

SPECTROSCOPY AND VIBRATIONAL PREDISSOCIATION OF HF VAN DER WAALS COMPLEXES AT $\nu_{HF} = 3$ VALENCE EXCITATION

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Spectra of OC-HF and OCO-HF have been observed via intracavity laser induced fluorescence for $\nu_{HF} = 3$. Two bands arising from the OC-HF molecule have been recorded, and correspond to the (30000) \leftarrow (00000) second overtone and the (30010) \leftarrow (00000) HF Π bend-stretch states. Relative to the $\nu_{HF} = 1$ fundamental, a rather large red shift of 478.3 cm^{-1} is observed at the second overtone, and is one of the largest shifts seen so far in this type of complex. Heavy atom separation shows a pronounced decrease upon valence excitation, as determined from a 7.44% increase in the rotational constant. Vibrational predissociation is extremely facile in both levels, inferred from the essentially Lorentzian lineshape fits, yielding values of 12 GHz for the overtone and 5 GHz for the bending state. The action spectrum of the OCO-HF complex is perhaps the most challenging to unravel. In total, six bands have been recorded, but only two have been tentatively identified. The second overtone HF ($\nu = 3$) valence band shows only a 198.1 cm^{-1} red shift, but a substantial increase of 8.12% in rotational constant relative to the ground state. The HF Π bend-stretch combination appears 364 cm^{-1} above the $\nu_{HF} = 3$ stretch mode. Predissociation linewidths for these two levels are 6 GHz and 3.3 GHz respectively, and are comparable to the OC-HF complex. Several strong features were recorded at -7, +7, +24, and +29 cm^{-1} from the fundamental, but have been as yet unidentified, and may well be linked to the non-linearity of the molecular geometry upon HF valence excitation. Preliminary electronic structure calculations show enhancement of the angular barrier to a linear complex at $\nu_{HF} = 3$, and efforts are currently underway to model the potential as a quartic oscillator to obtain the energy levels, providing a clearer picture of these unexplained emission features. Additionally, a new Michelson interferometer coupled to the intracavity laser induced fluorescence should provide new insight into the HF photoproduct rotational state distributions following the vibrational predissociation.