

A far infrared study of the Ar-HCl van der Waals molecule

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Results of far infrared measurements on the system HCl-Ar at low density and temperature are presented. Distinct spectral features are observed that must be attributed to Ar-HCl van der Waals molecules. Possible explanations of the observed spectra in terms of a simple picture of the internal motion of the complex are discussed. An estimate of the enthalpy of formation is made.

I. INTRODUCTION

Spectroscopic studies of van der Waals molecules may provide valuable information about the intermolecular potential between the constituents.¹ This method is of particular interest because the separations of energy levels directly reflect the precise shape of the potential surface, including anisotropic parts, over the region of the potential bowl. Line positions can be determined accurately from absorption spectra, and an analysis can result in realistic potentials that are hard to obtain otherwise.²

The Ar-HCl van der Waals molecule has received considerable attention. Klemperer and co-workers have presented results of molecular beam electric resonance experiments.³ They have determined radio frequency and microwave data associated with end-over-end rotation of the complex. The effective internal temperature of the Ar-HCl molecule was quite low (less than 20 K) and consequently all vibrational modes are in their ground states. From the measured quantities they could derive the stretching and bending force constants.⁴

Recently Dunker and Gordon⁵ have calculated energy levels and quantities measured in the molecular beam experiments using potentials as determined from scattering experiments. However, no quantitative agreement with the bound state data could be obtained. The suggestion is that more experimental data, in particular, on vibrationally excited states of this complex, might well give details of the Ar-HCl interaction which have not been obtained so far.

Studies of the absorption spectrum of Ar-HCl in the near infrared⁶⁻¹⁰ reveal a wealth of detail. The early reported *Q*-branch features have been discussed by Bratoz and Martin,^{11,12} the later very high resolution spectra on the other hand have not been completely analyzed. A straightforward analysis is complicated by the fact that the potential for ground state and vibrationally excited HCl may be different.

Far infrared studies of van der Waals molecules contain information about the potential and more generally probe the dynamics of the internal low frequency motions without the drawback of a change in the intermolecular potential caused by a high frequency excitation in one of the constituents. Thus far, measurements of this type have not been published. We here present far

infrared spectra of the Ar-HCl van der Waals molecule.

II. EXPERIMENTAL

The measurements of the spectra were performed on a Beckmann RIIC FS720 Michelson interferometer. A He cooled Texas Instruments Ge bolometer operating at 4.2 K was used as a detector. Gases were purchased from Matheson Gas Company and dried with molecular sieve and by freezing at 195 K. The Ar-HCl mixture was held in a 100 cm brass absorption cell with pure silicon windows. Temperature could be controlled within 1 K. 175 K was chosen for most temperatures. This choice was made to obtain a maximum concentration of van der Waals molecules without running into the danger of HCl condensation. Total gas densities were between 1 and 4 amagat. Every measurement consisted of 40-140 interferograms (depending on the spectral region involved). Because of the weak absorption associated with the complexes, much care was taken to reduce the noise level. Apodization with a $\cos^2(\pi x/2x_{\max})$ function was applied. The frequency region studied was 13-150 cm^{-1} with a resolution of 0.3 cm^{-1} .

III. RESULTS

Figure 1 shows the spectrum of a mixture of 0.07 amagat of HCl and 1.1 amagat of Ar. The strong absorption peaks around 21 and 42 cm^{-1} are due to the free HCl rotational transitions $J=0-1$ and $J=1-2$. Below 38 cm^{-1} one observes a series of weaker absorption peaks that appear to be equally spaced. Systematic errors in the data processing can be excluded as a possible cause of this structure as similar measurements on other gas mixtures (e.g., HCl-Kr) yielded completely different spectra. There was no absorption in the pure Ar, which is not surprising considering the high purity of the Ar (99.998%) and the way the gas mixtures were prepared.

The spectrum of pure HCl is shown in Fig. 2, curve *a*. It shows no absorption comparable to the structure in Fig. 1. The absorption feature at 32.3 cm^{-1} and a more intense one at 53.8 cm^{-1} (see Fig. 1) may be attributed to dimer absorption.^{10,13}

One must conclude that the absorption shown in Fig. 1 is due to the HCl-Ar combination. The sharpness of the features suggests that the occurrence of Ar-HCl

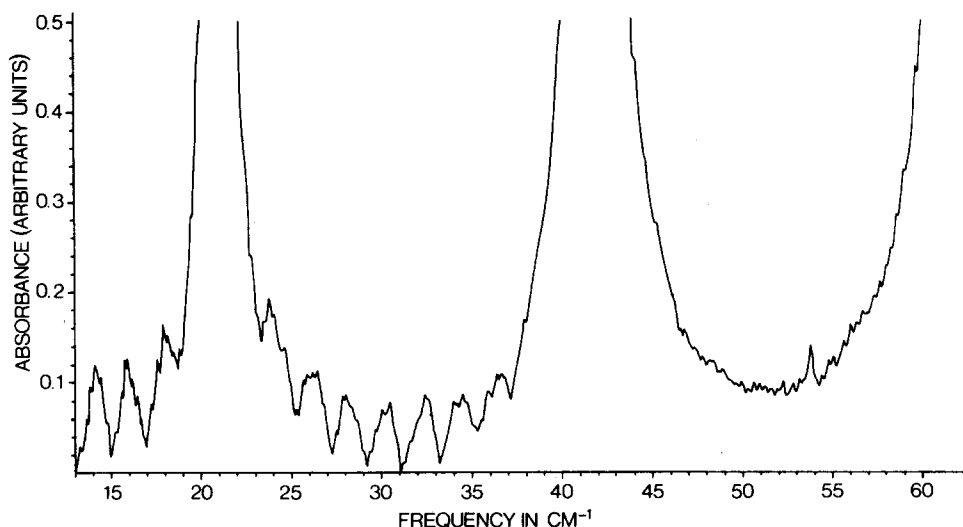


FIG. 1. Far infrared spectrum of a mixture of HCl and Ar. The strong absorption lines are due to HCl rotational transitions, the weaker ones to Ar-HCl van der Waals molecules. Experimental conditions are given in Table II.

van der Waals molecules of considerable lifetime is the cause of this absorption. If this were the case the intensity of the absorption would be expected to increase with increasing Ar density and decrease with increasing temperature at constant composition. This is indeed observed (see Figs. 2 and 3). The sharp line at 36.6 cm^{-1} in *a* of Fig. 3 is due to H_2O vapor and can be

used for calibration purposes and to obtain an estimate of the resolving power.

The observed peak frequencies are listed in Table I. There are ten equally spaced lines of an apparent half-width of 1 cm^{-1} and each $2.0 (\pm 0.1)$ apart. There is a rough agreement between the frequencies of some of the observed lines with the frequencies of some of the more pronounced features which have been observed in the near infrared. Of course, no complete agreement is expected because near infrared measurements probe transitions of van der Waals molecules superimposed on the HCl $v=0 \rightarrow v=1$ vibrational transition.

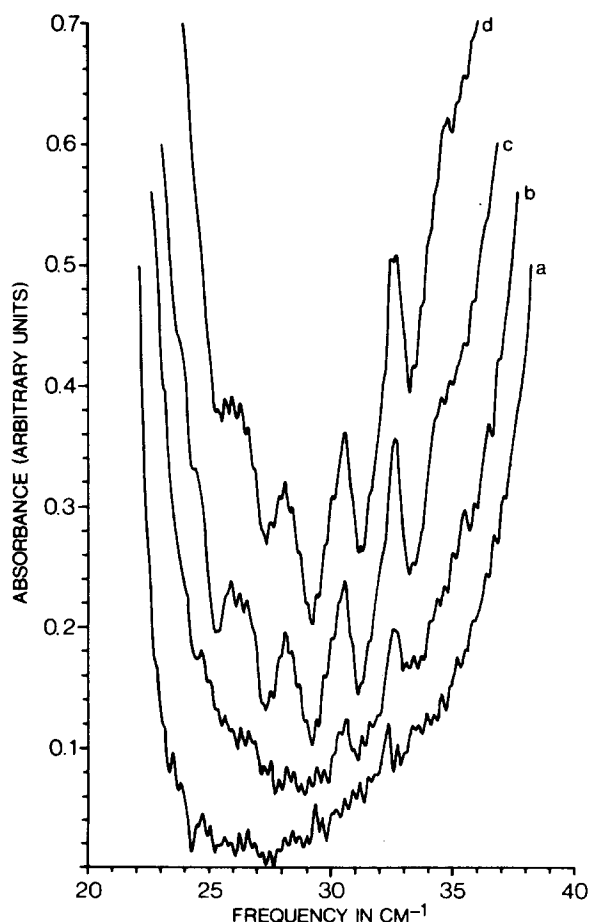


FIG. 2. Spectra of mixtures of HCl and Ar at different Ar densities. Spectrum *a* shows the absorption of pure HCl, the spectra *b*, *c*, and *d* show the effect of an increasing Ar density. Experimental conditions are given in Table II.

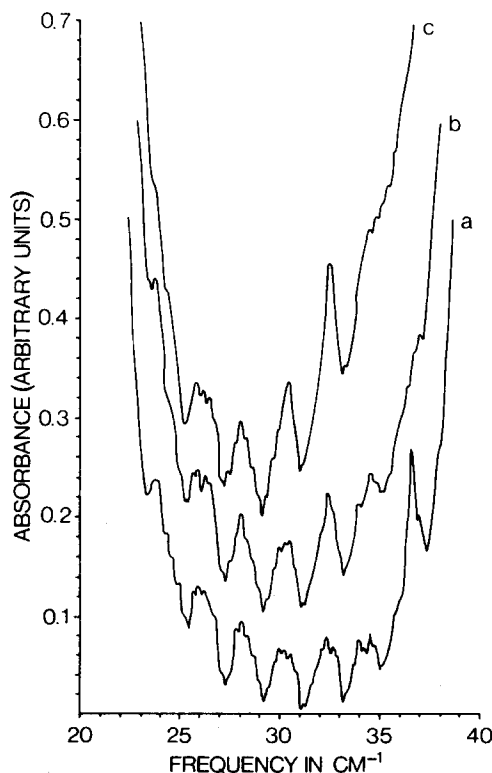


FIG. 3. Spectra of a mixture of HCl and Ar at different temperatures. Experimental conditions are given in Table II.

TABLE I. Observed frequencies of Ar-HCl in cm^{-1} .

From far infrared spectra This work	From near infrared spectra Refs. 6 and 7	Ref. 10
14.1 (± 1)	25.9	18.7
15.9	28.3	28.9
17.9	30.7	30.7
24.2	31.7	
26.3	32.6	
28.2		
30.2		
32.3		
34.2		
36.3		

IV. DISCUSSION

At the experimental temperature (175 K) kT is 122 cm^{-1} . From scattering and molecular beam experiments^{14,15} the depth of the isotropic potential well is estimated to be about 135 cm^{-1} , so we may expect all bound states to be thermally populated. This implies that the spectrum of such a complex will contain information over the entire region of the potential well.

An experimental quantity that can be estimated from the present data is the enthalpy of formation. Comparing Fig. 1 and spectrum *a* of Fig. 3 it is evident that the intensity of the absorption peaks is closely equal. If the densities of both measurements are considered, one can estimate the ΔH to be 1.4 kcal/mole. This value is in reasonable agreement with those determined by Rank⁷ (1.1 kcal/mole) and Pimentel¹⁶ (1.5 kcal/mole).

A description of the internal motion of the Ar-HCl complex is rather complicated. The analysis of the molecular beam data by Klemperer and co-workers³ indicates that, in its ground state, the Ar-HCl molecule is exceedingly nonrigid. It has high amplitude zero-point motion for both bending and stretching modes which are moreover coupled.¹⁵ Only for HCl internal rotatory levels that are well above the barrier for internal rotation, caused by the HCl-Ar anisotropic potential, one may describe the situation in terms of hindered rotation of the HCl subunit. At lower energies such a simple description is bound to fail. As a result the absorption spectrum of the complex is expected to be quite complicated and irregular. Remarkably enough, the spectrum below 40 cm^{-1} is dominated by a number of absorption peaks that are almost equally spaced. One is tempted by this aspect to analyze the spectrum in terms of a simple model in which a potential energy surface gives rise to lineary decreasing separations between energy levels. For a vibrational type of motion this could be brought about by a Morse potential, for a librational motion a potential well of the form $-(\cosh^2 x)^{-1}$ would be appropriate. From the observed succession of absorption peaks between 13 and 37 cm^{-1} (Table I) it follows that the total depth of a potential with such a level spacing must be about 380 cm^{-1} or 1.1 kcal/mole. When it is assumed that the motion involved is mainly a vibration between the Ar atom and

the HCl unit, it might seem that this value is in accordance with our value for the enthalpy of formation. Considering the rather high estimated transition probability, one might prefer to assume a more librational type of motion for which the angular motion of the HCl dipole contributes to the transition moment. Under this assumption, however, a value of 380 cm^{-1} for the depth of the potential well is in sharp contrast with estimates made for the height of the barrier for internal rotation. All estimates, e.g. 56 cm^{-1} at $R=4 \text{ \AA}$ for the fully optimized Neilsen and Gordon potential¹⁷ and a value of 63.5 cm^{-1} extracted from the molecular beam data,³ are much lower. Another point that seems to be in contradiction with this assumption is the fact that, in the case of a high rotational barrier, levels slightly above this barrier should give rise to separately observable absorption lines in the higher frequency region. However, distinct absorption features have not been found in the frequency region $40\text{--}150 \text{ cm}^{-1}$. This argument is, however, not conclusive because a more continuous distribution of absorption lines and a possible broadening by predissociation can blur a detectable structure. Quite generally, there is no unique way of determining a possible continuous absorption or the absolute intensity of an absorption peak because the precise shape of a pressure broadened free HCl rotational line in its wings is not known.

In Fig. 2 there is no clear variation of the apparent half-widths of the absorption peaks with pressure; they are much larger than those of the dimer absorption lines. The lifetime of a weakly bound van der Waals molecule is collision limited, so one should conclude that the observed lines are not due to one level-one level transitions; in the latter case the half-width should be linear in the collision frequency. It is therefore likely that the peaks result from a bundled superposition of single absorption lines.

Apparently one is forced to take recourse to less simple models to explain the observed spectrum. One possible qualitative picture would be that librational transitions occur in different vibrational states and hence have different frequencies. This would not demand a high barrier for internal rotation, but does not explain the equal spacing of the absorption peaks. It is clear that more experimental data and a more thorough theoretical investigation are needed. It seems, however,

TABLE II. Experimental conditions for the spectra shown in Figs. 1-3.

	Density (amagat)		Temperature (K)
	Ar	HCl	
Fig. 1	1.1	0.07	175
Fig. 2, <i>a</i>		0.24	175
<i>b</i>	0.7	0.24	175
<i>c</i>	1.6	0.24	175
<i>d</i>	4.0	0.24	175
Fig. 3, <i>a</i>	1.6	0.24	295
<i>b</i>	1.6	0.24	215
<i>c</i>	1.6	0.24	175

from the onset difficult to reconcile the large number of equally spaced lines with a more elaborate model.

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¹For an excellent review see G. E. Ewing, *Can. J. Phys.* **54**, 487 (1976).

²R. J. Le Roy and J. Van Kranendonk, *J. Chem. Phys.* **61**, 4750 (1974).

³S. E. Novick, P. Davies, S. J. Harris, and W. Klemperer, *J. Chem. Phys.* **59**, 2273 (1973).

⁴The bending force constant was published in a later paper on Kr-ClF: S. E. Novick, S. J. Harris, K. C. Janda, and W. Klemperer, *Can. J. Phys.* **53**, 2007 (1975).

⁵A. M. Dunker and R. G. Gordon, *J. Chem. Phys.* **64**, 354 (1976).

⁶D. H. Rank, B. S. Rao, and T. A. Wiggins, *J. Chem. Phys.* **37**, 2511 (1962).

⁷D. H. Rank, P. Sitaram, W. A. Glickman, and T. A. Wiggins, *J. Chem. Phys.* **39**, 2673 (1963).

⁸H. Vu and B. Vodar, *Z. Elektrochem.* **64**, 756 (1960).

⁹M. R. Atwood, H. Vu, and B. Vodar, *Spectrochim. Acta* **23A**, 553 (1967).

¹⁰M. Larvor, J. P. Houdeau, and C. Haeusler, *Spectrochim. Acta* **29A**, 971 (1973).

¹¹S. Bratoz and M. L. Martin, *J. Chem. Phys.* **42**, 1051 (1965).

¹²S. Bratoz, *Cahier Phys.* **175**, 105 (1965).

¹³D. H. Rank, W. A. Glickman, and T. A. Wiggins, *J. Chem. Phys.* **43**, 1304 (1965).

¹⁴J. M. Farrar and Y. T. Lee, *Chem. Phys. Lett.* **26**, 482 (1974).

¹⁵S. E. Novick, K. C. Janda, S. L. Holmgren, M. Waldman, and W. Klemperer, *J. Chem. Phys.* **65**, 1114 (1976).

¹⁶W. Klemperer, *Ber. Bunsenges.* **78**, 128 (1974).

¹⁷W. B. Neilsen and R. G. Gordon, *J. Chem. Phys.* **58**, 4149 (1973).