mirrors the fact that the $l = 1$ photoelectron amplitudes increase with vibrational excitation compared to the $l = 3$ components. *This is a direct*

^{a)} Contribution No. 8145.

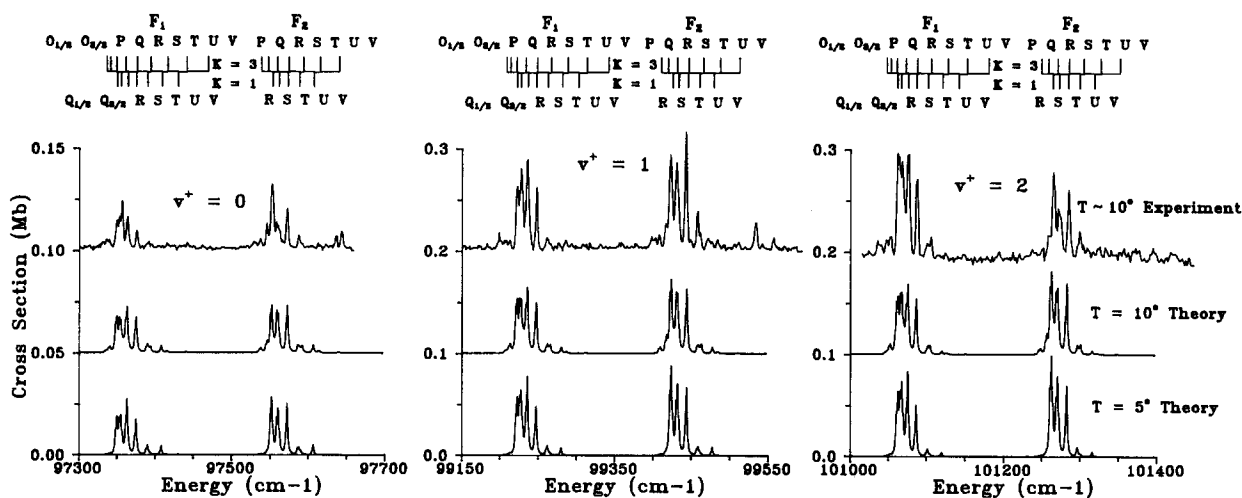


FIG. 1. Threshold photoelectron spectra for single-photon ionization of O_2 ($X^3\Sigma_g^-$) leading to O_2^+ ($X^2\Pi_g$). The branch designations refer to $\Delta K = (K^+ - K)$ transitions. For example, an "S" branch under F_1 on the bottom row of letters refers to a transitions from the $K = 1$ rotational level of the ground state to the $K^+ = 3$ level of the F_1 spin-orbit manifold of the ion. The theoretical spectra have an assumed linewidth of 2 cm^{-1} . The experimental spectra have arbitrary intensity units. The baselines of the 10° spectra have been shifted upward by a constant amount.

result of the internuclear distance dependence of the electronic transition moment due to the shape resonance. Without the shape resonance, we would expect the same ratio of $l = 1$ to $l = 3$ amplitudes for all vibrational levels and therefore the same relative peak heights in all spectra. It should be stressed here that an accurate description of the partial wave coupling between $l = 1$ and 3 in the σ_u shape resonance is critical in the analysis of these rotational intensities.

At $T = 10\text{ K}$, these differences in the rotational branch intensities with vibrational level are still evident in the theoretical and experimental spectra, but are more difficult to quantify due to the overlapping transitions originating from the $K = 3$ level, which now has an appreciable population (approximately 30% of the total intensity comes from $K = 3$ at 10°). The agreement between these 10° spectra is encouraging, especially for the $v^+ = 1$ and 2 levels. Some important differences do exist, and will be addressed in a future publication.²⁷

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