SLIT JET IR ABSORPTION SPECTROSCOPY OF MOLECULAR COMPLEXES

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ABSTRACT. The combination of high resolution ($\leq 10^{-3}$ cm$^{-1}$) cw tunable difference frequency generation, high sensitivity ($\leq 10^{-6}$/Hz) direct absorption methods, and long path length (2.54 cm) pulsed slit expansions provide a powerfully general technique for studying weakly bound complexes in a cold molecular beam environment. Transient absorption of the narrow band laser provides a nonintrusive probe of the quantum state, velocity, temporal and spatial dependence of cluster formation in the pulsed molecular beam. High resolution fundamental, combination and hot band spectra of ArHF, HFNO, and HFCO$_2$ complexes are presented. Detailed information on the molecular structure is determined for vibrationally excited states which sample the potential energy surface far from the ground state, near equilibrium geometry.

1. INTRODUCTION

Weak attractions between molecules and atoms control the rates and dynamics of a wide variety of chemical and physical phenomena. Consequently, a major effort in the past several years has been directed toward a detailed characterization of the potential energy surfaces in which weakly bound molecular complexes are formed. There has been an emphasis on simple molecular systems which can facilitate close comparison between theory and experiment; complexes of hydrogen halides with various inert gases, diatomic and small polyatomic molecules have therefore been of particular interest. Pressure broadening, crossed molecular beam and transport studies of the molecular constituents can address the behavior of "complexes" in highly vibrationally excited, i.e., unbound, scattering states. Microwave and radio frequency studies, using both molecular beam electric resonance detection and Fourier transform coherent transient methods, have greatly elucidated the ground vibrational state of many weakly bound

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complexes. Indeed, these high resolution rotational spectroscopic methods have proven invaluable in characterizing the shape of the potential energy surface at near equilibrium geometries, and hence determining molecular structures. Infrared spectroscopy offers a direct and complementary probe of the potential surface at molecular configurations away from the global energy minimum. The application of IR methods to the considerable range of bound, vibrationally excited states of complexes has only very recently become feasible, and form the focus of this paper.

In the past few years, there has been an explosive growth in the field of vibrational spectroscopy of complexes due to the development of several techniques with adequate sensitivity and resolution to observe low concentrations of weakly bound species in either cooled cell or supersonic beam environments. Pine and coworkers have used the high spectral resolution of a tunable difference frequency laser to investigate hydrogen halide dimers and van der Waals complexes in a cooled white cell, with 64-80 meter optical absorption path lengths. FTIR methods and mode hop scanning of a color center laser have also been used to study several strongly bound complexes in long path length cells. There have been several supersonic beam techniques developed for IR spectroscopy of complexes which exploit the tremendous cooling in the expansion to promote efficient synthesis and enhance populations in low quantum states. OPO and CO2 laser vibrational predissociation spectroscopy has been used to study complexes of hydrogen fluoride, water and several hydrocarbons. Bolometric methods pioneered by Scoles and coworkers that detect laser induced warming or predissociative deflection of the species in the molecular beam have shown excellent sensitivity for study of a variety of cluster molecules. Extensions of these methods by Miller and coworkers look very promising for sub-Doppler Stark spectroscopy on vibrationally excited states. Direct diode laser absorption spectroscopy of rare gas-OCS complexes has been recently demonstrated. Far infrared laser-microwave double resonance and intracavity laser Stark spectroscopic methods have been exploited to study low frequency, intermolecular vibrational modes in ArHCl.

Extension of direct absorption IR studies of weakly bound complexes into the molecular beam regime requires exceptional sensitivity to compensate for the roughly 5 orders of magnitude decrease in path length between a white cell and conventional pinhole expansion. Efforts in our laboratory have been directed toward combining near shot noise limited detection of IR laser direct absorption and supersonic expansion methods to achieve a general probe for high resolution (Δν < 0.001 cm⁻¹) IR spectroscopy of weakly bound complexes. Key advantages of this approach are that 1) jet temperatures are low enough to eliminate spectral congestion but can be controlled to populate very low frequency vibrations in the complexes, 2) velocity narrowing in the slit expansion permits sub-Doppler absorption linewidths in an unskimmed molecular beam, and 3) the slit jet geometry provides density absorption path lengths ~2 orders of magnitude longer than obtained in typical pinhole expansions. This paper describes the application of these techniques to a series of small HF-containing complexes (ArHF, HFN2 and
H$_2$O$_2$, in which fundamental, combination, and low frequency inter-
molecular hot bands are observed and serve to elucidate the shape of
the potential energy surface sampled in the vibrationally excited
state.

2. EXPERIMENTAL

Infrared spectra of molecular clusters, featuring sub-Doppler resolu-
tion at low (5-45 K) temperatures are obtained by high sensitivity,
direct absorption detection with a computer-controlled spectrometer
(Fig. 1) based on a tunable infrared laser and a pulsed slit sup-
sonic expansion. Detection limits are $\leq 3 \times 10^5$ molecules/cm$^3$/$\text{quantum}
state for HF-containing complexes over a 2.5 cm absorption pathlength.

2.1. Tunable IR Laser Spectrometer

A difference frequency laser provides CW infrared light, tunable from
2.2-4.2 $\mu$m, with a 0.0015 cm$^{-1}$ linewidth. The outputs of a single
frequency ring dye laser (0.25 W on Rhodamine 6G, horizontal polariza-
tion) and a single frequency Ar$^+$ laser (0.40 W, vertical polarization)
are combined with a polarization beamsplitter and focused with a 20 cm
focal length achromatic lens into a 90 degree phase matched, tempera-
ture tuned, 5 cm long LiNbO$_3$ crystal. This produces approximately 20
W of IR at the difference between the Ar$^+$ and dye laser frequencies.

![Fig. 1. Schematic of the tunable IR laser spectrome-
ter.](image-url)
The linewidths of the passively stabilized dye and Ar+ lasers are 46 ± 5 and 14 ± 5 MHz, respectively; the 50 ± 5 MHz infrared linewidth is the uncorrelated sum of the visible linewidths.

A 50% beamsplitter divides the IR output into sample and reference beams that are focused with 2.5 cm focal length CaF$_2$ lenses onto matched 0.04 mm$^2$ InSb photovoltaic detectors. IR-induced photocurrents are amplified in matched, home-built amplifiers with 100 kHz transimpedance. The difference signal between sample and reference is amplified, filtered with a 5 kHz center frequency bandpass, sampled by a boxcar integrator and displayed on an oscilloscope. Imperfect subtraction of fluctuations in infrared power leads to amplitude noise that corresponds to 0.01% absorption using a 500 µs boxcar gate and 5 kHz detection bandwidth. The observed absorption sensitivity is of the order 10$^{-6}$/Hz$^{1/2}$ at the detection frequency of 5 kHz, within a factor of 3 of the shot noise limit for 10 µW of infrared light at 2.6 µm.  

The visible frequencies are measured with a traveling Michelson interferometer constructed after the design of Hall and Lee. The reference laser is a 633 nm He-Ne laser polarization-stabilized to 1 MHz as determined by measuring the beat frequency offset from an iodine-stabilized He-Ne laser. Precision is increased 16-fold by phase-locking to the sinusoidal interferometer signal and counting the zero crossings of the phase-locked oscillator. The precision of each measurement is ±0.001 cm$^{-1}$, which is further improved by signal averaging to ±0.0004 cm$^{-1}$. The absolute frequency accuracy of the measurements is obtained from internal references absorbing in the IR; for all results reported herein the infrared frequencies are measured relative to HF monomer transitions. The techniques used reproduce the known frequency differences between reference lines separated by 80 cm$^{-1}$ to within 0.0010 cm$^{-1}$; we take this as a conservative estimate of the absolute frequency uncertainty.

2.2. Pulsed Slit Valve Construction and Performance

Van der Waals and hydrogen bonded clusters are produced in a supersonic expansion from a pulsed slit valve of our own design (see Fig. 2). The nozzle has a 1.25 cm slit length and a variable slit width, and produces a low-temperature expansion with a 2.5 cm double-pass absorption length. The nozzle holder consists of a stainless steel disk, 2.5 cm in diameter, into which a 350 µm, straight-walled slot with a knife-edged lip is formed by electroless discharge machining. Interchangeable nozzles are produced by cutting a 2.5 cm stainless steel disk in half along a diameter, machining the cut edges flat, and surface grinding a rectangular notch in each half. The two pieces are bolted onto the nozzle holder in contact with each other; the two notches form a sharp-edged slit with width uniform to 5 µm and with mirror-smooth surfaces contacting the gas flow. For the experiments reported in this paper, the slit width was 125 ± 12 µm; the thickness is 375 µm and the length 1.25 cm.

A fluorocarbon elastomer seal cut from a length of O-ring material is held in contact with the knife-edged lip of the nozzle holder by a leaf spring; the spring is compressed to maintain the closed
configuration. The valve is opened by passing a current pulse (30 A peak, 300 μs FWHM) through a solenoid. The resulting magnetic field gradient accelerates a ferromagnetic plunger against a rod connected to the seal. The elastomer seal is impulsively accelerated, travels approximately 250 μm before hitting a stop, and is then returned to the closed position by spring tension and recoil. The valve is acoustically quiet during operation, which is essential to reduce amplitude instability in the dual beam configuration.

The unskimmed wedge-shaped jet issuing from the nozzle is probed by two passes of the infrared sample beam at distances that can be varied from less than the 0.7 mm IR beam radius to several centimeters. Figure 3 depicts the time-dependent infrared absorption profile of a typical gas pulses. The absorption is due to the R(3) transition of the hydrogen-bonded species N₄HF, formed in a mixture of 2% N₂, 1% HF in Ar. The top trace is obtained 0.3 cm from the nozzle exit; the lower trace is obtained at 5.3 cm and shows clustering resulting in the concave structure on the top of the profile. The pulse fall time of 70 μs is consistent with the single-exponential decay of the pressure in the dead volume between the seal and the nozzle; the 10% to 90% rise time is 40 μs. The pulse width may be varied from 150 μs to over 1 ms, controlled by varying the distance between the seal and stop and by varying the current pulse. The pulse width is 450-600 μs for the experiments described in this paper.

Molecular velocity components parallel to the slit are quenched by collisions among molecules issuing from adjacent regions of the expansion. This collimation of velocities reduces the Doppler contribution to the linewidth measured along the slit axis. The residual
Fig. 3. Time-resolved IR absorption of typical gas pulse. The absorption is due to the $R(3)$ transition of the $v_1$ fundamental band of the hydrogen-bonded species $N_2HF$; maximum absorbance is 2.1%. Pulse rise and fall times are determined by dead volume in nozzle holder; pulse width is variable (see text). Upper trace: 0.3 cm from nozzle exit. Lower trace: 5.3 cm from nozzle exit. Travel time corresponds to velocity of $6.1 \times 10^4$ cm s$^{-1}$. Dip in lower pulse is due to clustering during the travel; clustering is enhanced at higher backing pressures and lower nozzle temperatures.

Doppler contribution is estimated from observed rotational temperatures to be $\leq 0.001$ cm$^{-1}$ for our expansion conditions and geometry. With the above apparatus and the probe beam less than 1 cm from the nozzle, observed infrared linewidths for stable species (HF, methane, etc.) are 0.0015 cm$^{-1}$, limited at present by the infrared laser linewidth. This represents a factor of 5 to 7 improvement over the direct absorption Doppler widths from an unskimmed pinhole expansion, and results in a comparable increase in the peak absorption intensity. A skimmed molecular beam also provides a small Doppler width, but only at the expense of number density and pathlength; there is no corresponding enhancement in the peak absorption.

2.3. Clustering Behavior in the Expansion

The optimum conditions for formation of molecular complexes are determined by observing the time-dependent absorption of monomer or cluster species as the composition or pressure is varied. This ability to monitor concentrations of particular quantum states spectroscopically permits a completely nonintrusive probe of the spatial and time-dependent clustering processes. In addition, due to the high frequency
resolution of the IR laser, one can monitor relative populations of various velocity groups resolved along the probe axis, and thereby obtain a full velocity map of the species in the beam. By way of example, Fig. 4 displays frequency scans across the HF $R(0)$ absorption line in the slit as a function of backing pressure. The probe laser geometry is along the long axis of the linear expansion, and roughly 0.6 cm ($x/d = 50$) downstream from the slit; the HF/Ar ratio is 1:100. At low backing pressures the absorption lines are single, intense peaks, with sub-Doppler widths corresponding to perpendicular velocities of order $10^4$ cm/s. As the backing pressure increases, there is a systematic reduction in the absorption at line center, which implies a selective removal of $J=0$ monomer species with low perpendicular velocities. At pressures above 500 Torr, this selective elimination of low velocity absorbers is sufficient to split the peak into fully resolved doublets. It is important to note that the peak absorption strength per unit pressure decreases by 500 fold over the same pressure range, indicating that the low velocity absorbers are not simply being redistributed into higher perpendicular velocity groups. Investigation of higher $J$ states in the expansion verify that the absorption loss of $R(0)$ is also not due to selective rotational excitation away from $J=0$.

![Pressure Dependence of Line Splitting in HF $R(0)$](image)

Fig. 4. Lineshape behavior on $R(0)$ of HF monomer (1% HF/Ar) as a function of backing pressure. In the absence of clustering, the absorbanee would grow linearly with pressure, instead a rapid drop in intensity is observed. The colder central region of the expansion clusters preferentially, which due to the Doppler effect greatly reduces absorption intensity at line center and produces the characteristic doubling of the lineshape. More than half of the HF is clustered at $>300$ Torr; at 1000 Torr more than 99% of the monomer is bound in complexes, but less than 1% in either Ar-HF or (HF)$_2$ (see Fig. 5).
The severe loss of HF is by clustering in the expansion to form ArHF, HF dimer, and higher molecular weight species. Due to extensive fragmentation upon electron impact, accurate characterization of the relative populations of various clusters in an expansion has been difficult to obtain. By way of contrast, absorption spectroscopy permits a direct measure of the concentrations of HF monomer, (HF)₂ and ArHF as a function of expansion conditions. The integrated absorption signals for HF monomer R(0) and ArHF R(7), normalized to backing pressure are displayed in Fig. 5. In these plots, clustering behavior is evidenced by deviations from a horizontal line; nonlinear growth or removal is indicated by positive or negative derivatives, respectively. The HF monomer J=0 populations exhibit a monotonic depletion above 150 Torr of the 1% HF/Ar mixture, i.e., the same pressure regime in which the ArHF population grows. The ArHF signal strengths roll off at higher backing pressures due either to sequential clustering to larger molecular weight species or by loss of free HF precursors with which to form ArHF. The absorption signal behavior for HF dimer, which is also observed in this spectral region, is quite similar to ArHF. The signal strengths for ArHF and HF dimer, corrected for partition functions, translate into total number densities of less than 1% of the HF monomer number density lost through clustering. This behavior indicates extensive sequential

Fig. 5. Pressure dependence of integrated absorption signals for R(0) of HF monomer and R(7) of ArHF. The ArHF data have been multiplied by 420. The behavior of (HF)₂ has also been measured and is quite similar. If one corrects for partition function effects, less than 1% of the clustered HF monomer (see Fig. 4) can be accounted for in either (HF)₂ or ArHF for the optimum backing pressure, indicating a predominance of higher oligomers in the beam.
clustering occurs which preclude substantial population in the small cluster, ArHF and (HF)$_2$ species even under optimized expansion conditions. Qualitatively similar behavior is noted for expansions of other hydrogen halides and small hydrocarbons such as acetylene and methane. These observations are consistent with recent scattering experiments on ammonia complexes by Buck and coworkers, which indicate consistently low populations of dimer species in their beams.

3. RESULTS AND DISCUSSION

The direct absorption slit expansion methods described above have been used in our laboratories to investigate several complexes of hydrogen halides and small hydrocarbons. In this section results are presented for ArHF, HFN$_2$, and HFCU, which illustrate the richness of dynamical (and hence spectral) behavior that is exhibited in this series of three-, four-, and five-atom complexes.

3.1. ArHF $v_1$ Fundamental and $v_1+v_2$ Combination Band

The ArHF high frequency stretch fundamental spectrum $(10^00) + (00^00)$ occurs near 3952 cm$^{-1}$, and exhibits a simple P and R branch structure of a molecule with linear equilibrium geometry. The regularly spaced lines and null gap between R(0) and P(1) permit unambiguous numbering of the J assignment. Sample data with typical signal to noise on R(3)-R(1) are shown in Fig. 6. Peak absorption strengths in this figure correspond to 0.2% absorption; the noise background is $10^{-4}$ absorbance in a 5 kHz bandwidth.

Fig. 6. Sample data scan of R(3)-R(1) of ArHF on the $(10^00) + (00^00)$ fundamental transition. Peak absorption is a few tenths of a percent; baseline noise corresponds to a $10^{-4}$ absorbance in a 5 kHz bandwidth. The entire scan segment takes roughly 40 seconds. The rotational temperature of the ArHF is approximately 10 K.
Transition frequencies for R(2u) through P(19) of the fundamental are obtained. In order to decrease systematic and statistical errors, each transition is observed and measured in two to three separate experimental runs; each individual measurement represents an average of at least five IR frequency measurements. Combination differences for the ground and v1 excited state are fit to a standard power series expression in J(J+1) to extract the rotational constants; the pure vibrational frequency is then obtained by a fit to the observed transitions with the rotational constants held fixed. A summary of the nonlinear least-squares fits of the molecular constants is shown in Table 1. The ground state B and D constants obtained for ArHF are in excellent agreement (1 part in 10^5) with the early microwave work.\(^3,6\) This agreement, in conjunction with the simple mixture of gases, establishes beyond any reasonable doubt the chemical identity of the complex observed in these IR experiments.

Noteworthy is the 3.49(12) \times 10^{-4} \text{ cm}^{-1} increase in the B rotational constant between the (00^00) and (10^00) vibrational states. This result is in contrast with the negative ΔB observed in rare gas-HCl species excited in the v1 vibrational mode.\(^3\) The predicted shift in B due simply to vibrational elongation of the HF bond is approximately -1.6 \times 10^{-5} \text{ cm}^{-1}, i.e., of opposite sign and more than 20 times smaller than experimental observation. The observed 0.34% increase in B for v1 excited ArHF is more than can be accounted for by rotation of the HF unit around its center of mass (ΔB \ll 0.25%) hence some contraction in the vibrationally averaged van der Waals bond must occur. If \(θ_{\text{cm}}\) is held at the vibrationally averaged angle (41.6°) determined for the ground state, \(R_{\text{cm}}\) would decrease by 0.006 Å (from 3.510 to 3.504 Å).

Table 1. Molecular constants (in \text{ cm}^{-1}) obtained for ArHF.

<table>
<thead>
<tr>
<th></th>
<th>(00^00)</th>
<th>(10^00)</th>
<th>(11^10)^f</th>
<th>(11^10)^g</th>
<th>(10^02)</th>
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<tr>
<td>(δ)</td>
<td>0.102251(20)</td>
<td>0.102609(18)</td>
<td>0.100325(25)</td>
<td>0.102651(34)</td>
<td>0.08183(14)</td>
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<tr>
<td></td>
<td>(0.10226100(3))^g</td>
<td></td>
<td></td>
<td></td>
<td>(0.0817)^b</td>
</tr>
<tr>
<td>(D)</td>
<td>2.34(11) \times 10^{-6}</td>
<td>2.07(8) \times 10^{-6}</td>
<td>3.32(19) \times 10^{-6}</td>
<td>4.14(13) \times 10^{-6}</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>(2.361(3) \times 10^{-6})^g</td>
<td></td>
<td></td>
<td></td>
<td>---</td>
</tr>
<tr>
<td>(Ω)</td>
<td>2.6(17) \times 10^{-10}</td>
<td>2.7(13) \times 10^{-10}</td>
<td>6.0(38) \times 10^{-10}</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>(E_v-E_0)</td>
<td>3951.7680(30)</td>
<td>4022.1047(30)</td>
<td>4022.1062(30)</td>
<td>4023.3880(30)</td>
<td></td>
</tr>
<tr>
<td>(g_{111}u)</td>
<td>(-2.33(6) \times 10^{-3})</td>
<td></td>
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</tr>
</tbody>
</table>

Coriolis interaction between (11^10)^g and (10^02)^g = 0.01664(20) \sqrt{J(J+1)}.

\(^a\)Ref. 3.
\(^b\)Calculated from a Lennard-Jones potential fit to (10^00) data in the pseudo-diatomic approximation.
to induce the observed shift in B. If $\theta_{cm}$ decreases upon $v_1$ excitation, the decrease in $R_{cm}$ would only need to be $>0.003 \AA$. In light of the enhanced van der Waals attraction in the excited state, it is likely that the geometric shifts will involve both a shrinking of the van der Waals bond and greater alignment of the HF in the complex. Some recent Stark measurements on ArHF indicate an increase in the molecular dipole moment in the $v_1$ excited state which is consistent with a decrease in $\theta_{cm}$.\(^{18}\)

An increased attraction between Ar and HF in the vibrationally excited complex is also exhibited in the decreased centrifugal distortion constant. Based on the often used pseudo-diatomic approximation,\(^3\) one predicts a harmonic stretch frequency of 45.7 cm\(^{-1}\) for the $v_1$ excited state i.e., 7.4% higher than the 42.6 cm\(^{-1}\) ground state prediction. For a Lennard-Jones 6-12 potential, the binding energy of the complex in this diatomic approximation is readily shown to be

$$V_e = \frac{R_e^2 \mu}{4n^2\omega_e^2c^2},$$  \(1\)

where $R_e$ is the equilibrium Ar-HF center-of-mass separation and $\mu$ is the Ar-HF reduced mass. This expression predicts roughly a 15% increase in the vibrationally averaged van der Waals well depth from 117 to 135 cm\(^{-1}\) upon $v_1$ excitation. Subsequent studies by Fraser and Pine on ArHF complexes in a cooled White cell have provided rotational energies up to the dissociation limit ($J = 40$).\(^{23}\) Line position and predissociation linewidth fits to a four-parameter Hatiand-Smith potential yield well depths of 125 and 136 cm\(^{-1}\) for the ground and $v_1$ excited state, respectively, in surprisingly good agreement with the predictions of the present study.

Although the difference frequency spectrometer cannot excite the low frequency van der Waals modes directly, these modes can be observed in combination, difference and hot bands built on the higher frequency vibrational modes of the van der Waals constituenst. In ArHF, the large amplitude zero point motion in the bending vibration modulates the projection of the HF dipole moment derivative along the molecular axis, and hence transfers intensity from the fundamental ($10^{0}\) + (00$^0$) into the combination ($11^{1}\) + (00$^0$) and difference ($10^{0}\) + (01$^0$) bands. In the limit of a free internal rotor, these three "vibrations" correlate with Q(0), R(0) and P(1) of the HF monomer respectively, and the fundamental transition is forbidden. In the jet spectrometer at $<10$ K, only the ground vibrational state is appreciably populated; we therefore look for the van der Waals bending mode in the $v_1$+$v_2$ combination. Since the degenerate bend has one unit of vibrational angular momentum around the principal axis, one anticipates the P, Q and R branch structure characteristic of a $\Pi$-$\Pi$ perpendicular transition.

Such a spectrum is indeed observed approximately 70 cm\(^{-1}\) to the blue of the $v_1$ origin. Signal strengths on the combination band Q branch are 37% as strong as the fundamental, which permit R(0)-R(16), Q(1)-Q(17) and P(2)-P(18) to be observed. Since the upper state has a minimum of J=1, P(1) and Q(0) are not anticipated and do
not occur. A stick plot of the $v_1 + v_2$ combination band is shown in Fig. 7.

The $v_2$ bending vibration in ArHF is doubly degenerate and split by first and second order Coriolis interactions into a $\Pi^e$ and $\Pi^o$ manifold. As a result of the $J$ dependence of parity, the $\Delta J = 0$ (Q branch) transitions access only the $\Pi^o$ component of the doublets, while the $\Delta J = \pm 1$ (R and P branch) transitions access the $\Pi^e$ component of the doublets. Term values for $J=1$ to $J=8$ in the $(11^10)$ $\Pi^e$ manifold are obtained as the sum of observed Q branch transition frequencies and the measured term values for the lower ($00^00$) state. These terms have been fitted to standard Hamiltonian expressions for a $\Pi$ state ($\ell = 1$); the results are summarized in Table 1.

If one neglects off-diagonal anharmonicity, an approximate bending frequency of 70.3 cm$^{-1}$ can be obtained from the blue shift of the $v_1 + v_2$ versus $v_1$ origins. This frequency is remarkably close to the

![Fig. 7. Stick plot of the observed transition frequencies for the Q(upper) and P/R(lower) branches, respectively. Relative intensities are shown for a 10 K rotational distribution. Transitions to the $\Pi^e$ component of the $(11^10)$ manifold are seen exclusively in the Q branch (displaced for clarity). The P/R branch represents only transitions to the $\Pi^o$ component, which exhibit a strong localized Coriolis perturbation near $J' = 8$ by the $(10^02)$ $\Sigma^+$ vibrational manifold. Transitions to states strongly mixed by this interaction are indicated by dotted lines with arrows.](image)
prediction of 67.7 cm$^{-1}$ based on the anisotropic potential surfaces of Hutson and Howard. The harmonic prediction of Kiemper and coworkers based on vibrationally averaged spin-spin HF hyperfine interactions in the ground state is also quite close but somewhat higher, 79.8 cm$^{-1}$. The B constant for the (1110) $\eta^4$ bend excited state is lower by 1.9% than the ground state, which is responsible for the extreme red shifting of the Q branch. This shift is nearly six times larger than, and of opposite sign to, the shift observed in the fundamental transition. Changes in the vibrationally averaged $\theta_{cm}$ of the HF unit can account for at most 13% of the observed shift; hence the major contribution to $\Delta B$ must be due to a growth in $R_{cm}$. If $\theta_{cm}$ is held at the ground state value of 41.6°, $R_{cm}$ would have to increase by 0.034 Å (from 3.510 to 3.544 Å) to achieve the observed 1.9% decrease in B. Again, it is a more likely scenario that both $\theta_{cm}$ and $R_{cm}$ will increase an $v_2$ excitation, which would be physically reasonable since a significant source of the binding is due to anisotropic dipole-induced dipole interactions. It would be extremely useful to have Stark data on either $v_1$+$v_2$ or $v_2$ excited states to clarify these issues. In any event, this large change in vibrationally averaged separation with bending excitation is in sharp contrast with observations for ArHCl, $31,32,37$ and is indicative of strong bend-stretch couplings in the ArHF potential.

In addition to the Q branch lines, 35 transitions attributed to the P and R branch are observed to the red and blue of the vibrational origin. Fairly regular spacing in the rotational structure is evident, but with dramatic irregularities over a highly localized region of intermediate J values. Unambiguous J assignment of the transitions is made from measured combination differences in the ground state; agreement is consistently within the measurement uncertainty of 0.001 cm$^{-1}$. These assignments show that P(9) and R(7) are each split into a doublet of transitions, revealing a strong, but localized perturbation in J=8; such behavior is completely absent in the Q branch measurements. As discussed above, the P/R branch and Q branch transitions from the ground state terminate on levels in the $\Pi^e$ and $\Pi^g$ manifolds, respectively. The localized perturbation in the $\Pi^e$ state can be assigned to Coriolis couplings with the (1002) $\Sigma^+$ overtone of the van der Waals stretch; the “extra” lines observed are transitions directly to the states mixed by the interaction. The $\Pi^g$ state observed in the Q branch, on the other hand, should be unperturbed by the (1002) state, as is observed to be the case.

B-type Coriolis interaction between a $\Sigma^+$ and $\Pi^e$ state requires $\Delta J = 0$, $\Delta \Omega = \pm 1$ and scales as

$$\langle \Omega, J-1 | \hat{G}_{\text{cor}} | \Omega, J \rangle \propto \beta (J(J+1))^{1/2}$$

(2)

Term values for the mixed $\Sigma^+$ and $\Pi^e$ state are therefore least-squares fit to a 2x2 Hamiltonian matrix with elements given by

$$H_{11} = v_{1110} + \delta_{1110} (J(J+1) - \Omega^2) - D_{1110} (J(J+1) - \Omega^2)^2$$

(3a)
\[ H_{22} = v_{10^0_2} + B_{10^0_2} J(J+1) \]  
(3b)

\[ H_{12} = B_{J(J+1)} \]  
(3c)

where \( B_{11^10}, v_{10^0_2}, B_{11^10}, B_{10^0_2} \) and \( D_{11^10} \) are adjustable parameters. The results for the deperturbed molecular constants are shown in Table 1.

The \( B \) rotational constant for the \( v^f (11^10) \) state is significantly higher than for the \( v^e (11^10) \) state, which indicates a negative \( \pm \) doubling constant of \(-69.8(18) \) MHz. This is contrary to what is observed in "normal" molecules, where both first and second order vibration-rotation interactions lead to positive \( \pm \) doubling since the bend excited state is usually the lowest \( \pm \) vibration.\(^{38}\) From the Hutson and Howard surfaces,\(^{12}\) however, the van der Waals stretch \((10^0_1)\) and parallel bend \((12^0_0)\) are predicted to be lower in energy and to have the correct \( \pm \) symmetry to perturb the \( v^e \) component of the perpendicular bend \((11^10)\). Negative \( \pm \) doubling have also been observed in far IR experiments on ArHCl on the \((01^10)\) state,\(^{31,32}\) although, surprisingly, not in the analogous White cell, near IR studies on the \((11^10)\) excited state.\(^{37}\) Finally, the centrifugal distortion in the \( v^e \) manifold is significantly larger than the ground state value. This is in agreement with the behavior in the \( v^e \) manifold and again indicates a weakening of the van der Waals attraction with excitation of the perpendicular bend.

The deperturbed vibrational origin of the \((10^0_2)\) excited state is 71.6 cm\(^{-1}\) above the \( v_1 (10^0_0) \) excited state. This is in good agreement with numerical integration of the Schrödinger equation for the vibrationally averaged Lennard-Jones 6-12 potential fits for the \((10^0_0)\) manifold. Using these \( C_6 \) and \( C_{12} \) parameters, one calculates a vibrational origin of 65 cm\(^{-1}\) and a \( 10^0_2 \) rotational constant of 0.0817 cm\(^{-1}\), in very close agreement with the observed values of 71.6 cm\(^{-1}\) and 0.0818 cm\(^{-1}\), respectively. Efforts by Fraser and Pine\(^{23}\) to fit the vibrationally averaged van der Waals well to a one-dimensional Maitland-Smith potential predict 72.25 cm\(^{-1}\) for the \( 10^0_2 \) vibrational origin and 0.08264 cm\(^{-1}\) for \( 10^0_{10} \). These consistency checks leave little doubt that the \((10^0_2)\) state is responsible for the observed Coriolis perturbations in the \((11^10)\) \( v^e + (00^0_0) \) combination band.

3.2. HF\(_2\): Stretching and Bending Vibrations in a Nearly Linear Polyatomic Complex

The HF\(_2\) complex offers a nice comparison with ArHF for several reasons. The hydrogen bond is much stronger\(^{11,12}\) than the van der Waals bond, leading to potentially more anisotropic interactions between the constituents. However, the larger reduced mass of \( N_2 \) with respect to HF allows much lower frequency bending motions to occur, and may be sufficiently populated in the slit jet to observe directly.

The origin of the \( v_1 \) HF stretch of HF\(_2\) is observed at 3918.2434(2) cm\(^{-1}\), red-shifted by 43.1795(2) cm\(^{-1}\) from the rotationless vibration frequency of HF monomer, but blue-shifted by
37 cm\(^{-1}\) from observations in a matrix. Initial conditions for searching for the complex are determined by monitoring the absorption of the van der Waals complex Ar-HF in an expansion of 1\% HF in Ar as \(N_2\) is added to the mixture. Strong HFN\(_2\) transitions are immediately observed; optimization of expansion conditions shows a broad maximum at 20\% to 50\% \(N_2\), 1\% HF with intensity monotonically increasing from 100 to 1150 Torr backing pressure. Figure 8 is a stick plot of the observed transition frequencies. The spectrum displays the P and R branches, center gap, and regular spacing characteristic of a \(\Delta + \Delta\) transition of a linear molecule; these features provide unambiguous \(J\) assignment. Transition frequencies for R(37) to P(35) (inclusive) are obtained; all spectral features are isolated and unblended. Unambiguous identification of the absorbing species is made by the excellent agreement (\(\pm 0.001\) cm\(^{-1}\)) between the observed spacing and combination differences generated using the microwave rotational constants. The HF P(1) transition at 3920.3119 cm\(^{-1}\) is the reference for all frequencies reported.

Analysis of the transition frequencies for the \(v_1\) fundamental follows closely the method described for \(v_1 = 1+0\) in ArHF. Table 2 lists the molecular constant coefficients obtained from our data, along with the corresponding values for the ground state determined by microwave spectroscopy. The infrared-determined \(B''\) and \(D''\) are in

![Diagram](image)

Fig. 8. Stick plot of the observed HFN\(_2\) transitions in the \(v_1\) fundamental (upper) and \(v_1 + v_5 - v_5\) bend excited hot band (lower). The \(v_1\) fundamental transitions from R(37)-P(35) are observed. The hot band transitions are all split by \(\pm\)-doubling too small to be observed in this figure. The 60:15 intensity ratio between fundamental and hot band transitions is consistent with a \(v_5\) bending vibrational frequency of 100±25 cm\(^{-1}\).
Table 2. Molecular constants (in cm\(^{-1}\)) obtained for HFN\(_2\).

<table>
<thead>
<tr>
<th></th>
<th>(v_1=0, v_5=0)</th>
<th>(v_1=0, v_5=1)</th>
<th>(v_1=1, v_5=1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(B)</td>
<td>0.108562(84)</td>
<td>0.1071781(84)</td>
<td>0.107356(18)</td>
</tr>
<tr>
<td>(V)</td>
<td>5.67(13) \times 10^{-7}</td>
<td>5.28(12) \times 10^{-7}</td>
<td>6.64(33) \times 10^{-7}</td>
</tr>
<tr>
<td>(H)</td>
<td>1.37(39) \times 10^{-11}</td>
<td>-1.42(52) \times 10^{-11}</td>
<td>---</td>
</tr>
</tbody>
</table>

\[ E_0 - E_0' \] \(U\) \(3918.2434(30) \) \(v_5 \approx 100\pm25 \text{ cm}^{-1}\) \(c\)

\(3920.9594(30) + v_5 \)

\(|q| = 4.61(7) \times 10^{-4}\) \(|q| = 4.44(6) \times 10^{-4}\)

\(X_{15} = -2.710(b)\)

\(^a\)Ref. 7.
\(^b\)Ref. 15.
\(^c\)Estimated from relative intensities, based on equilibrated rotations and low frequency vibrations.

excellent agreement with the microwave results.\(^7\) The contribution from the sextic terms is 0.039 cm\(^{-1}\) at the highest \(J\) observed, which is approximately 50 times the experimental uncertainty.

The rotational constant \(B\) increases 0.6% and the centrifugal distortion constant decreases by 6% on excitation of the \(v_1\) stretch. Both changes are indicative of a stronger hydrogen bond in the excited state. The binding energy calculated for the ground state of HFN\(_2\) is 600 cm\(^{-1}\), using the diatomic approximation and increases by 8% to 650 cm\(^{-1}\) in the excited state. To estimate the low frequency stretching vibration, a Lennard-Jones 6-12 potential is assumed and eigenvalues of the pseudodiatomic Hamiltonian are obtained by numerical integration. The intermolecular stretch frequency is estimated to be 91 cm\(^{-1}\) in the ground state, increasing to 95 cm\(^{-1}\) in the \(v_1\) excited state. These calculations predict a redshift of the \(v_1\) transition of 48 cm\(^{-1}\) from the rotationless frequency of the HF monomer, in fair agreement with the experimental value of 43 cm\(^{-1}\). With the assumption of unchanged equilibrium bond angles, the separation between the centers of mass of the subunits is determined to decrease by 0.010 Å upon \(v_1\) excitation; again, this value would be slightly smaller if \(\theta_{cm}\) for the HF unit decreases with excitation of \(v_1\).

In addition to the strong \(v_1\) transitions, the high sensitivity of the direct absorption/slit expansion technique permits observation of a much weaker series of doublets that becomes progressively more intense in the warmer region of the expansion close (\(\lesssim 0.4\) cm) to the nozzle. The spectrum is assigned as a \(\Pi + \Pi\) hot band of N\(_2\)HF, in
which the lower and upper levels each have one unit of vibrational angular momentum \(|\ell| = 1\) around the figure axis. Since in a standard analysis of \(\ell\) doubling, the splitting increases as \(J(J+1)\) and is zero for the rotationless molecule, the ro-vibrational transitions can be unambiguously assigned by fitting the splittings to

\[
\Delta v = q'J'(J'+1) - q''J''(J''+1)
\]

and varying the \(J\) assignment. For only one trial value does the predicted splitting vanish at \(J = 0\), and the standard deviation of the fit is also observed to reach a sharp minimum at that value. Based on this assignment, the rotational constants and vibrational frequency can be extracted as for \(\text{ArHF}\); the results are summarized in Table 2.

The band origin is blue-shifted by 2.7160(4) cm\(^{-1}\) from the fundamental, indicating that the interaction between the HF and nitrogen subunits is relatively weaker upon bend excitation, in contrast to the effect observed for the \(v_1\) stretch. The average of the rotational constants for the two states is 0.9% larger than for the ground state, and increases by 0.5% on \(v_1\) excitation. The centrifugal distortion constants for the bend-excited states are also 13% larger than for the ground and \(v_1 = 1\) states, again, consistent with a weakening of the bond upon bend excitation.

There are two bending vibrations in \(\text{N}_2\text{HF}\) that might produce such a spectrum, the \(\nu_5\) HF bend and the \(\nu_2\) \(\text{N}_2\) bend. The identification of the hot band as the \(\nu_5 + \nu_1 - \nu_5\) transition is made from two estimates of the bending vibration frequency obtained from our data that yield values in general agreement with other estimates of the \(\nu_2\) bend but much lower than the 262 cm\(^{-1}\) observed for the HF bend.\(^{15}\) The first estimate of the bending frequency is obtained from a Boltzmann analysis of the relative intensities (60±15) of the two bands. This yields an estimate of the bend frequency of 100±25 cm\(^{-1}\), assuming the vibrational degrees of freedom are in equilibrium at the rotational temperature of the fundamental. A confirming estimate of the bend frequency comes from analysis of the \(\ell\)-doubling parameter. In the absence of a first-order perturbation of the \(\Pi^0\) state by nearby states of \(\Sigma^+\) symmetry, the \(\ell\)-doubling parameter \(q\) is approximately related to the bend frequency \(\omega_b\) by\(^{46}\)

\[
\omega_b = \frac{2B_0^2}{q} \left[ 1 + 4 \sum_i \xi_i \frac{\omega_i^2 - \omega_b^2}{\omega_i^2} \right]
\]

where \(B_0\) is the equilibrium value of the rotational constant, and the HF subunit is treated as a point mass to make use of the above linear triatomic expression. In Eq. (5), \(\xi_i\) is the Coriolis coupling constant for the \(i\)th vibration interacting with the bend, and \(\omega_i\) are the corresponding harmonic stretch frequencies. Coriolis coupling constants for both the \(\text{N}_2\) and the HF bends are calculated using the experimental values for the bond lengths and for the HF and \(\text{N}_2\) stretch frequencies; the van der Waals stretch frequency is estimated from the diatomic approximation (see above) as 91 cm\(^{-1}\). Cross coupling terms are not known and therefore not included. This procedure yields
\( \nu_0 = 80 \text{ cm}^{-1} \) for the \( \text{N}_2 \) bend and predicts that the \( \tilde{J} \)-doubling parameter is positive. In contrast, the \( \tilde{J} \)-doubling parameter predicted for the \( \nu_1 \) HF bend using the known bend frequency determined from matrix isolation studies is 8 times smaller than the observed value. This calculation, in conjunction with harmonic estimates based on observed \( \text{N}_2 \) quadrupolar couplings in microwave studies, leaves little doubt that the lower state of the hot band transition is the lowest bending frequency, \( \nu_5 = 1 \), i.e., the \( \text{N}_2 \) librational mode. Based on these estimates, we hope to be able to locate the \( \nu_1 + \nu_5 \) combination band in the slit jet spectra, from which a more direct bend frequency measurement can be made.

3.3. \( \text{HFCO}_2 \): Stretching and Bending Vibrations in a Highly Nonrigid Polyatomic Complex

The IK spectroscopy of \( \text{HFCO}_2 \) serves as an intriguing comparison with both \( \text{ArHF} \) and \( \text{HFN}_2 \). All three complexes have been investigated by microwave studies; the equilibrium structures have been determined to be linear. This result was unanticipated for \( \text{HFCO}_2 \) in light of the \( sp^2 \) lone pair electron distribution on oxygen and a Lewis acid-base description of the hydrogen bonding. This proved particularly surprising since \( \text{HFN}_2 \text{O} \), which is isoelectronic with \( \text{HFCO}_2 \), was subsequently determined to have a bent equilibrium structure. Ab initio calculations further served to verify these structural predictions. If, however, the linear equilibrium geometry in \( \text{HFCO}_2 \) results from a nearly balanced competition between on-axis and off-axis contributions, one would anticipate a shallow bending potential which could be elucidated via hot band absorption spectra in the slit jet apparatus.

A relatively strong series of absorption transitions is observed (peak absorbances \( \gtrsim 10^{-3} \)) near 3909 cm\(^{-1} \) which can be assigned to the \( \nu_1 = 1+0 \) HF stretch fundamental spectrum of \( \text{HFCO}_2 \). A stick plot of the observed frequencies is shown in Fig. 9. The clear R and P branch progression and the null gap between R(0) and P(1) permit unambiguous J labeling of the spectral transitions. Combination differences for the ground state consistently agree with values calculated from microwave data to within experimental error. To extract the molecular constants, combination differences for the upper and lower states are fit to standard Hamiltonian expressions for a semirigid linear complex, and analyzed in a similar manner as for \( \text{ArHF} \) and \( \text{HFN}_2 \). The molecular constants thus obtained are presented in Table 3.

The \( \text{HFCO}_2 \) molecular constants indicate several interesting points. Firstly, there is a significant increase (+1.75%) in the \( B \) rotational constant upon \( \nu_1 \) vibrational excitation. This is immediately evident from the stick plot in Fig. 7, where a compression in the P versus K branch line spacings is quite evident. The sign of the change is identical to what is observed in several other HF containing complexes, and has been interpreted as an indication of stronger bonding in the vibrationally excited state. The magnitude of the change, however, is much greater than what has been observed for any of the linear HF complexes. If one constrains the complex to the nearly linear geometry suggested from the microwave data, the observed change
Fig. 9. Stick plot of the observed transitions in the $v_1$ fundamental (lower) + $v_1 + v_6 - v_6$ bend excited hot band (lower) in HFCO$_2$. The bunching of lines in the P branch is evidence for a large increase in B upon $v_1$ excitation. Doubling in the hot band spectra is clearly visible and due to rotational splitting of the doubly degenerate bend vibration. The 2.5:1 intensity ratio between fundamental and hot band transitions is consistent with a $v_6$ bending vibration of 10±5 cm$^{-1}$, i.e., an order of magnitude smaller than indicated in HF$_2$ (see Fig. 8).

In B would require a 0.041 Å decrease (from 1.921 to 1.879 Å) in the hydrogen bond length. This should be compared to the 4–7 times smaller change (0.010 and 0.006 Å) in the bond length indicated by the N$_2$HF and ArHF infrared data, respectively.

Secondly, if the increase in B were in fact reflective of a greatly enhanced well depth in the upper state, then one would expect a comparably dramatic reduction in the centrifugal distortion constant due to tighter binding. What is observed, in fact, is a 55% increase in D upon $v_1$ excitation. Again, this is inconsistent both in sign and magnitude with the observed behavior for ArHF and N$_2$HF in which D is observed to decrease by roughly 10%.

It is worth noting that the observed dependences of B and D on vibrational excitation are contradictory only in the context of a nearly linear geometry. An increase in both B and D would in fact be predicted for nonlinear geometries where the CO$_2$ is bent away from the HF. An increase in B would result from a foreshortened projection of the nuclei on the A axis. The dramatic increase in D, on the other hand, could be the consequence of J dependent centrifugal straightening of the complex against a weak bending potential. There would be a
Table 3. Molecular constants (in cm\(^{-1}\)) obtained for HFCO\(_2\).

<table>
<thead>
<tr>
<th>Ground State</th>
<th>(v_1=1, v_6=0)</th>
<th>(v_1=0, v_6=1)</th>
<th>(v_1=1, v_6=1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>0.06511(10)</td>
<td>0.066247(11)</td>
<td>0.064709(13)</td>
</tr>
<tr>
<td></td>
<td>(0.06506401(4))(^a)</td>
<td></td>
<td>0.065804(41)</td>
</tr>
<tr>
<td>U</td>
<td>3.43(15)\times10^{-7}</td>
<td>5.33(16)\times10^{-7}</td>
<td>2.79(9)\times10^{-7}</td>
</tr>
<tr>
<td></td>
<td>(3.56(2)\times10^{-7})(^a)</td>
<td></td>
<td>4.21(15)\times10^{-7}</td>
</tr>
</tbody>
</table>

\(E_{v-v'}^0\) U

\[ v_6 = 1 \pm 5 \text{ cm}^{-1} \quad c \quad v_6 + 3906.3659(30) \]

\[(3871)^b \]

\[ |q| = 4.21(15) \times 10^{-4} \quad |q| = 5.78(15) \times 10^{-4} \]

\(X_{10} = 2.954(2)\)

\(^a\text{Ref. 5.}\)

\(^b\text{Ref. 14.}\)

\(\text{Estimated from relative intensities in the } v_1 \text{ fundamental and hot band, based on equilibrated rotations and low frequency vibrations.}\)

The magnitude of this centrifugal straightening effect can be estimated analytically for a semiclassical model of a semirigid complex with harmonic restoring forces in the bend coordinate to be\(^{26}\)

\[ D_{\text{cent. straight.}} = \frac{\frac{\partial B}{\partial \theta}^2}{\frac{\partial^2 B}{\partial \theta^2}} \]

Since \(\frac{\partial B}{\partial \theta} = 0\) as \(\theta_{eq} = 0\), it is clear from Eq. (6) that significant \(D\) enhancement from this model requires both 1) a nonlinear geometry and 2) a very soft bending potential. For example, if one attributes the change in \(B\) and \(D\) solely to bending of the complex (holding center-of-mass separations of the constituents fixed), the data would be consistent with an upper state bend angle of roughly 15 degrees and a corresponding bending force constant of 0.1 cm\(^{-1}\)/degree\(^2\). This translates into a predicted frequency for the \(\text{CO}_2 v_6\) librational mode of approximately 10 cm\(^{-1}\), which is low enough to be significantly populated in the jet expansion.
It bears stressing that Eq. (6) applies strictly for a model of the bending vibration with a nonlinear equilibrium geometry. Due to vibrational averaging, however, this centrifugal straightening mechanism should also be important for a linear but highly nonrigid equilibrium geometry. In the latter case the wave function in the bend coordinate would simply be more diffuse at low J, and narrowing toward small θ with increasing J. From these observations alone, therefore, one cannot distinguish between an equilibrium, or simply a vibrationally averaged bent geometry. Both potential surface topologies, however, would require weak restoring forces in the bending coordinate in order to reproduce the observed trends. We are presently pursuing fully quantum close coupled calculations on model potentials to test the accuracy of these classical predictions, and to characterize the correct shape of the energy surface.

We see further evidence for a weak bending potential by a closer inspection of the HFCO$_2$ spectrum. In the P branch of the $\nu_1 = 1\to 0$ fundamental a progression of hot band doublet transitions is observed with a clear P and R branch structure and an origin that is red-shifted from the $\nu_1$ fundamental by 2.954(2) cm$^{-1}$. The roughly 0.065 cm$^{-1}$ spacing identifies the spectrum as belonging to HFCO$_2$; the doubling of the spectra is characteristic of a parallel transition out of an excited HFCO$_2$ complex with a doubly degenerate bend vibration excited.

The intensity ratio between the fundamental and each component of the corresponding doublets is approximately 2.5:1. This ratio rules out the possibility that the excited vibration correlates to the free $\nu_6$ vibration in CO$_2$, since even at 300 K the fractional population would be only 6%. The HF bend, $\nu_6$, has been seen in matrix studies at 313 cm$^{-1}$, and would be negligibly populated at the 16 K jet temperatures. This leaves $\nu_6$, i.e., the CO$_2$ librational mode, as the only candidate; if one assumes that the vibrational and rotational degrees of freedom are equilibrated, the observed intensity ratio between the fundamental and hot band correspond to a $\nu_6$ frequency of 10±5 cm$^{-1}$. This value is in qualitative agreement with the predictions made previously which considered only changes in B and D upon $\nu_1$ excitation.

As was performed for the HPH$_2$ hot band data, J assignment of the transitions is achieved by fitting the splittings to $q^{J'}(J'+1)-q^{J'}(J +1)$ and shifting the J labeling until the curve intersects the origin. With the J assignment determined, the average line frequency for each doublet is least-squares fit to standard expressions for a $|J| = 1$ H-H transition; the molecular constants obtained from these fits are shown in Table 3.

There are several features worth noting about the spectral fits. First as in the case of the fundamental transition, the rotational B constant for the bend excited states increases (+1.7%) with $\nu_1$ vibrational excitation. This is consistent with the previous observation in the $\nu_1$ fundamental, and indicates a shortening of the center-of-mass separations between HF and CO$_2$, which could arise via a greater vibrationally averaged bend CO$_2$ bend angle or a deeper attractive well. However, bend excitation consistently decreases the fitted B constants over the corresponding values observed in the $\nu_1$ fundamental, which
suggests the following simple physical interpretation. Excitation of bending modes in the complex bends the constituents further away from the energy minimum, and places a node in the orientation of strongest interactions. This tends to weaken the intermolecular bond, and hence increase the center-of-mass displacements of the complexed species. A similar effect is evident in both the ArHF and HFN₂ complexes.

Secondly, the vibrational origin for the transition is red-shifted by 2.95 cm⁻¹ from the v₁ fundamental. This implies a positive off diagonal anharmonicity with respect to the low frequency bend. This would be somewhat inconsistent with the previous explanation of the overall decrease in B upon bend excitation, which relied on a weakening of the bonding interactions between HF and CO₂, and which would tend to blue-shift the HF stretching back in the direction of the free HF monomer.

Thirdly, centrifugal distortion for the bend excited complexes increases dramatically upon v₅+v₁-v₁ excitation, similar to what is observed on the fundamental transition. Again, this increase in both B and D is in contrast with expectations based on nearly linear complexes and suggests a significant shift in the vibrationally averaged geometry in the v₁ excited state.

Finally, the magnitude of the centrifugal distortion constants consistently decreases on excitation of the bend. Note that the exact opposite behavior is observed in both ArHF and HFN₂, and was attributed to a weakening of the bond upon bend excitation. However, this behavior in HFCO₂ would be completely consistent if a major contribution to D comes from centrifugal straightening of a highly nonrigid complex. For finite angular momentum around the figure axis, there will be a centrifugal barrier which goes to infinity at the linear geometry; this can compete effectively with the tendency to straighten the complex with increasing end-over-end rotation, and hence reduce the centrifugal distortion. It is noteworthy that the decrease in D on excitation of the bend occurs for both v₁ = 0 and 1. This would suggest a significant contribution to D even for the ground state occurs from centrifugal straightening, which may explain the anomalously large values measured in the early microwave studies.⁵

4. SUMMARY AND CONCLUSION

A general method for direct IR absorption spectra of weakly bound complexes in slit supersonic expansions is described which permits high detection sensitivity (≤ 3 × 10⁹/cm²/quantum state) and high spectral resolution (Δν ≤ 0.001 cm⁻¹). Advantages of the approach are 1) lack of spectral congestion in the cooled jet, 2) control of expansion temperature for observation of low frequency intermolecular cluster vibrations, 3) sub-Doppler resolution from velocity narrowing in the slit expansion, 4) long path length × number density for direct absorption, and 5) applicability of the method with low power high resolution light sources. Fundamental, combination and low frequency intermolecular hot band spectra have been obtained and analyzed for ArHF, HFN₂ and HFCO₂. The vibrational state dependence of the rotational constants
provides information on structural shifts in the molecules upon excitation. An enhancement in intermolecular bonding upon HF stretch excitation is consistently observed. Excitation of bending nodes in the complex, on the other hand, consistently weakens the bonding. In HFN₂, the observed behavior of the rotational constants and vibrational frequencies is consistent with a nearly linear geometry and a relatively strong restoring potential with respect to N₂ rotation. For HFCO₂, however, the behavior suggests a very nonrigid potential for CO₂ libration (ν₆), and hence a significantly bent vibrationally averaged geometry, at least in the ν₁ excited state. The ν₆ bend frequency is comparable to the time scale for end-over-end rotation for high J's in the HFCO₂ complex, which calls into question the validity of standard analyses of vibration-rotation spectral structure. Full quantum calculations on trial potentials are presently being performed to fit the data and thereby infer the topology of the true potential energy surface.

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