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

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We have recently observed transitions to 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] By exciting selected rotational levels in intermediate states belonging to the progressions 2_0^n, $1_0^1 2_0^n$, and $2_0^n 3_0^1$, a variety of B^1A' state levels have been observed, extending to an energy of 7000 cm^{-1} above the B^1A' state origin. In this talk, we will focus on the dynamics of the B^1A' state. All of the observed lines are predissociated, as evidenced by Lorentzian lineshapes, and the linewidths increase with increasing energy. A pronounced mode specificity is observed; levels containing CF stretching excitation dissociate more rapidly than nearly isoenergetic bending levels. The implications of these 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).