PREDISSOCIATION OF THE D STATE OF CaI. INVESTIGATION OF CaBr and CaI BY CAVITY RING DOWN SPECTROSCOPY.

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A Cavity Ring Down Spectroscopy has been set up to investigate predissociation in the alkaline earth monohalides MX (M = Mg, Ca, Sr, Ba, X = (Br, I) [a]. Preliminary experiments were carried out on the B-X transition of CaBr, formed by chemical reaction in a Broida oven, where the effective path length was extended from 1 cm to 1 m. The rotational structure of the CRDS and laser excitation B-X spectra recorded under identical experimental conditions are different, pointing out specific effects of the CRDS technique. Laser excitation studies of the D-X transition of CaBr and CaI have revealed important differences between the $D^2\Sigma^+$ states of CaI and its homologues of the CaX series. The main difference arises from the fact that the dissociation limit of CaI lies much lower than in the case of the other CaX. The anomalous structure of the D-X transition of CaI is most likely due to the interaction with the $D'^2\Sigma^+$ repulsive state which dissociates to Ca($^1$S) + I($^2$P) neutral atoms. CRDS experiments are in progress to investigate quantitatively this predissociation. The position of the repulsive $D'^2\Sigma^+$ state potential curve can be determined through the use of trial-and-error Frank-Condon calculations and matrix elements governing the D-D' interaction obtained.

[a] R. G. Sadygov, J. Rostas, G. Taieb and D. R. Yarkony, J. Chem. Phys., 106 (1997), 4091-4101