

ANOMALOUS Q BRANCH INTENSITY IN THE 2+1 REMPI SPECTRUM OF THE ${}^1\Pi-{}^1\Sigma^+$ TRANSITION IN HIGHLY ROTATIONALLY EXCITED CO PHOTOFRAGMENTS FROM OCS PHOTODISSOCIATION AT 215 NM

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Nascent CO ($X\ {}^1\Sigma^+$) photoproducts formed in the dissociation of OCS at 215 nm were probed using 2+1 resonance enhanced multiphoton ionization (REMPI) through the $E\ {}^1\Pi$ state. This photodissociation produces a highly rotationally excited CO distribution, with fragment rotational levels ranging from $J=48$ to $J=77$. The resulting REMPI spectrum contains a prominent Q branch, despite negligible line strength factors for high J, two-photon, $\Pi-\Sigma$, Q branch transitions. The presence of a Q branch in the spectrum is explained by intensity borrowing from the nearby $C\ {}^1\Sigma^+$ state, as coupling between the C and E states is well documented, and two photon, $\Sigma-\Sigma$, Q branch transitions are intense for high J states. The observed relative intensities of the Q and S branch lines are well described by extrapolation to high J of the J-dependent mixing of C and E states inferred from the E state lambda doublet splittings at lower J. Improved D_e and D_f constants have been derived through the incorporation of this high J data.