# Infrared Spectra of HF Complexes in Noble-gas Solids

## Lester Andrews

*Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901, U.S.A.*

The very weak hydrogen-bonded complex of molecular hydrogen and HF has been prepared by condensing the neon-diluted reagents at 5 K. Infrared spectra of the $H_2\cdots HF$ complex revealed a $\nu_s(HF)$ stretching mode at 3938 cm$^{-1}$ and $\nu(H_2)$ mode at 4155 cm$^{-1}$, which are bathochromically shifted from the isolated molecule values of 15 and 6 cm$^{-1}$, respectively. The very strong $NH_3\cdots HF$ complex has been studied in solid neon and solid argon. The $\nu_s(HF)$ mode at 3215 cm$^{-1}$ in the gas phase is shifted to 3106 cm$^{-1}$ in solid neon and 3041 cm$^{-1}$ at solid argon. The $\nu_l(HF)$ librational mode appeared at 916 cm$^{-1}$ with $2\nu_1$ at 1679 cm$^{-1}$, while $\nu_2(NH_3)$ was hypsochromically shifted to 1093 cm$^{-1}$ in solid argon. The antihydrogen-bonded arrangement is the more stable structure for the $HF\cdots Cl_2$ complex in the gas phase; however, solid argon and neon samples reveal both antihydrogen-bonded and hydrogen-bonded complexes. In the $Cl_2\cdots HCl$ case, evidence for only the hydrogen-bonded form was observed in solid argon

Matrix-isolation studies of reactive molecules and complexes can make unique contributions to the spectroscopy of these species by taking advantage of the matrix host. These advantages include accumulation of sufficient sample to observe weak absorptions, long cooling time to ensure that minimum temperature is reached by the sample, and fast relaxation of new energized species to prevent decomposition. In addition, a complete low-resolution spectrum can be recorded to provide a useful guide for diode laser studies. This report will describe chemical systems that exploit these advantages of matrix-isolation spectroscopy.

## The $NH_3\cdots HF$ Complex

The strong $NH_3\cdots HF$ complex was one of the first hydrogen-bonded complexes studied in our group and it remains one of the most interesting.[1,2] The $\nu_s(HF)$ fundamental and microwave spectrum have been observed in the gas phase (unpublished work by Thomas and Clements *et al.*), and the complex has three-fold symmetry. A series of matrix experiments was performed with isotopic ammonia and hydrogen fluoride samples in argon at 12 K, and the new absorptions are collected in table 1. The spectrum recorded for DF/HF and $NH_3$ identifies the HF submolecule modes due to the appearance of DF counterparts and the $NH_3$ submolecule mode ($\nu_2^C$), which shows only a very small effect for the acid isotope.[1,2] The strong $\nu_s(DF)$ band at 2278 cm$^{-1}$ (f.w.h.m. = 4 cm$^{-1}$) has a $\nu_s(HF)$ counterpart at 3041 cm$^{-1}$ (f.w.h.m. = 16 cm$^{-1}$). Sharp librational $\nu_1$ bands were observed for HF and DF at 916.0 and 696.7 cm$^{-1}$ with their overtones at 1679.4 and 1315.9 cm$^{-1}$. The HF submolecule fundamentals observed for the complex are the $\nu_s(HF)$ stretching fundamental and the $\nu_l(HF)$ librational mode derived from rotational degrees of freedom from the isolated diatomic. The doubly degenerate nature of this librational motion is maintained by the $C_{3v}$ symmetry of the complex. The $\nu_s(HF)/\nu_s(DF) = 3041/2278 = 1.334$ ratio is characteristic of the HF stretching mode in a hydrogen-bonded complex. The overtone ratio $2\nu_1(HF)/2\nu_1(DF) = 1679/1316 = 1.276$ is less than the fundamental ratio $\nu_1(HF)/\nu_1(DF) = 916/697 = 1.314$ owing to increased

**Table 1.** Absorptions ($cm^{-1}$) for the ammonia–hydrogen fluoride complex in solid neon and argon

| neon | | argon | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $NH_3 + HF$ | $NH_3 + DF$ | $NH_3 + HF$ | $NH_3 + DF$ | $^{15}NH_3 + HF$ | $^{15}NH_3 + DF$ | $ND_3 + HF$ | $ND_3 + DF$ | assignment |
| 3106 | 2309 | 3041 | 2278 | 3042 | 2277 | 3017 | 2269 | $\nu_s$ |
| 1676 | 1317 | 1679 | 1316 | 1678 | 1314 | 1664 | 1272 | $2\nu_1$ |
| 1090 | 1091 | 1093 | 1094 | 1087 | 1088 | 849 | 849 | $\nu_2^c$ |
| 912 | 695 | 916 | 697 | 915 | 695 | 906 | 675 | $\nu_1$ |

anharmonicity in the overtone. The positions of the $\nu_s$ and $\nu_1$ modes provide a measure of the interaction between acid and base as the $\nu_s$ mode is decreased from the 3919 $cm^{-1}$ stretching fundamental and the $\nu_1$ mode is increased from the 44 $cm^{-1}$ rotational fundamental of the diatomic.

The ammonia submolecule mode $\nu_2^c$ in the complex follows $^{15}NH_3$ and $ND_3$ substitution, as does $\nu_2$ of ammonia. The $\nu_2^c$ mode is not split by inversion as $\nu_2$ for $NH_3$ is split; this shows that the acid ligand presents inversion of the ammonia submolecule in the complex **1**. Note the effect of $^{15}NH_3$ and $ND_3$ substitution on the HF submolecule modes; this verifies that a reagent complex has been formed in the matrix.

The $NH_3\cdots HF$ complex has been prepared in solid neon for comparison with the argon-matrix data (table 1). First, the strong $\nu_s$ band at 3106 $cm^{-1}$ (f.w.h.m. = 10 $cm^{-1}$) is sharper than in solid argon and it falls approximately midway between the gas-phase (3215 $cm^{-1}$) and argon-matrix (3041 $cm^{-1}$) values. The $2\nu_1$ and $\nu_1$ modes are shifted only a slightly and the ratio is essentially unchanged from the solid-argon value. The $\nu_2^c$ band at 1090 $cm^{-1}$ is also shifted only slightly from the solid-argon value, but the shift above $NH_3$ in solid neon, 122 $cm^{-1}$, is essentially the same as in solid argon, 120 $cm^{-1}$. The HF/DF ratios in solid neon are essentially unchanged from solid-argon values. The neon medium is more inert, and the argon matrix effect is clearly seen to be greater on $\nu_s$ than on $\nu_1$ and $\nu_2^c$. This probably arises from the greater polarizability of argon and the large dipole change in the $\nu_s$ vibration.
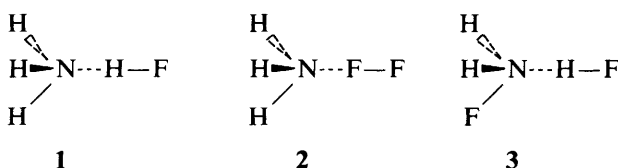


**NH₃···F₂ and NH₂F···HF Complexes**

The fluorine–ammonia matrix system yielded two interesting new complexes.[3] On codeposition of Ar/NH₃ and Ar/F₂ samples, new bands appeared at 966 and 781 $cm^{-1}$. These bands increased threefold on sample annealing and decreased markedly on photolysis that produced the $NH_2F\cdots HF$ complex to be described below, hence assignment of the strong 966 and weak 781 $cm^{-1}$ bands to the $NH_3\cdots F_2$ complex **2** follows. The strong 966 $cm^{-1}$ band is within 1 $cm^{-1}$ of the median of the inversion-split Q branches of $NH_3$ in solid argon,[4] which demonstrates that even the weak $NH_3\cdots F_2$ interaction prevents inversion of the $NH_3$ submolecule in the complex. The weak 781 $cm^{-1}$ band is below the 892 $cm^{-1}$ Raman fundamental of $F_2$ in solid argon, which suggests a weak charge-transfer interaction between $NH_3$ and $F_2$.

The major photolysis product bands in the $NH_3\cdots F_2$ system appeared at 3389 $cm^{-1}$ ($\nu_s$), 3269 $cm^{-1}$ ($\nu_1$), 1568 $cm^{-1}$ ($\nu_2$), 1314 $cm^{-1}$ ($2\nu_1$), 1244 $cm^{-1}$ ($\nu_3$), 934 $cm^{-1}$ ($\nu_4$) and

**Table 2.** Infrared absorptions (cm$^{-1}$) for the amine-bonded $H_2FN\cdots HF$ complex in solid argon

| $H_2FN\cdots HF$ | $H_2F^{15}N\cdots HF$ | $HDFN\cdots HF$ | $D_2FN\cdots DF$ | assignment |
|---|---|---|---|---|
| 3389 | 3388 | 3384 | 2505 | $\nu_s$ |
| 3269 | 3264 | | 2399 | $\nu_1$ (N—$H_2$ str) |
| 1568 | 1566 | 1429 | 1151 | $\nu_2$ (N—$H_2$ bend) |
| 1314 | 1314 | 1312 | 998 | $2\nu_1$ |
| 1244 | 1238 | | 968 | $\nu_3$ (NH$_2$ wag) |
| 934 | 916 | 933 | 924 | $\nu_4$ (N—F str) |
| 750 | 750 | | 561 | $\nu_l$ (in-plane) |
| 723 | 723 | | 540 | $\nu_l$ (out-plane) |

750, 723 cm$^{-1}$ ($\nu_l$), which are listed in table 2 along with their ND$_3$ and $^{15}$NH$_3$ counterparts. The $\nu_s$ and $\nu_l$ bands are clearly due to acid submolecule and the $\nu_1$, $\nu_2$, $\nu_3$ and $\nu_4$ bands to base submolecule modes in a new complex with the structure proposed in **3** based on the spectrum. This nitrogen lone-pair complex $H_2FN\cdots HF$ is weaker than $H_3N\cdots HF$ as $\nu_s$ is displaced less (to 3389 cm$^{-1}$) and the $\nu_l$ modes are increased less (to 750 and 723 cm$^{-1}$). The base has less than threefold symmetry based on splitting of the librational mode into two bands. The other four bands show isotopic shifts and components for the NH$_2$F vibrations as assigned in the table. Unfortunately isolated NH$_2$F has not been characterized owing to its extremely great reactivity, and it is observed here because of efficient quenching of the reaction exothermicity by the cold matrix.

### Hydrogen Molecule–HF Complex

Very weak, hydrogen-bonded complexes of molecular hydrogen and HF have been prepared by condensing the neon-diluted reagents at 5 K. Infrared spectra of an Ne/H$_2$/HF sample in fig. 1 reveal HF monomer, dimer (D) and trimer (T) bands at 3992, 3953, 3919, 3848 and 3706 cm$^{-1}$, a strong, sharp $\nu_s$ band at 3838 cm$^{-1}$, a weak $\nu^c$ band at 4155 cm$^{-1}$, a weaker $\nu^{cc}$ band at 4146 cm$^{-1}$ and split $\nu_{sa}$ and $\nu_{sb}$ bands at 3889 and 3840 cm$^{-1}$.[5,6] Changes in reagent concentration and sample annealing show that the $\nu^{cc}$, $\nu_{sa}$ and $\nu_{sb}$ bands are due to a higher-order complex than $\nu^c$ and $\nu_s$. Accordingly, the primary product complex is identified as $H_2\cdots HF$ (**4**) and the higher-order complex as $H_2\cdots(HF)_2$ (**5**). Vibrational assignments are aided by the isotopic data given in table 3. The $\nu_s$ band is displaced 15 cm$^{-1}$ below isolated HF in solid neon (3953 cm$^{-1}$) and exhibits an HF/DF ratio of 1.364; which is appropriate for an HF complex; the $\nu^c$ band is shifted 6 cm$^{-1}$ below the H$_2$ fundamental in the gas phase and exhibits an H$_2$/D$_2$ ratio of 1.389, near that for the gaseous diatomics (1.390). Accordingly, the $\nu_s$ and $\nu^c$ bands are assigned to the H—F and H—H fundamentals in the $H_2\cdots HF$ complex, and in like fashion, the $\nu^{cc}$, $\nu_{sa}$ and $\nu_{sb}$ assignments follow as well. Comparison of fundamentals for **4, 5** and (HF)$_2$ is of chemical interest. The $H_a$—F and $H_b$—F fundamentals of (HF)$_2$ at 3919 and 3848 cm$^{-1}$ are displaced to 3889 and 3840 cm$^{-1}$ by the addition of H$_2$ to form **5**; note the greater effect for the $H_a$—F mode where H$_2$ is attached. Likewise, when $H_b$—F binds to **4** the H—F mode is shifted from 3938 to 3889 cm$^{-1}$ owing to the fluoride affinity of $H_b$—F.
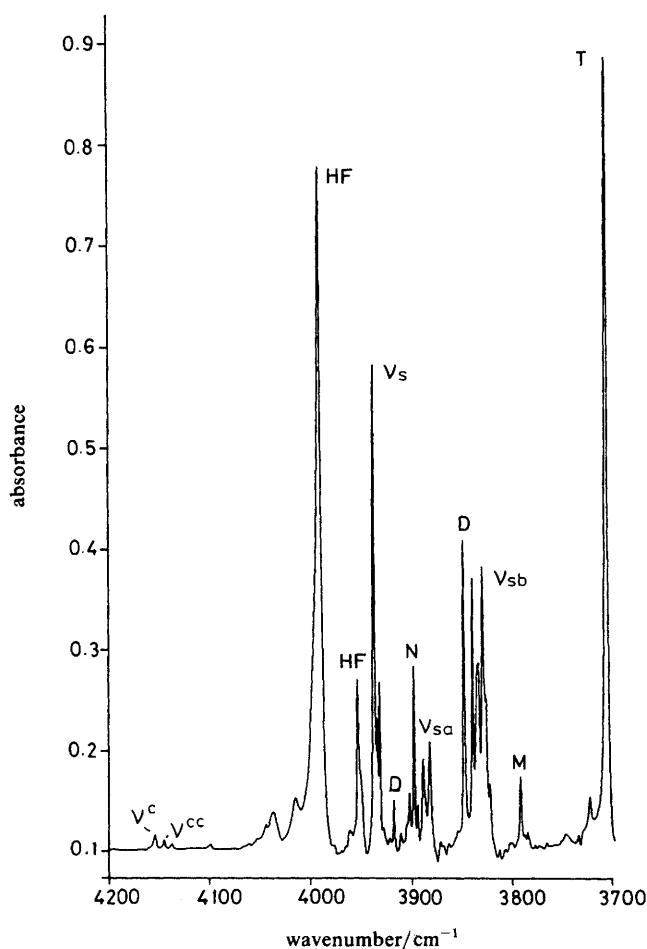
H
| ⋯⋯H—F        **4**
H

H
| ⋯⋯$H_a$—F        **5**
H                ⋰
                $H_b$
                  ＼
                    F

*HF Complexes in Noble-gas Solids*
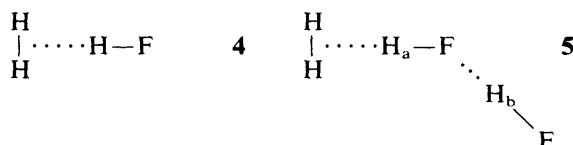


**Fig. 1.** Infrared spectra (4200–3700 cm$^{-1}$) for hydrogen and hydrogen fluoride in solid neon: 11 mmol of Ne/H$_2$ = 50/1 and 11 mmol of Ne/HF = 200/1 codeposited at 4 K.

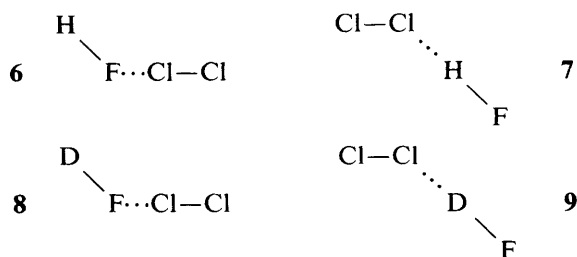**Table 3.** Absorptions (cm$^{-1}$) for molecular hydrogen and hydrogen fluoride complexes in solid neon at 5 K

| H$_2$ + HF | H$_2$ + DF | D$_2$ + HF | D$_2$ + DF | assignment |
|---|---|---|---|---|
| 4155 | 4152 | 2991 | 2988 | $\nu^c$ (**4**) |
| 4146 | 4143 | 2983 | 2980 | $\nu^{cc}$ (**5**) |
| 3938 | 2887 | 3938 | 2886 | $\nu_s$ (**4**) |
| 3889 | 2850 | 3887 | 2848 | $\nu_{sa}$ (**5**) |
| 3840 | 2814 | 3838 | 2813 | $\nu_{sb}$ (**5**) |

Note the relatively larger effect of DF on $H_2$ and $D_2$ than HF, which is listed in table 3. This is due to the shorter time-average distance of D from $H_2$ than H owing to the smaller librational amplitude of DF. In the $D_2 \cdots HF$ complex the $\nu^c$ mode was bathochromically shifted only 3 cm$^{-1}$ below the gas-phase fundamental for $D_2$. Clearly the $D_2$ oscillator is less susceptible to electrical interactions than $H_2$ since $D_2$ is substantially lower in the potential well.

Initial studies on $H_2$—HF were performed in solid argon. The $H_2 \cdots HF$ complex gave a $\nu_s$ mode shifted hypsochromically 8-17 cm$^{-1}$ above the HF fundamental in solid argon, and the value of these results was confused by interaction with the argon matrix. Replacing one argon atom by $H_2$ provided a repulsive contribution to the HF intramolecular potential function and hypsochromic shift resulted since $H_2$ is only slightly more physically inert than argon. Neon is, however, still more inert and neon-matrix studies of very weak complexes are representative of gas-phase studies. Accordingly, the neon-matrix work, taking the weak $Ar \cdots HF$ complex as a model, predicts a gas-phase band at 3950 cm$^{-1}$ for $H_2 \cdots HF$,[5] which has subsequently been observed.[7,8] The gas-phase spectrum has been analysed in terms of a $j = 1$ hindered $H_2$ rotor in an anisotropic potential with a minimum energy at the T-shaped geometry; no evidence was found for the corresponding $para - H_2 \cdots HF$ complex.[7] The neon-matrix experiments provide data for only one 1:1 complex, which is most probably the same $ortho - H_2 \cdots HF$ complex characterized in the gas phase. In other words, HF 'traps' $H_2$ in the *ortho* spin state, whereas in a matrix with trace $O_2$ present, conversion to the *para* spin state eventually occurs for $H_2$ molecules isolated in the matrix.[5]

## Chlorine–Hydrogen Halide Complexes

The HF—$Cl_2$ complex has been studied in a molecular beam[9] and by theoretical calculations.[10] Both conclude that the anti-hydrogen-bonded $HF \cdots Cl_2$ arrangement (**6**) is more stable than the hydrogen-bonded $Cl_2 \cdots HF$ structure (**7**); however, the energy difference is calculated to be small ($<100$ cm$^{-1}$). In an argon matrix at 5 K, HF/$Cl_2$ mixtures[11] gave sharp new bands at 3901 and 2864 cm$^{-1}$ (labelled $a\nu_s$) above the $N_2 \cdots HF$ and $N_2 \cdots DF$ complexes (labelled N)[12] and sharp multiplets at 3860, 3853, 3848 and 2831, 2826, 2822 cm$^{-1}$ ($\nu_s$) between N and hydrogen fluoride dimer (D), fig. 2(*a*). In an argon matrix at 12 K, the $a\nu_s$ bands were stronger relative to $\nu_s$, and on sample annealing to 23 K, both $a\nu_s$ and $\nu_s$ features increased, fig. 2(*b*) and (*c*), but the $a\nu_s$ band increased more than $\nu_s$ in the case of HF.

$$
\begin{matrix}
\text{H} & & & \text{Cl—Cl} & & \\
\quad\diagdown & & & \quad\diagdown\raisebox{-1ex}{\tiny .} & & \\
\textbf{6} \quad & \text{F}\cdots\text{Cl—Cl} & & & \text{H} & \textbf{7} \\
& & & & \quad\diagdown & \\
& & & & \quad\text{F} & \\
\end{matrix}
$$

$$
\begin{matrix}
\text{D} & & & \text{Cl—Cl} & & \\
\quad\diagdown & & & \quad\diagdown\raisebox{-1ex}{\tiny .} & & \\
\textbf{8} \quad & \text{F}\cdots\text{Cl—Cl} & & & \text{D} & \textbf{9} \\
& & & & \quad\diagdown & \\
& & & & \quad\text{F} & \\
\end{matrix}
$$

The new absorptions in HF/DF/$Cl_2$ matrix samples are considered for 1:1 complexes between HF and $Cl_2$. It is expected that the $HF \cdots Cl_2$ arrangement perturbs the H—F fundamental less than the $Cl_2 \cdots HF$ structure since this vibration is primarily a hydrogen motion. The $a\nu_s$ band at 3901 is bathochromically shifted 18 cm$^{-1}$ from the HF-induced Q branch[2] at 3919 cm$^{-1}$, not as much as the $HF \cdots HCN$ complex[13] at 3891 cm$^{-1}$, and the strongest $\nu_s$ band at 3860 cm$^{-1}$ is bathochromically shifted 59 cm$^{-1}$, more than $N_2 \cdots HF$ at 3881 cm$^{-1}$. These data are consistent with assignment of the $a\nu_s$ band to **6** and the $\nu_s$ bands to **7**. Parallel studies with ClF support these assignments as ClF is a
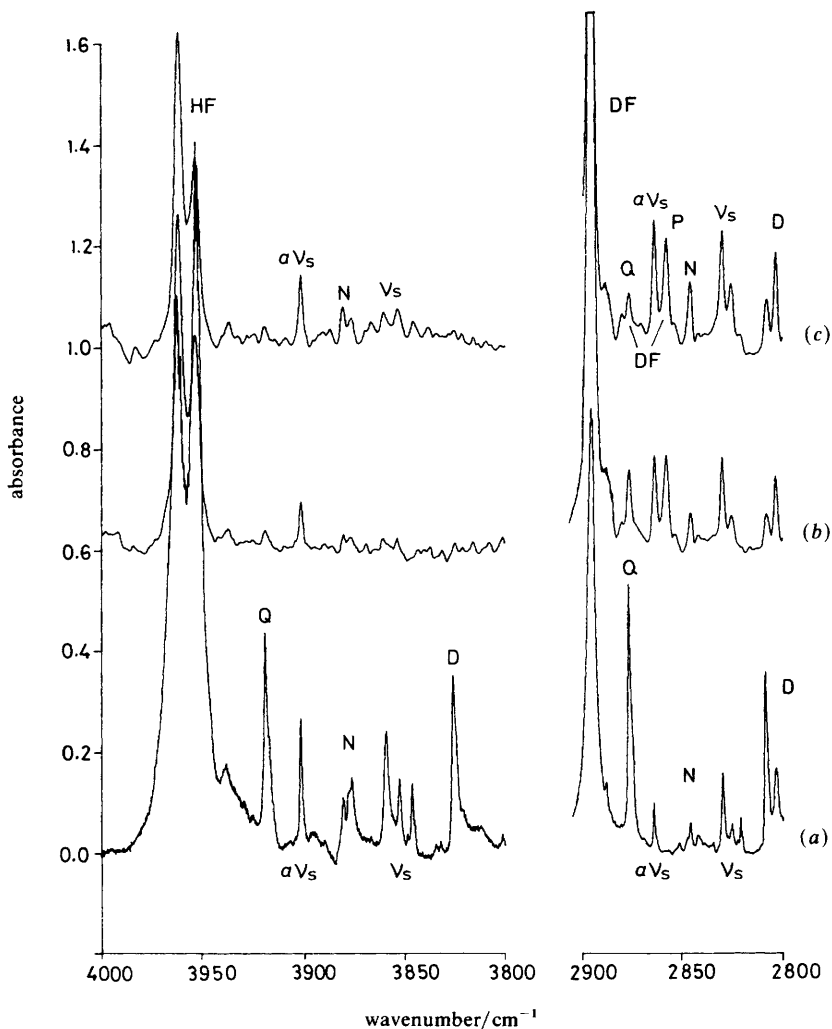
*HF Complexes in Noble-gas Solids*

**Fig. 2.** Infrared spectra in the HF and DF regions for $Cl_2$ mixtures in solid argon: (*a*) after codeposition of Ar/(HF + DF) = 200/1 (60% DF) and Ar/$Cl_2$ = 200/1 at 5 K for 3 h, (*b*) after deposition of Ar/(HF + DF) = 200/1 (90% DF) and Ar/$Cl_2$ = 200/1 at 12 K for 4 h, (*c*) after warming to 23 K and recooling to 12 K.

stronger Lewis acid but a weaker Lewis base than $Cl_2$ owing to the inductive effect of fluorine.[11] The HF$\cdots$ClF complex absorption at 3896 cm$^{-1}$ indicates a stronger interaction than **6**, and FCl$\cdots$HF band at 3870 cm$^{-1}$ denotes a weaker interaction than that found for **7**.

The greater relative yield of the more stable **6** arrangement compared to **7** in 12 K argon matrices is consistent with beam experiments and calculations. However, freezing the samples more quickly at 5 K gives more absorbance for the **7** species, and this is more pronounced for DF than HF. Similar observations[11] were found in solid neon at 5 K. Apparently the lower temperature does not allow thermodynamic equilibrium to be established between structures and traps relatively more of the less stable arrangement. The matrix results suggest that **9** is closer in energy to **8** and perhaps even lower and invite gas-phase and theoretical studies on the DF species **8** and **9** to test this hypothesis.
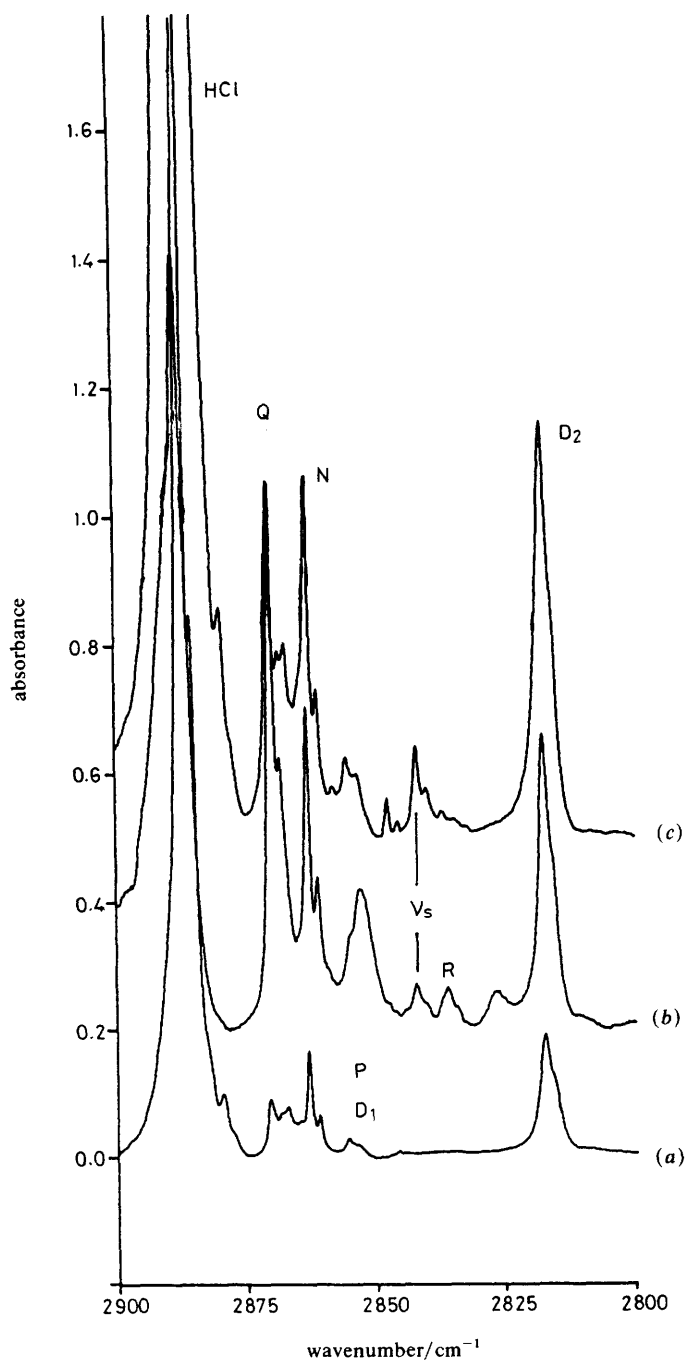
**Fig. 3.** Infrared spectra (2900–2800 cm$^{-1}$) for chlorine and hydrogen chloride in solid argon: (*a*) 6 mmol of Ar/HCl = 200/1 deposited at 5 K, (*b*) Ar/HCl = 200/1 codeposited at 12 K with Ar/Cl$_2$ = 100/1 sample passed through microwave discharge and (*c*) continuation of (*a*) with 7 mmol of Ar/HCl = 200/1 codeposited at 5 K with 3.5 mmol of Ar/Cl$_2$ = 100/1 sample.

Similar experiments have been performed with the $HCl/DCl/Cl_2$ system to prepare the analogous complexes.[14] Fig. 3 illustrates spectra for Ar/HCl: the strong HCl R(0) band, the induced Q doublet, the $N_2\cdots HCl$ complex, the HCl P(1) and $(HCl)_2$ bands are in agreement with earlier studies.[15] On deposition with $Ar/Cl_2$ a new chlorine isotopic doublet was observed at 2842.2, 2840.1 $cm^{-1}$ [labelled $\nu_s$ in fig. 3(c)] between the N doublet (2863.5, 2861.3 $cm^{-1}$) and $(HCl)_2$ (2817.5, 2815.4 $cm^{-1}$ sh); no new features were observed between the Q doublet (2871.0, 2868.7 $cm^{-1}$) and the N doublet. In a separate experiment the $Ar/Cl_2$ stream was passed through a microwave discharge to dissociate chlorine and was subsequently codeposited with an Ar/HCl stream, and in addition a new doublet was observed at 2836.4, 2834.5 $cm^{-1}$ (labelled R) [fig. 3(b)] and $HCl_2^-$ appeared at 696 $cm^{-1}$.[16] The chlorine isotopic doublet between $N_2\cdots HCl$ and $(HCl)_2$ is assigned to the $Cl_2\cdots HCl$ complex and the new band in the discharge experiments is due to the $Cl\cdots HCl$ complex. Again comparison with the ClF system,[14] which reveals a new doublet at 2849.9, 2848.1 $cm^{-1}$ for the $FCl\cdots HCl$ complex, supports this identification of $Cl_2\cdots HCl$ because $FCl\cdots HCl$ is expected to be a weaker complex and exhibit a smaller shift in the H—Cl fundamental than the $Cl_2\cdots HCl$ complex. Finally, comparison of the HCl fundamental in the $Cl_2\cdots HCl$ complex at 2842.2 $cm^{-1}$ with HCl fundamentals in the $Br_2\cdots HCl$ and $I_2\cdots HCl$ complexes at 2820.2 and 2783.9 $cm^{-1}$ in solid argon, respectively,[17] defines a trend of increasing hydrogen-bonding interaction with increasing halogen molecule size and polarizability. In addition the heavy halogen atom complexes with HCl exhibit stronger interactions with HCl than the diatomic,[17] as found for chlorine.

Three points are noteworthy: (1) the chlorine atom inteaction with HCl is slightly stronger than the $Cl_2$ molecule interaction, (2) the anion electron makes a significant difference in the bonding and structure of the weak $Cl\cdots H$—Cl complex and the strongly hydrogen-bonded centrosymmetric anion $HCl_2^-$, and (3) with HCl the favoured structure is the $Cl_2\cdots HCl$ hydrogen-bonded form, whereas with HF the anti-hydrogen-bonded form $HF\cdots Cl_2$ discussed above is the more stable arrangement. Although HCl forms a weaker hydrogen bond than HF, the much larger covalent radius of chlorine results in a much weaker Lewis acid–base interaction $HCl\cdots Cl_2$, which allows the $Cl_2\cdots HCl$ arrangement to be more stable in this system.

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