MODE SPECIFIC DYNAMICS IN THE PREDISSOCIATED, QUASILINEAR B^1A' STATE OF CHF AND CDF PROBED BY OPTICAL-OPTICAL DOUBLE RESONANCE SPECTROSCOPY

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Last year at this meeting, we reported studies of the predissociated, quasilinear B^1A' state of a halocarbene, CHF, using a fluorescence dip detected optical-optical double resonance technique via the A^1A'' state.[a] Recently, we have extended these observations to the deuterated isotopomer, CDF. The pronounced mode selectivity observed in CHF, where levels containing a combination of C-F stretch and bending excitation dissociate more rapidly than nearby levels, is reversed in CDF. Here we find that overall the mode selectivity is dramatically reduced, and the pure bending states now display the largest widths. These results will be discussed in light of the excited state bending potentials, and bend-stretch interactions, as viewed from an analysis of the vibronic term energies. Such an analysis for CDF yields a barrier height which is in good agreement with high level $ab\ initio$ calculations. The implications of our results for the dissociation mechanism will be emphasized.

[a] C. Tao, S. A. Reid, T. W. Schmidt, and S. H. Kable, J. Chem. Phys. 125, 051105 (2007).