

FTIR observation of the N₂HF complex in solid argon

Lester Andrews, Benue J. Kelsall, and Robert T. Arlinghaus

Citation: *The Journal of Chemical Physics* **79**, 2488 (1983); doi: 10.1063/1.446093View online: <http://dx.doi.org/10.1063/1.446093>View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/79/5?ver=pdfcov>Published by the [AIP Publishing](#)

Articles you may be interested in[Two-dimensional laser induced fluorescence spectroscopy of van der Waals complexes: Fluorobenzene-Ar *n* \(*n* = 1,2\)](#)*J. Chem. Phys.* **136**, 134309 (2012); 10.1063/1.3697474[Observation of the lead carbonyls, Pb *n* CO \(*n*=1–4\): Reactions of lead atoms and small clusters with carbon monoxide in solid argon](#)*J. Chem. Phys.* **122**, 034505 (2005); 10.1063/1.1834915[Accurate intermolecular ground state potential of the Ar-N₂ van der Waals complex](#)*J. Chem. Phys.* **121**, 10419 (2004); 10.1063/1.1809606[Accurate intermolecular ground state potential of the Ar–N₂ complex](#)*J. Chem. Phys.* **110**, 8525 (1999); 10.1063/1.478760[FTIR observation of N≡N stretching fundamentals in hydrogenbonded complexes in solid argon](#)*J. Chem. Phys.* **83**, 4983 (1985); 10.1063/1.449763



sition was assigned to be at 255.07 nm from the analysis of the hot bands observed at a higher sensitivity and the emission data by Kielkopf and Miller.⁷ From this assignment and the energy of the dissociation limit (252.78 nm, 39 548 cm⁻¹) discussed below, the potential depth (D_0) of the corresponding excited state was determined to be 356 ± 3 cm⁻¹. In the higher energy region of the 253.7 nm Hg line, the 0_0^0 band of the other electronic transition was assigned to be at 253.21 nm. The spacing of the vibrational progression of this transition starts from 11 cm⁻¹ and converges into continuum as the progression proceeds. Birge-Sponer's plots of those individual bands give a 66 ± 3 cm⁻¹ dissociation energy (D_0) and the convergence limit of 252.78 nm for the upper state.

From the observed spectroscopic data and the emission data by Kielkopf and Miller,⁷ the potential depth (D_0) and the vibrational frequency (1-0 transition) in the ground electronic state were determined to be 135 ± 3 and 18 cm⁻¹, respectively.

According to Behmenburg,² the 253.7 nm atomic line of Hg (3P_1) is expected to split into two optical transitions by the formation of the complex with rare gases, namely, $A^3\Pi_1-X^1\Sigma_0$ and $B^3\Sigma_0-X^1\Sigma_0$ in the order of the transition energy. The observed absorption bands starting at 255.07 and 253.21 nm are clearly assigned to these two transitions.

The potential depth and the relative displacement (qualitative) of individual electronic states (X , A , and B) are shown in Fig. 1(b). The fact that the X and B

state are not stable at room temperature, while the A state is deeply bounded is in good agreement with the prediction by Behmenburg.^{2,4}

When the fluorescence is monitored with a high sensitivity in the near UV region (300 to 350 nm), the fluorescence excitation spectrum of freely expanded Hg and Ar mixture exhibits a spectrum different from that of the Hg-Ar complex. The spectrum also splits into two different transitions below and above the 253.7 nm Hg resonance line. It was tentatively assigned by us to Hg₂ because of the spectral pattern and the wavelength of the emission. Detailed analyses of Hg₂, Hg-Ne, and Hg-Kr as well as Hg-Ar are in progress in our laboratory.

We thank Professor I. Ohmine of the Institute for Molecular Science for his critical reading of the manuscript. Acknowledgment is also made to Mitsubishi Science Foundation for the financial support to this research project.

¹J. P. Fohr, W. L. Wiese, and L. J. Rosgnan, Bibliography on Atomic Line Shapes and Shifts, Nat. Bur. Stand. (U.S.) Spec. Pub. (1972), Suppl. 1 (1974) and Suppl. 2 (1975).

²W. Behmenburg, Z. Naturforsch. Teil A 27, 31 (1972).

³O. P. Strausz, J. M. Campbell, S. De Paoli, H. S. Sandhu, and H. E. Gunning, J. Am. Chem. Soc. 95, 732 (1981).

⁴H. C. Petzold and W. Behmenburg, Z. Naturforsch. Teil A 33, 1461 (1978).

⁵T. Gryczuk and E. Czerwosz, Physica C 106, 431 (1981).

⁶D. Perrin, Z. B. Lakhdar, J. C. Jeannet, and R. Lennuier, J. Phys. (Paris) 43, 45 (1982).

⁷H. F. Kielkopf and R. A. Miller, J. Chem. Phys. 61, 3304 (1974).

NOTES

FTIR observation of the N₂--HF complex in solid argon

Lester Andrews, Benue J. Kelsall, and Robert T. Arlinghaus

Chemistry Department, University of Virginia, Charlottesville, Virginia 22901

(Received 4 April 1983; accepted 24 May 1983)

During a series of matrix isolation studies of base-HF complexes,¹⁻⁶ spectra of (HF)₂ and (HF)₃ were observed in solid argon.^{7,8} Matrix samples containing HF were doped with N₂ to check for a possible impurity N₂--HF complex, and strong sharp absorptions¹ at 3881.5 and 262 cm⁻¹ were found to be related to N₂ present in the matrix. The linear N₂--HF complex (1) recently characterized by pulsed-nozzle microwave studies,⁹ has a weaker



hydrogen bond than the isoelectronic OC--HF and HCN--HF species.^{10,11} The vibrational spectrum of N₂--HF in solid argon, reported here, provides complementary spectroscopic information.

In FTIR experiments with HF in solid argon,¹⁻⁶ the sharp 3881.5 and 262 cm⁻¹ bands exhibited variable in-

tensity relative to (HF)₂ absorptions.^{7,8} The argon-HF system was reexamined with a Beckman IR-12 (4000-200 cm⁻¹)¹² and great care was taken to reduce the background pressure; very weak bands were observed at 3881 and 262 cm⁻¹ which increased markedly when N₂ was added to the matrix in subsequent experiments; sample warming increased both bands with approximately the same relative absorbances. FTIR experiments that exhibited a moderate yield ($A=0.3$) of the 3881.5 cm⁻¹ band in the freshly deposited sample produced a sharp, new 3787.7 cm⁻¹ band on warming and recooling the sample.⁷ The latter band was observed ($A=0.1$) in a Ar/HF=200/1 and Ar/N₂=300/1 sample deposited at 12 ± 1 K where the 3881.5 cm⁻¹ band was intense ($A=0.7$); this sample was warmed to 16, 20, and 24 K over a 4 h period and the 3881.5 cm⁻¹ band reached maximum absorbance after 40 min at 16 K, the 3825

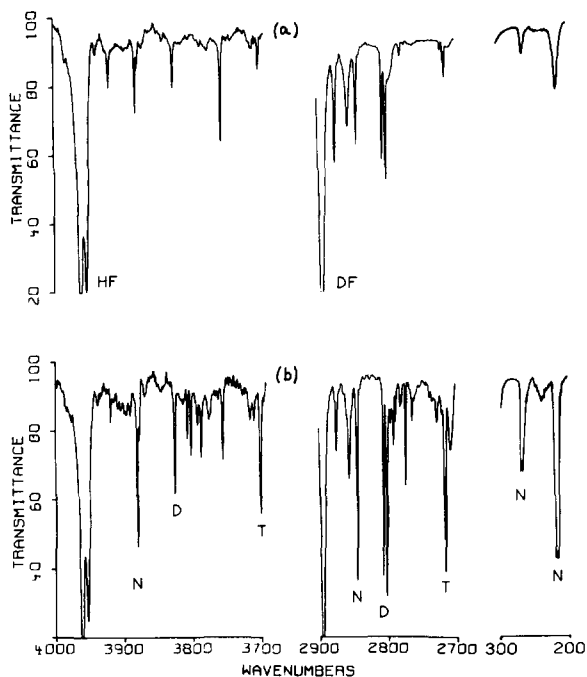


FIG. 1. FTIR spectra in the 4000–3780, 2900–2770, and 300–200 cm^{-1} regions for $\text{Ar}/(\text{HF}+\text{DF})=300/1$ samples, 75% DF enriched. (a) Samples deposited at 12 ± 1 K, (b) samples warmed to 26 ± 1 K and re-cooled to 12 ± 1 K.

cm^{-1} $(\text{HF})_2$ band peaked after 20 min at 20 K and the 3787.7 cm^{-1} band maximized after 60 min at 20 K.

The sharpest bands of interest were observed in HF and DF experiments with trace nitrogen contamination, and Fig. 1(a) illustrates such a spectrum for a 75% DF enriched sample. A single sharp DF counterpart was observed at 2846.2 cm^{-1} for the N band at 3881.5 cm^{-1} (FWHM = 1.0 cm^{-1}), the 3825.5 cm^{-1} $(\text{HF})_2$ band labeled D exhibited a $(\text{DF})_2$ counterpart at 2803.6 cm^{-1} and a (HF) (DF) satellite at 2808.0 cm^{-1} , and the 3702.0 cm^{-1} , open- $(\text{HF})_3$ band^{7,8} labeled T exhibited a $(\text{DF})_3$ counterpart at 2717.4 cm^{-1} with intermediate satellites. Similar HF and DF studies in solid krypton at 18 K gave sharp N bands at 3880.3 and 2845.4 cm^{-1} .

The far-infrared region yielded a 262 cm^{-1} band (FWHM = 5.0 cm^{-1}) with a DF counterpart at 214 cm^{-1} (FWHM = 3.5 cm^{-1}). Warming this sample to 26 ± 1 K and recooling to 12 ± 1 K produced changes in the spectra, as shown in Fig. 1(b); the N and D bands increased three fold, the T bands increased fivefold and the lower frequency bands split into sharp 263.2 , 260.7 cm^{-1} and 214.9 , 212.9 cm^{-1} doublets, and new M bands were

produced at 3787.7 and 2776.5 cm^{-1} (FWHM = 2.0 cm^{-1}).

The above experiments conclusively demonstrate that the 3881.5 and 262 cm^{-1} bands require N_2 , as shown by earlier workers for the 3881 cm^{-1} band,¹³ and the DF shifts verify that HF is present in the absorbing species. The fact that the 3881.5 cm^{-1} band reached a maximum in a warm argon matrix before the 3825 cm^{-1} $(\text{HF})_2$ band indicates that a single HF molecule is involved, a point further supported by the lack of mixed isotopic satellites near the 3881.5 and 2846.2 cm^{-1} bands. The 3881.5 and 262 cm^{-1} bands are, therefore, assigned to the $\text{N}_2\text{--HF}$ complex. The $\text{HF}/\text{DF} = 3881.5/2846.2 = 1.3637$ ratio is appropriate for the H–F stretching mode ν_s , and the small displacement from the 3953.7 cm^{-1} HF value ($\Delta\nu_s = 72 \text{ cm}^{-1}$) indicates a relatively weak hydrogen bond, weaker than in the OC--HF complex ($\Delta\nu_s = 164 \text{ cm}^{-1}$).¹⁴ The substantially lower $\text{HF}/\text{DF} = 1.224$ ratio is expected for the H–F librational mode ν_l of this weak hydrogen bond owing to considerable anharmonicity in the librational potential function. The ν_l mode for OC--HF is higher and less anharmonic ($\text{HF}/\text{DF} = 389.5/305.0 = 1.277$).¹⁴ The small splitting on the sharp ν_l mode, also observed for OC--HF in solid argon,¹⁴ is probably due to asymmetry in the argon matrix site, and is not inconsistent with a degenerate ν_l mode for this linear complex.

The diffusion data demonstrate that the 3787.7 cm^{-1} M band requires more HF than complex (1), and N_2 doping shows that N_2 is involved, which suggests the higher aggregate complex (2). This complex is simply $(\text{HF})_2$ with a slight



perturbation at $\text{H}_a\text{--F}$. The 3787.7 cm^{-1} band, which is slightly below the 3825 cm^{-1} $\text{H}_b\text{--F}$ mode for $(\text{HF})_2$, fits this model for the $\text{H}_b\text{--F}$ mode in complex (2). The lack of mixed isotopic satellites suggests that the interaction between $\text{H}_a\text{--F}$ and $\text{H}_b\text{--F}$ in complex (2) is minimal which could be explained by a 90° $\text{H}_a\text{--F--H}_b$ angle. On the other hand, the “inversion” found¹⁵ for $(\text{HF})_2$ is prevented in complex (2) by the N_2 molecule and this mechanism for interaction between H–F submolecules is not available for complex (2). The $\text{H}_a\text{--F}$ mode in complex (2) is expected to be considerably weaker, based on $(\text{HF})_2$ band intensities, and it was not detected here.

Chemical comparisons for the isoelectronic series of linear complexes are summarized in Table I. The matrix infrared spectra are consistent with the micro-

TABLE I. Spectroscopic data for a series of isoelectronic linear hydrogen bonded complexes.

	Argon matrix at 12 K ^a					Gas phase ^b		
	ν_s (cm^{-1})	HF/DF	$\Delta\nu_s$	ν_l	HF/DF	ν_s	R(B–H–F)	PA(B)
$\text{N}_2\text{--HF}$	3881	1.364	72	262	1.224	...	3.082	114
OC--HF	3789	1.362	164	389	1.277	3844	3.047	143
HCN--HF	3626	1.359	328	586	1.347	3710	2.795	170

^aThis work and Refs. 6 and 14.

^b ν_s in cm^{-1} , from Refs. 18 and 19; R in Å, from Refs. 9–11; PA in kcal/mol, from Ref. 16.

wave data,⁹⁻¹¹ base proton affinities,¹⁶ and recent *ab initio* calculations¹⁷ in characterizing increasing hydrogen bond strength with increasing $\Delta\nu_s$ for the complexes. Note the substantial increase in anharmonicity in the ν_i mode (as reflected in the HF/DF ratio) for the weaker hydrogen bond that is not matched in the ν_s mode.

Finally, gas-phase ν_s data^{18,19} for the more strongly bound complexes show that the gas-to-matrix shift appears to correlate with $\Delta\nu_s$, which predicts a gas-phase origin for ν_s of $\text{N}_2\cdots\text{HF}$ near $3890 \pm 10 \text{ cm}^{-1}$.

The authors gratefully acknowledge financial support from the National Science Foundation and a Fulbright Senior Research Fellowship for L.A.

¹L. Andrews and G. L. Johnson, J. Chem. Phys. **76**, 2875 (1982).

²G. L. Johnson and L. Andrews, J. Am. Chem. Soc. **104**, 3043 (1982).

³L. Andrews, G. L. Johnson, and B. J. Kelsall, J. Chem. Phys. **76**, 5767 (1982).

⁴L. Andrews, G. L. Johnson, and B. J. Kelsall, J. Phys. Chem. **86**, 3374 (1982).

⁵L. Andrews and G. L. Johnson, J. Phys. Chem. **86**, 3380 (1982).

⁶G. L. Johnson and L. Andrews, J. Am. Chem. Soc. **105**, 163 (1983).

⁷L. Andrews and G. L. Johnson, Chem. Phys. Lett. **96**, 133 (1983).

⁸L. Andrews and G. L. Johnson, J. Phys. Chem. (to be published).

⁹P. D. Soper, A. C. Legon, W. G. Read, and W. H. Flygare, J. Chem. Phys. **76**, 292 (1982).

¹⁰A. C. Legon, P. D. Soper, M. R. Keenan, T. K. Minton, T. J. Balle, and W. H. Flygare, J. Chem. Phys. **73**, 583 (1980).

¹¹A. C. Legon, D. J. Miller, and S. C. Rogers, Proc. R. Soc. London Ser. A **370**, 213 (1980).

¹²G. L. Johnson and L. Andrews, J. Am. Chem. Soc. **102**, 5736 (1980).

¹³M. T. Bowers, G. I. Kerley, and W. H. Flygare, J. Chem. Phys. **45**, 3399 (1966).

¹⁴L. Andrews, R. T. Arlinghaus, and G. L. Johnson, J. Chem. Phys. **78**, 6347 (1983).

¹⁵T. R. Dyke, B. J. Howard, and W. Klemperer, J. Chem. Phys. **56**, 2442 (1972).

¹⁶J. L. Beauchamp, in *Interactions Between Ions and Molecules*, edited by P. Ausloos (Plenum, New York, 1975).

¹⁷M. A. Benzel and C. E. Dykstra, J. Chem. Phys. **78**, 4052 (1983).

¹⁸R. K. Thomas, Proc. R. Soc. London Ser. A **325**, 133 (1971).

¹⁹E. K. Kyro, P. Shoja-Chaghervand, K. McMillan, M. Eliades, D. Danzeiser, and J. W. Bevan, J. Chem. Phys. **79**, 78 (1983).

COMMENTS

Rotational *R*-branch Raman spectroscopy in CO_2

K. Altmann,^{a)} W. Klöckner,^{b)} G. Strey,^{a)} H. Finsterhölzl, and H. W. Schrötter

Sektion Physik der LMU München, Schellingstr. 4, D 8000 München 40, West Germany
(Received 4 April 1983; accepted 17 May 1983)

Godfried and Silvera¹ have recently reported their Raman intensity measurements in the *R* branch of the pure rotational spectrum of vibrationally excited CO_2 molecules in a supersonic molecular beam. They claim this to be the first observation of these *R* branch lines.

We should like to draw attention to the fact that these lines have already been observed in static samples several years ago. Barrett and Weber² mentioned that they saw faint indications of the *R* branch lines on their photographic plates and later Wang³ confirmed this observation. Moreover, the *R* branches of vibrationally excited CO_2 and N_2O molecules at room temperature were resolved by three of us (KA, WK, and GS)⁴ up to $J=9$ with a photoelectrically recording Raman spectrometer.⁵ The intensities were calculated⁴ and found to be in agreement with theory taking into account only the $\bar{\alpha}_{zz}^{(2)}$ component of the anisotropic part of the polarizability tensor, as was now confirmed by Godfried and Silvera.¹ Further studies of rotational Raman spectra of vibrationally excited linear molecules include carbon disulfide,^{6,3} acetylene,^{7,8} and cyanogen.⁹

It may also be mentioned that the intensities in the

vibration-rotation Raman spectrum of several isotopic species of CO_2 were recently studied by one of us (HF).¹⁰

^{a)}Present address: Messerschmitt-Bölkow-Blohm, Ottobrunn.

^{b)}Present address: Elektronik System GmbH, München.

¹H. P. Godfried and I. F. Silvera, J. Chem. Phys. **78**, 121 (1983).

²J. J. Barrett and A. Weber, J. Opt. Soc. Am. **60**, 70 (1970).

³C. H. Wang, dissertation, Fordham University, New York, 1975.

⁴K. Altmann, W. Klöckner, and G. Strey, Z. Naturforsch. Teil A **31**, 1311 (1976).

⁵H. Finsterhölzl, H. W. Klöckner, K. Srinivasan, H. W. Schrötter, and J. Brandmüller, Indian J. Pure Appl. Phys. **16**, 370 (1978).

⁶W. J. Walker and A. Weber, J. Mol. Spectrosc. **39**, 57 (1971).

⁷H. Finsterhölzl, J. G. Hochenbleicher, and G. Strey, J. Raman Spectrosc. **6**, 13 (1977).

⁸I.-Y. Wang and A. Weber, Indian J. Pure Appl. Phys. **16**, 358 (1978).

⁹I.-Y. Wang and A. Weber, J. Chem. Phys. **67**, 3084 (1977).

¹⁰H. Finsterhölzl, Ber. Bunsenges. Phys. Chem. **86**, 797 (1982).