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Author
Lisy, J.M.

Publication Date
1981-07-01
Submitted to the Journal of Chemical Physics

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Prepared for the U.S. Department of Energy under Contract W-7405-ENG-48
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VIBRATIONAL PREDISSOCIATION SPECTRA OF (HF)_n
n = 2 to 6

James M. Lisy^a, Andrzej Tramer^b, Matthew F. Vernon^c, and Yuan T. Lee

Materials and Molecular Research Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

July 1981

ABSTRACT

Using molecular beam techniques and a tunable infrared laser, the vibrational predissociation spectra for (HF)_n, n = 2 to 6, in the 3000 to 4000 cm\(^{-1}\) range are presented. The vibrational bands have been assigned to intramolecular HF stretching modes and combinations of intra- and intermolecular modes. The structures of (HF)_n, n = 3 to 6, were found to be cyclic, i.e. each HF molecule is both a proton donor and acceptor.

\(^a\) National Science Foundation Postdoctoral Fellow, 1979-80.
\(^b\) Permanent Address: Laboratoire de Photophysique Moleculaire, Batiment 213, Universite de Paris-Sud, 91405 Orsay, France.
\(^c\) Also associated with the Department of Chemistry, University of California, Berkeley, California 94720.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract Number W-7405-ENG-48.
Hydrogen bonding is an interesting, unique and important interaction in chemical and biochemical systems. Detailed molecular beam studies of \((\text{H}_2\text{O})_2\)^1 and \((\text{HF})_2\)^2 have established the vibrationally averaged ground state structures and provided information on the potential energy surface near the minimum. Infrared absorption studies of small hydrogen-bonded clusters have been hindered by uncertainty in assigning features to a specific cluster. We wish to report molecular beam studies of the vibrational predissociation spectra of \((\text{HF})_n\), \(n = 2\) to \(6\) in the 3000 to 4000 cm\(^{-1}\) range, associated primarily with the covalent HF stretching motion, using a tunable infrared laser.

Molecular beams containing small clusters of HF are prepared by supersonic expansion of 0.5 to 3.0% HF in a carrier of He, Ne or Ar. The electron impact quadrupole mass spectrometer monitors the molecular beam directly, with the axis of the quadrupole perpendicular to the molecular beam axis. This permits the infrared laser to propagate coaxially with the molecular beam from the ionizer to the nozzle source (65 cm). For monitoring a given cluster, \((\text{HF})_n\), the predominant ionization product \((\text{HF}_{n-1})^+\) is detected. The infrared laser is a Nd-YAG pumped \(\text{LiNbO}_3\) optical parametric oscillator. As the laser is tuned through the frequency region of interest, the absorption of an infrared photon by \((\text{HF})_n\), which then predissociates, is detected by the depletion of the \((\text{HF}_{n-1})^+\) mass spectrometer signal after the laser pulse. Vibrational predissociation lifetimes between 1 \(\mu\)sec and 1 msec can be determined directly by this apparatus. Details may be found elsewhere.
Figure 1 contains the (HF)$_2$ spectrum and the vibrationally averaged ground state structure as determined by Klemperer et al. The bandwidths are laser linewidth limited (~8 cm$^{-1}$). The spectra of (HF)$_n$ $n = 3$ to $6$ displayed in Fig. 2 are broader than the laser linewidth, with a pronounced red shift from the HF monomer fundamental at 3960 cm$^{-1}$. No other features were observed in the 3000 to 4000 cm$^{-1}$ region. The signals were observed to have a linear dependence on photon number. Depletion of the molecular beam signal was found to occur directly after the laser pulse, indicating predissociation lifetimes of less than 1 µsec for all (HF)$_n$.

The assignment of spectra to specific clusters was done through a series of experiments by varying the source pressure, carrier gas and seeding ratio. The mass spectrometer was essential in confirming the assignments by comparing spectra at different m/e settings. For example, the (HF)$_3$ bands are observed only at m/e = 41, while (HF)$_4$ bands can be found at both m/e = 41 and 61.

The dimer bands are assigned as follows: the 3720 cm$^{-1}$ band to the H-F stretch of the hydrogen-bonded proton, the 3878 cm$^{-1}$ band to the H-F stretch of the "free" proton and the 3970 cm$^{-1}$ band to a combination band involving intra- and intermolecular modes. The latter two bands have been previously observed in the gas phase$^{5,6}$ and our results confirm their assignment to dimer bands. The observed rotational structure$^6$ of the 3970 cm$^{-1}$ band with linewidths of approximately 0.15 cm$^{-1}$, combined with our results, enables the predissociation lifetime, $\tau$, to be limited to 30 psec $\leq \tau \leq$ 1 µsec. The predicted
lifetime of \((HF)_2\), based on an empirical treatment\(^7\) of vibration to translation energy transfer, is 200 psec, which falls within the above range. Predictions based on Ewing's method\(^8\) of 10 to 100 sec underscore his observation that quantitative agreement must await better knowledge of the potential energy surface.

The \((HF)_n\), \(n = 3\) to 6, clusters exhibit a larger frequency shift from the HF fundamental than was observed for the dimer. No absorption was observed above 3500 cm\(^{-1}\), indicating the absence of a terminal \(--\text{H-F}\) or \(--\text{F-H}\) group. Therefore, we conclude \((HF)_n\), \(n = 3\) to 6, to have cyclic structures with each HF as both a proton donor and acceptor. This is in agreement with previous molecular beam deflection\(^2\) results.

The \((HF)_n\), \(n = 3\) to 6, spectra have a similar structure fit by \(\nu_n = \nu'_n + mv''_n\) \((m = 0,1,2)\), where \(\nu'_n\) decreases and \(\nu''_n\) increases with cluster size, \(n\). It seems likely that those progressions are combination bands involving coupled \(\text{H-F} (\nu'_n)\) and \(\text{F-H---F} (\nu''_n)\) modes. The frequency variations with cluster size, \(n\), are in accord with the strengthening of the intermolecular interactions and weakening of the intramolecular bands in progressively larger clusters.

The spectrum of \((HF)_4\) shows a peculiar doublet structure, where the relative intensity of the components depends on the expansion conditions. Each component appears to belong to a separate \(\nu = \nu'_4 + mv''_4\) series, with the lower frequency component exhibiting a larger \(\nu''_4\). Increasing the source pressure, enhancing the adiabatic cooling, increases the relative intensity of the lower frequency component. This could be due
to two (cyclic) tetramer structures, distinguishable on the predissociation timescale, with the lower frequency components assigned to the more stable isomer.

Further experiments involving (DF)\textsubscript{n} and (DF)\textsubscript{n}(HF)\textsubscript{m} are planned, inducing predissociation by excitation of the fundamental and overtone bands. This information will be used to understand the intermolecular potentials, binding energies and structures of HF clusters.

ACKNOWLEDGMENT

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract Number W-7405-Eng-48.
REFERENCES


FIGURE CAPTIONS

Fig. 1. Vibrational predissociation spectrum of (HF)$_2$ corrected and normalized for the photon number, with the structure of (HF)$_2$ as determined by molecular beam electric resonance spectroscopy.

Fig. 2. Vibrational predissociation spectra of (HF)$_n$, $n = 3-6$, corrected and normalized for photon number. The peaks marked with asterisks in the m/e = 41 spectrum are from (HF)$_3$, the other peaks are due to larger clusters.
Fig. 2
This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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