OVERTONE SPECTRUM AND VIBRATIONAL PREDISSOCIATION IN $(HF)_2$ FROM CLASSICAL TRAJECTORY CALCULATIONS ON A 6-DIMENSIONAL ELECTRONIC POTENTIAL ENERGY SURFACE

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The hydrogen fluoride dimer $(HF)_2$ is widely used as prototype system to describe and model dynamics in hydrogen bonded systems. This dimer has the advantage to be particularly ”simple” and therefore allows for both high-resolution rovibrational spectroscopy[a,b] and full dimensional quantum dynamical calculations on accurate potential hypersurfaces[c]. An interesting property and a real challenge for experimentalists and theoreticians is the investigation of the mode selectivity of the predissociation dynamics as well as the relative intensities in the spectra. For instance, using highly resolved pulsed jet CW cavity-ring down experiments[b], we have shown that the lifetime of the 2_1 state involving two quanta of the bonded HF stretching mode is only ~ 50 ps whereas that of the 2_2 state involving two quanta of the free HF stretching mode is more than 1 ns. The 2_3 state exhibits an intermediate behavior ($\tau_{\mathrm{PD}} \simeq 200$ ps).

In this paper[d], we study the vibrational predissociation in the HF dimer with classical trajectory calculations using the accurate fully 6D SO-3 electronic potential hypersurface established previously in our group[c]. Our goal is to obtain a more detailed understanding of the dynamics in this dimer and to provide a benchmark investigation for classical dynamics simulations. We present here our results of lifetimes and absorption spectra for $N = 1, 2, 3$ polyads of the HF stretching modes and compare them with experimental results.

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