SPECTROSCOPY OF GLYOXAL NEAR THE THRESHOLD FOR FORMATION OF HCO

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Fluorescence excitation spectrum for transition $A^1\mathrm{A}_u$-$X^1\mathrm{A}_g$ of $trans-$glyoxal in a supersonic jet is recorded with laser excitation in the wavelength region 394-395 nm. With resolution 0.04 cm^{-1}, most lines in the spectrum are resolved and can be assigned rotationally; in total, six bands are assigned, three having c-type rotational structure, and another three having types a/b hybrid, a, and b, respectively. Fluorescence decays with quantum beats, resulting from coherent excitation of S_1 and T_1 states, are observed for most rotational levels. From the spectra transformed to the frequency domain for these decays, the widths increase relative to that obtained at low excitation energy. The widths from non-zero frequency lines, reflecting mostly the triplet character, are broad indicating that the triplet state is dissociating. Fragment HCO is detected with technique of laser-induced fluorescence, confirming that the dissociation channel correlated to the triplet surface of glyoxal is formation of radical products. The threshold for dissociation to form two HCO from $trans-$glyoxal is therefore determined to be 394.4 nm with an exit barrier 2.5 kcal/mol. The state-resolved appearance rates of HCO for various rotational states for the vibrational state near dissociation threshold are measured. Some gateway states with strong singlet/triplet interaction are observed to show the fast intersystem crossing rate, consequently enhancing yields of HCO that are produced from the triplet surface.