OZONE PHOTODISSOCIATION IN THE SINGLET CHANNEL AT 226 NM

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Ozone photodissociation plays an important role in atmospheric chemistry and has been the focus of many experimental and theoretical studies. In the Hartley band (200-300 nm) there are two spin-allowed dissociation channels, one forming excited state, singlet products (O2(a 1Δg) + O(1D)), and one forming ground state, triplet products (O2(X 3Σg-) + O(3P)). The singlet channel is the primary dissociation channel in the Hartley band, and numerous studies have characterized the dissociation at longer wavelengths within the Hartley band. There has been considerable interest in the triplet channel dissociation at 226 nm following the observation of low velocity O(3P) fragments, but the singlet channel dissociation dynamics at 226 nm has not been previously reported. We report the rotational state distribution and vector correlations of the O2(a 1Δg, v=0) fragments arising from the 226 nm photodissociation of jet-cooled O3. Consistent with previously reported trends, the rotational distribution is shifted to higher rotational states with decreasing wavelength. We observe highly suppressed odd rotational state populations due to a strong Λ-doublet propensity. The measured rotational distribution is in agreement with classical trajectory calculations for the v=0 products, although the distribution is narrower than predicted. The spatial anisotropy follows the previously observed trend of decreasing β with increasing photon energy with β = 0.72 $\pm$ 0.14 for v=0, j=38. As expected for a triatomic molecule, the v-j correlation is consistent with v perpendicular to j, but the measured correlation is non-limiting due to rotational and translational depolarization. The j-dependent linewidth of the O2(a 1Δg) REMPI spectrum is also discussed in connection with the lifetime of the resonant O2(d 1Πg) state and predissociation via the II 1Πg valence state.