

The multiplet state distribution of $O(^3P_J)$ produced in the 193 nm photodissociation of SO_2

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The ultraviolet photodissociation of SO_2 has been the subject of numerous dynamical studies, all of which were concerned with the momentum and internal state distributions of the SO fragment.¹⁻⁵ It is now well established that at 193 nm ~50% of the available energy appears as translation,^{1,5} 10% in rotation,⁵ and the remainder in vibration with a distribution sharply peaked at $v = 2$.^{1,4,5} It has also been found that the spin of SO ($^3\Sigma^-$) is aligned along the SO rotational angular momentum vector. In the present note we report the multiplet state distribution for the $O(^3P)$ fragment at 193 nm.

The apparatus will be described in detail in a future publication. Briefly, a gas mixture consisting of either 2 or 28 mTorr SO_2 and 0 to 0.8 Torr of He was flowed slowly through a cubical cell. The SO_2 component was dissociated by single-photon excitation, using a collimated ArF laser (30–50 mJ/pulse). The $O(^3P)$ fragments were probed by two-photon laser-induced fluorescence at 226 nm.⁶ This was accomplished with a tunable UV dye laser which was aligned perpendicular to the 193 nm beam and pulsed after a variable time delay. The 226 nm radiation was produced with a Nd:YAG pumped dye laser, using a 532 nm pulse to pump a mixture of Rhodamine 590 and 610 dyes to generate 572 to 575 nm light. This radiation was then frequency doubled and mixed with the Nd:YAG fundamental. The resulting 226 nm radiation had a pulse energy of 50 μ J, which was focused with a 25 cm focal length lens.

The probe laser beam induced the $3p^3P-2p^3P$ transition in the oxygen atoms. The 130 nm fluorescence from the $3s^3S-2p^3P$ transition was monitored with a solar blind photomultiplier tube fitted with a narrowband interference filter. The dye laser was tuned to the peaks of each of the three multiplet states in succession. For each state the delay time was scanned continuously from 0 to several hundred ns. The fluorescence signal and the intensities of each laser beam were recorded separately, using a three channel gated integrator and a laboratory computer.

The two-photon absorption cross sections for all three $2p$ multiplet states are expected to be equal.^{6,7} This was confirmed experimentally by quenching the $O(^3P_J)$ atoms with Ar and measuring the resulting state distribution. A 300 K Boltzmann distribution was observed at long times. Moreover, the sum of the intensities of all three states were constant over this interval. These tests confirm that no external calibration is needed to obtain the relative concentrations of the multiplet states.

The results of a typical set of scans are shown in Fig. 1. For the pressure used in this experiment the oxygen atoms did not undergo any quenching collisions during the scan, and the signal strengths reflect the nascent populations of the three multiplet states. The data shown in this figure were

normalized as follows. First, the data points in each scan were divided by the 193 nm intensity and by the square of the 226 nm intensity for each laser shot. Each scan was then multiplied by a scale factor chosen so that the sum of the populations averages to unity.

For each scan an average over all of the laser shots was calculated for each multiplet state. From an average of five such experiments we find that the populations are $59.2\% \pm 5.0\%$, $29.5\% \pm 3.2\%$, and $11.4\% \pm 3.3\%$ for $J = 2$ (ground state), $J = 1$ (158.5 cm^{-1}), and $J = 0$ (226.5 cm^{-1}), respectively, with error bars of two standard deviations. These results are nearly in the same ratio as the multiplet degeneracies, namely 5:3:1.

The multiplet state distribution can have two limiting forms, depending on the amount of energy available. At low recoil energy the distribution is governed by the adiabatic Born-Oppenheimer potential energy surfaces. In this limit symmetry correlation selects one or two of the multiplets. At

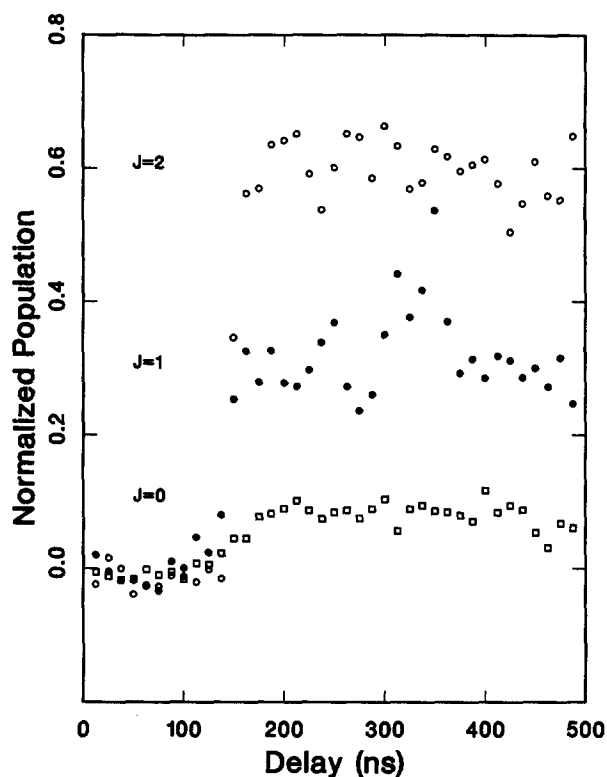


FIG. 1. Laser-induced fluorescence signal from $O(^3P_0)$, $O(^3P_1)$, and $O(^3P_2)$ as a function of the delay between the pump and probe lasers. A neat SO_2 pressure of 28 mTorr was used in this run. The excimer laser was fired at a fixed time of 151 ns, while the YAG laser was triggered with a variable delay time which was incremented by 5 ns after every 20 laser shots. The gated integrators recorded a running average of 30 shots. The resulting digital signal was normalized and averaged as described in the text. The plotted points each represent an average of 50 laser shots.

the high energy limit a frame transformation produces a statistical distribution with all three states populated in proportion to their degeneracies.⁸ Further restrictions will result if not all of the fine structure states are excited by the laser, or if the molecule predissociates. In the latter case the matrix elements for the operator coupling the two potential energy surfaces may favor specific multiplet states.

The present results are to our knowledge the first report of a statistical distribution of atomic multiplet states produced in a photodissociation reaction. Examples of nonstatistical distributions are the photodissociation of HCl,⁹ O₂,¹⁰ CdXe,¹¹ CS₂,¹² and NO₂.¹³ The observation of a statistical distribution for SO₂ is surprising in light of the observed spin polarization of the SO fragment.⁴

A question we wish to address is whether the observed SO₂ distribution is due to a sudden frame transformation or to some other mechanism. A simple measure of the suddenness of the dissociation is given by the adiabaticity parameter,¹⁴⁻¹⁷ $A = t_n/t_e$, where t_n is the time it takes the nuclei to recoil a characteristic distance R , t_e is the electron precession time $\hbar/\Delta E_{SO}$, and ΔE_{SO} is the spin-orbit splitting. Using theoretical calculations as a guide we find that the statistical limit is reached at $A = 1.1$ for HCl¹⁸ (with $R = 2 \text{ \AA}$) and at 0.65 for NaAr¹⁵ (with $R = 3.7 \text{ \AA}$), while the ratio of multiplet populations is double the statistical value at $A = 1.6$ and 1.4.

In the case of SO₂, using the experimental peak recoil velocity¹ and taking $\Delta E_{SO} = 226.5 \text{ cm}^{-1}$, $A < 1$ is obtained only for $R < 0.6 \text{ \AA}$. Thus even though $E = 14\Delta E_{SO}$, there is no compelling reason to believe that the molecule is in the high energy limit. Moreover, it is thought that SO₂ predissociates by curve crossing from the \tilde{C}^1B_2 state to either a $^3A'$ or a $^1A'$ state.⁴ As mentioned previously, the matrix elements of the coupling operator should produce a nonstatistical distribution of multiplet states at any energy.¹⁹ Thus a sudden recoil is not a valid explanation of the observed statistical distribution. Adiabatic dissociation is also not a possible explanation; symmetry correlation predicts that most of the

atoms should be in the $J = 2$ state and none in $J = 0$. A more likely explanation is the existence of exit-channel effects, such as bend-stretch interaction at short distances and spin-orbit and coriolis coupling at long distances, which can uncouple the spin and orbital angular momentum vectors of the oxygen atom. In contrast, the spin of the SO product is coupled to the rotational angular momentum vector and retains a memory of the nascent conditions.

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Phase measurements of optical second harmonic generation on Au(111) during thallium underpotential deposition

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In surface studies of metals and semiconductors the intensity of the second harmonic (SH) response has been used to monitor surface structure and adsorption.¹ Additional information is available in the phase of the second harmonic fields. This is of particular interest when resonant optical transitions are involved. We present here the first use of phase measurements in investigating adsorbate contributions to the anisotropic second harmonic response of single

crystal metals. By using polarized light, the nonlinear response parallel to the interface is isolated from the response of a Au(111) electrode. The phase and intensity of the SH light is then monitored as the surface is modified by electrochemical adsorption of thallium. Intensity changes are accompanied by a pronounced phase shift as the coverage exceeds a monolayer, documenting the formation of new interfacial states with a significant nonlinear response. These