

Infrared spectra of CIF, Cl₂, and Cl complexes with HCl in solid argon

Lester Andrews and Rodney D. Hunt

Citation: *The Journal of Chemical Physics* **89**, 3502 (1988); doi: 10.1063/1.454921

View online: <http://dx.doi.org/10.1063/1.454921>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/89/6?ver=pdfcov>

Published by the AIP Publishing

Articles you may be interested in

[A new ab initio potential energy surface and infrared spectra for the Ar-CS₂ complex](#)

J. Chem. Phys. **141**, 104306 (2014); 10.1063/1.4894504

[Coherent spin control of matrix isolated molecules by IR+UV laser pulses: Quantum simulations for CIF in Ar](#)

J. Chem. Phys. **120**, 11522 (2004); 10.1063/1.1753256

[Depolarization as a probe for ultrafast reorientation of diatomics in condensed phase: CIF versus I₂ in rare gas solids](#)

J. Chem. Phys. **117**, 5 (2002); 10.1063/1.1486444

[Photochemical reactions of CIF and BrF with hydrogen in solid argon. Infrared spectra of mixed hydracid dimers](#)

J. Chem. Phys. **88**, 3599 (1988); 10.1063/1.453909

[Extraatomic relaxation in HCl, CIF, and Cl₂ from xray photoelectron spectroscopy](#)

J. Chem. Phys. **78**, 5437 (1983); 10.1063/1.445472



Infrared spectra of ClF, Cl₂, and Cl complexes with HCl in solid argon

Lester Andrews and Rodney D. Hunt

Chemistry Department, University of Virginia, Charlottesville, Virginia 22901

(Received 6 May 1988; accepted 17 June 1988)

Argon mixtures of ClF, Cl₂, and Cl atoms have been codeposited with Ar/HCl at 5 and 12 K. Infrared spectra in the HCl stretching region give evidence for the FCl-HCl, Cl₂-HCl, and Cl-HCl hydrogen-bonded complexes. The molecular complexes are more stable in the hydrogen-bonded than antihydrogen-bonded forms as no evidence for the latter were observed. The Cl-HCl radical hydrogen-bonded complex is considerably different from the centrosymmetric (Cl-H-Cl)⁻ anion.

INTRODUCTION

Hydrogen bonding and Lewis acid-base interactions play significant roles in intermolecular interactions. Competition between these two means of intermolecular binding is typified by the Cl₂ and ClF complexes with HF. Molecular beam electric resonance spectroscopy has determined the most stable structures to be antihydrogen bonded HF-Cl₂ and HF-ClF.¹⁻² Theoretical calculations have suggested that the hydrogen bonded isomers are of almost identical stability,³⁻⁵ and the most recent *ab initio* calculations find slightly greater stability for the antihydrogen bonded forms. Very recent matrix infrared studies provide evidence for both structural arrangements and support the greater stability for the antihydrogen bonded forms.⁶ The present study reports infrared observation and characterization of the Cl₂ and ClF complexes with HCl.

For the last two decades, attempts to identify and characterize hydrogen dihalide radicals XHX have not been successful since the controversy^{7,8} over (ClHCl) radical has been settled in favor of (ClHCl)⁻ with further matrix⁹ and gas phase¹⁰ characterizations of the anion. Nevertheless, evidence has been found for weakly bound complexes Cl-HF, Br-HF, and F-HF using matrix photochemistry.^{6,11,12} The matrix infrared evidence for F-HF as a weak hydrogen bonded complex is completely in accord with LCAO-MO-SCF calculations.¹³ The analogous Cl-HCl complex has been prepared and will also be reported here.

EXPERIMENTAL

The matrix infrared experiments have been described previously⁶; HCl (Matheson) and DCl (MSD Isotopes) were codeposited from specially treated stainless steel manifolds. Chlorine atoms were produced by microwave discharge of the Ar/Cl₂ stream.¹⁴ Air products Displex (two-stage) and Heliplex (three-stage) closed-cycle refrigerators were used for 12 and 5 K experiments, respectively. Infrared spectra were recorded on a Nicolet 7199 FTIR spectrometer at 0.24 cm⁻¹ resolution; reported bands are accurate to ± 0.1 cm⁻¹.

RESULTS

Figure 1(a) shows the spectrum of an Ar/HCl = 200/1 sample codeposited at 5 K; the band positions are in agree-

ment with earlier studies^{15,16} (the trimer band at 2787 cm⁻¹ was weak). At 12 K the *P*(1) band of HCl at 2853.5 cm⁻¹ is much more intense than the (HCl)₂ band at 2855.8 cm⁻¹ [Fig. 1(b)] supporting its assignment. Figure 1(c) illustrates the spectrum of Ar/HCl and Ar/Cl₂ samples codeposited at 5 K, which reveals new chlorine isotopic doublets at 2847.9, 2845.8 cm⁻¹ and 2842.2, 2840.1 cm⁻¹ (labeled ν_s). Figure 1(d) shows a similar spectrum of Ar/HCl and Ar/ClF samples; a new doublet was observed at 2849.9, 2848.1 cm⁻¹ along with the HF-HCl complex¹¹ at 2834.5, 2832.5 cm⁻¹ from HF impurity in the ClF sample and ClF itself¹⁷ at 770 and 763 cm⁻¹. Figure 1(b) illustrates the spectrum of Ar/HCl codeposited with Ar/Cl₂ passed through a coaxial microwave discharge to dissociate Cl₂; a new doublet was observed at 2836.4, 2834.5 cm⁻¹ (labeled *R*), traces of atomic chlorine species (ClO₂, ClCO, NCl) were detected,¹⁴ and HCl₂⁻ was observed at 696 cm⁻¹ in solid argon,⁹ near the recently reported 722 cm⁻¹ gas phase value.¹⁰ Sample warming to 27-39 K to allow diffusion and association of trapped species^{15,16,18} substantially increased (HCl)₂, (HCl)₃, N₂-HCl, and N₂-(HCl)₂ at the expense of HCl, and increased the *R* doublet by 30% and the ν_s doublet by 150%.

The lower region in the figure shows spectra from corresponding DCl experiments. The stronger new ν_s doublet for Cl₂ and DCl appeared at 2057.4, 2054.4 cm⁻¹ and a weaker band appeared at 2063.9 cm⁻¹. The discharge experiment produced a new *R* isotopic doublet at 2053.5 and 2050.4 cm⁻¹. The ClF experiment gave a new 2065.3, 2062.3 cm⁻¹ doublet (ν_s) plus HF-DCl at 2052.2, 2049.3 cm⁻¹. The magnitude of the deuterium and chlorine isotopic shifts identify H-Cl and D-Cl fundamental vibrations. The N₂-HCl complex bands are sharp and resolved;¹⁸ the H³⁵Cl/D³⁵Cl ratio (1.3812) and H³⁷Cl/D³⁷Cl ratio (1.3821) for this species are typical. Note the larger ratio for ³⁷Cl owing to the larger ³⁵Cl-³⁷Cl shift for chlorine vibrating against D than against H. The ν_s and *R* bands exhibit almost identical isotopic frequency ratios which are characteristic of H-Cl and D-Cl fundamental vibrations.

DISCUSSION

Cl₂-HCl and FCl-HCl complexes

The codeposition of Ar/Cl₂ and Ar/HCl samples produced two new chlorine isotopic doublets, the stronger at

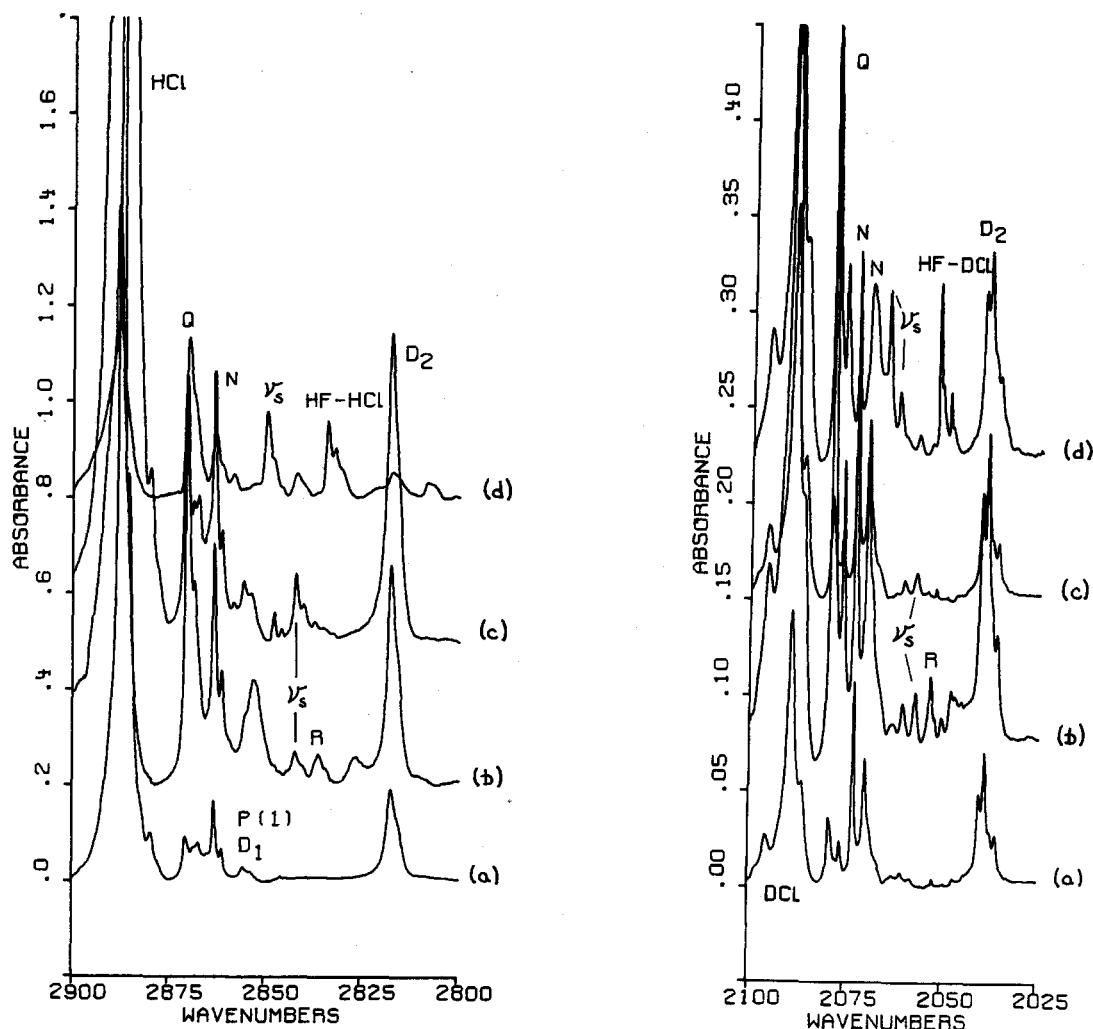


FIG. 1. Infrared spectra in the 2900–2800 cm^{-1} region for hydrogen chloride, chlorine, and chlorine monofluoride in solid argon: (a) 7 m mol of $\text{Ar}/\text{HCl} = 200/1$ deposited at 5 K, (b) 28 m mol $\text{Ar}/\text{HCl} = 200/1$ codeposited at 12 K with 12 m mol $\text{Ar}/\text{Cl}_2 = 100/1$ sample passed through microwave discharge, (c) continuation of (a) with 8 m mol of $\text{Ar}/\text{HCl} = 200/1$ codeposited at 5 K with 4 m mol of $\text{Ar}/\text{Cl}_2 = 100/1$ sample, and (d) 11 m mol $\text{Ar}/\text{HCl} = 200/1$ codeposited at 10 K with 12 m mol of $\text{Ar}/\text{ClF} = 200/1$ sample. Infrared spectra in the 2100–2025 cm^{-1} region for comparable experiments with DCl (approximately 80% deuterium enrichment).

TABLE I. Infrared absorptions (cm^{-1}) in argon matrix samples containing HCl , ClF , and Cl_2 .

HCl	$\text{HCl} + \text{ClF}$	$\text{HCl} + \text{Cl}_2$	DCl	$\text{DCl} + \text{ClF}$	$\text{DCl} + \text{Cl}_2$	Ident.
2888			2089			$\text{HCl } R(0)$
2871.0			2079.3			$\text{H}^{35}\text{Cl } Q$
2868.7			2076.4			$\text{H}^{37}\text{Cl } Q$
2863.4			2073.1			$\text{N}_2\text{--H}^{35}\text{Cl}$
2861.3			2070.2			$\text{N}_2\text{--H}^{37}\text{Cl}$
2855.8						$(\text{HCl})_2(\text{D}_1)$
2853.3						$\text{HCl } P(1)$
	2849.9			2065.3 ^d		$\text{FCl--H}^{35}\text{Cl}$
	2848.1			2062.3		$\text{FCl--H}^{37}\text{Cl}$
		2842.2 ^a			2057.4 ^b	$\text{Cl}_2\text{--H}^{35}\text{Cl}$
		2840.1			2054.4	$\text{Cl}_2\text{--H}^{37}\text{Cl}$
		2836.4 ^c			2053.5 ^c	$\text{Cl--H}^{35}\text{Cl}$
		2834.5 ^c			2050.4 ^c	$\text{Cl--H}^{37}\text{Cl}$
2817.5			2039.2			$(\text{HCl})_2(\text{D}_2)$

^a Weaker matrix site at 2847.9, 2845.8 cm^{-1} .

^b Weaker matrix site at 2063.9 cm^{-1} .

^c Bands produced when Ar/Cl_2 stream subjected to microwave discharge; additional band at 2827 cm^{-1} may also be due to R species.

^d Additional broader band at 2069 cm^{-1} may also be due to ν_s .

2842.2, 2840.1 cm^{-1} and the weaker at 2847.9, 2845.8 cm^{-1} . These new H-Cl absorptions are below the hydrogen bonded $\text{N}_2\text{--HCl}$ complex¹⁸ H-Cl fundamental at 2863.4, 2861.3 cm^{-1} and it is, therefore, probable that the new bands are due to different matrix sites of a more strongly interacting hydrogen-bonded complex than $\text{N}_2\text{--HCl}$. The new bands are red shifted 23.1 and 28.8 cm^{-1} from the HCl induced Q branch (2871.0 cm^{-1}) whereas the $\text{N}_2\text{--HCl}$ complex is red shifted only 7.6 cm^{-1} . No new absorptions were observed elsewhere in the H-Cl stretching region.

The appearance of one new chlorine isotopic doublet at 2849.9, 2848.1 cm^{-1} in the ClF experiment, above the major product in Cl_2 experiments, supports identification of these new bands as hydrogen-bonded complexes. Chlorine monofluoride is a stronger Lewis acid and a weaker Lewis base than Cl_2 owing to the inductive effect of fluorine. The $\nu_s(\text{HCl})$ fundamental of the hydrogen-bonded complex $\text{Cl}_2\text{--HCl}$ (2842.2 cm^{-1}) is expected to be displaced more from the HCl induced Q branch (2871.0 cm^{-1}) than the ν_s fundamental of FCl--HCl (2849.9 cm^{-1}). The relative ordering of the ClF and Cl_2 product bands is not consistent with their assignment to antihydrogen bonded complexes, because in this case, HCl--ClF should exhibit a larger displacement than HCl--Cl_2 , which was not observed in these experiments.¹⁹

The greater stability of the hydrogen-bonded arrangement for $\text{Cl}_2\text{--HCl}$ in solid argon, in contrast to the more stable antihydrogen bonded arrangement for HF--Cl_2 , is of interest. Since very little charge transfer is expected in either arrangement of the Cl_2/HCl complex, the matrix is unlikely to stabilize either structural form appreciably more than the other. The larger covalent radius of chlorine in HCl probably accounts for the reduced stability of the HCl--Cl_2 arrangement and the failure to observe it in the matrix experiment.¹⁹ Molecular beam and theoretical studies on the Cl_2/HCl complex system are suggested to test this interpretation of the matrix infrared observations.

Cl--HCl radical complexes

The new doublet at 2836.4, 2834.5 cm^{-1} in the matrix formed by codepositing discharged Ar/Cl_2 with Ar/HCl is assigned to the Cl--HCl radical complex. This band is displaced slightly more than the $\text{Cl}_2\text{--HCl}$ band at 2842.2, 2840.1 cm^{-1} . A similar relationship was found for the $\text{Cl}_2\text{--HF}$ (3860 cm^{-1}) and Cl--HF (3858 cm^{-1}) complexes.^{6,11} It appears that the chlorine atom interacts slightly more strongly with the hydrogen-bonding acids than does the Cl_2 molecule. Finally, the Cl--H-Cl radical is a weak hydrogen-bonded complex analogous to the F--H-F radical, for which calculations have predicted a weak (3 kcal/mol) hydrogen bond.¹³ The fact that Cl atom is a stronger base than the F atom, based on infrared spectra of F--H-F (3901 cm^{-1})⁶ and Cl--H-F (3858 cm^{-1})¹¹ suggests that Cl--H-Cl might exhibit a slightly stronger hydrogen bond than does F--H-F. The shift in H-X fundamentals in these species (18 cm^{-1} for HF_2 and 35 cm^{-1} for HCl_2) supports this hypothesis.

The anion electron makes a significant difference in the ground state bonding and structure of the weak Cl--H-Cl complex and the strongly hydrogen bonded centrosymmetric $(\text{Cl--H--Cl})^-$ anion. This difference is much more significant than inferred from simple molecular orbital treatments of the bichloride anion.⁷ The centrosymmetric transition state of HCl_2 reached by vertical photodetachment²⁰ from HCl_2^- is considerably different from the present weak ground state hydrogen-bonded complex.

CONCLUSIONS

The matrix isolation technique has been used to trap the ClF/HCl and Cl_2/HCl complexes at 5 K. Infrared spectra in the HCl region shows only hydrogen bonded complexes FCl--HCl and $\text{Cl}_2\text{--HCl}$ and suggests that this arrangement is more stable than the antihydrogen bonded forms observed in the gas phase for the analogous HF complexes. The chlorine atom--HCl complex shows a similar infrared spectrum, namely that of a weak hydrogen bonded complex Cl--H-Cl. This ground state complex is considerably different from the centrosymmetric $(\text{ClHCl})^-$ anion or the transition state reached by photodetachment. The matrix technique is useful for preparing reactive atom complexes with small molecules where the reactive atoms and small molecules can be condensed with excess argon, which traps the resulting weak complex.

ACKNOWLEDGMENT

The authors gratefully acknowledge financial support from National Science Foundation Grant No. CHE 85-16611.

- ¹F. A. Baiocchi, T. A. Dixon, and W. Klemperer, *J. Chem. Phys.* **77**, 1632 (1982).
- ²S. E. Novick, K. C. Janda, and W. Klemperer, *J. Chem. Phys.* **65**, 5115 (1976).
- ³H. Umeyama, K. Morakuma, and S. Yamabe, *J. Am. Chem. Soc.* **99**, 330 (1977).
- ⁴P. Hobza, M. M. Szczesniak, and Z. Latajka, *Chem. Phys. Lett.* **82**, 469 (1981).
- ⁵A. P. L. Rendell, G. G. Bacskay, and N. S. Hush, *J. Chem. Phys.* **87**, 535 (1987).
- ⁶R. D. Hunt and L. Andrews, *J. Phys. Chem.* **92**, 3769 (1988).
- ⁷P. N. Noble and G. C. Pimentel, *J. Chem. Phys.* **49**, 3165 (1968).
- ⁸D. E. Milligan and M. E. Jacox, *J. Chem. Phys.* **53**, 2034 (1970).
- ⁹C. A. Wight, B. S. Ault, and L. Andrews, *J. Chem. Phys.* **65**, 1244 (1976) and references therein.
- ¹⁰K. Kawaguchi, *J. Chem. Phys.* **86**, 4186 (1988).
- ¹¹R. D. Hunt and L. Andrews, *J. Chem. Phys.* **88**, 3599 (1988).
- ¹²B. S. Ault, *J. Chem. Phys.* **68**, 4012 (1978).
- ¹³P. N. Noble and R. K. Kortzeborn, *J. Chem. Phys.* **52**, 5375 (1970).
- ¹⁴R. O. Carter III and L. Andrews, *J. Phys. Chem.* **85**, 2351 (1981).
- ¹⁵D. Maillard, A. Schriver, and J. P. Perchard, *J. Chem. Phys.* **71**, 505 (1979).
- ¹⁶J. P. Perchard, J. Cipriani, B. Silvi, and D. Maillard, *J. Mol. Struct.* **100**, 317 (1983).
- ¹⁷L. Andrews, F. K. Chi, and A. Arkell, *J. Am. Chem. Soc.* **96**, 1997 (1974).
- ¹⁸L. Andrews and S. R. Davis, *J. Chem. Phys.* **83**, 4983 (1985).
- ¹⁹The HCl--Cl_2 complex is expected (Ref. 6) to absorb between Q and N where a weak band might be masked.
- ²⁰R. B. Metz, T. Kitsopoulos, A. Weaver, and D. M. Neumark, *J. Chem. Phys.* **88**, 1463 (1988).