

# Microwave and radio frequency spectrum of XeHCl<sup>a)</sup>

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Microwave and radio frequency spectra of <sup>132</sup>XeH<sup>35</sup>Cl are measured by molecular beam electric resonance spectroscopy. The spectroscopic constants determined for this complex are  $B = 989.262$  (5) Mhz,  $D_J = 3.84$  (32) kHz,  $(eqQ)_\alpha$ , <sup>35</sup>Cl =  $-34.640$  (20) MHz,  $\mu_\alpha = 1.0901$  (30) D. Only a single vibrational level, with zero angular momentum along the heavy atom axis, has been observed. The results are interpreted in terms of a linear complex with large amplitude oscillation. The structure is assumed to have atomic arrangement XeHCl. The average Xe-Cl distance is 4.258 Å. The average angle of the HCl subunit with the heavy atom axis is 34.8°. The stretching frequency of the weak bond is 33.5 cm<sup>-1</sup>.

## INTRODUCTION

The study of the interaction of HCl with the inert gases is extensive. In this article we report rotational spectroscopy of the complex XeHCl. While there have been a number of studies of collisional phenomena involving Xe and HCl, relatively little structural data for the species XeHCl exist. Rank, Sitaram, Glickman, and Wiggins<sup>1</sup> have reported infrared absorption spectra of ArHCl and XeHCl in the region 2885 cm<sup>-1</sup>. The complexity of the system at 195°K virtually ensured that rotational analysis of this spectrum is not practical.

Pressure broadening and spectral line shifts of the 0-1 and 0-2 bands of HCl induced by xenon have been measured by several groups at high resolution.<sup>2,3</sup> Gordon<sup>4</sup> has pointed out to us that these experiments show clearly that vibrational effects are large for Xe-HCl collisions. Thus, without elaborate analysis it is not possible to obtain even a qualitative grasp of anisotropic terms in the intermolecular potential from these data.

The present study of XeHCl is quite similar in nature and results to a more complete study of the ArHCl molecule. Both ArHCl and XeHCl contain two heavy atoms which virtually define the inertial coordinate system, irrespective of the position of the hydrogen. The most important vibrational level in the present work is the ground state. Although it is expected from the results for ArHCl that large amplitude zero point motions occur, an average structure with appreciable dipole moment along the  $a$  inertial axis (approximately the Xe-Cl line) exists. This is sufficient to define both rotational energy levels and electric dipole selection rules, including the Stark effect.

## EXPERIMENTAL

The spectra were taken with a recently constructed Rabi-type electric resonance spectrometer having a quadrupole  $A$  field and a dipole  $B$  field, operating in the flop-in mode.<sup>5</sup> The  $A$  field is 35 cm long, with an aperture of 0.261 cm. The  $B$  field is 25 cm long, with a 0.4 cm gap, a convex radius of 0.678 cm, and a concave ra-

dius of 0.556 cm. The source-detector distance is 140 cm.<sup>6</sup>

The resonance region is constructed from a pair of  $5.08 \times 10.16$  cm quartz optical flats. The flats are gold coated by vacuum deposition and spaced apart by three 1.0033 cm precision quartz spacers. They were aligned by a standard interference technique to be parallel within several wavelengths of sodium  $D$  light. The spacing of 1.00311 (54) cm, determined by calibration with the OCS  $J=1$  Stark effect, is well within the experimental error of that of the precision spacers.

A uniform electrostatic field is established between the flats for Stark effect measurements. Radio frequency radiation, with components parallel and perpendicular to the electrostatic field, can be applied to the 7.6 cm central portion of the flats. An S-band horn with polarization axis perpendicular to the flats couples microwave radiation into the resonance region.

The detector is a mass spectrometer with a Weiss-type electron bombardment ionizer<sup>7</sup> followed by a 30.5 cm radius, 60° sector magnetic analyzer,<sup>8</sup> and an electron multiplier particle detector. Resonances are detected by square wave amplitude modulation of the radiation at 10 Hz followed by phase sensitive detection of the mass spectrometer signal.

XeHCl is produced from a supersonic nozzle of 33  $\mu$  diameter. A room temperature expansion of 2.5 atm of a 5% HCl, 10% Xe, 85% Ar mixture is used. This is a compromise between maximization of XeHCl production and the expense of using Xe. Cooling the nozzle did not significantly increase XeHCl production or signal on resonance. The total amount of XeHCl<sup>+</sup> detected is 5% of the Xe<sup>+</sup> signal.

Although unessential for the present radio spectroscopy, it is interesting to note that fragmentation of <sup>132</sup>XeH<sup>35</sup>Cl in the ionizer produced an XeCl<sup>+</sup> ( $m/e=167$ ) signal approximately the same size as the XeHCl<sup>+</sup> ( $m/e=168$ ) signal. All resonances used in the <sup>132</sup>XeH<sup>35</sup>Cl analysis were detected at both of the above mass positions. The resonance frequencies of <sup>131</sup>XeH<sup>35</sup>Cl are quite different from those of <sup>132</sup>XeH<sup>35</sup>Cl. Thus the signal strengths of <sup>132</sup>XeH<sup>35</sup>Cl radio frequency resonances detected at  $m/e=167$  and  $m/e=168$  provide fragmentation ratios for XeHCl<sup>+</sup> and XeCl<sup>+</sup>. That a substantial amount of the complex will cleave at the strong, chemical bond under electron bombardment is rather surpris-

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ing. Unfortunately, we could not determine what fraction of the XeHCl fragmented to produce XeH<sup>+</sup>, Xe<sup>+</sup>, Cl<sup>+</sup>, or HCl<sup>+</sup>. A significant amount of ArXe is present in the same mass range as XeHCl, but it does not interfere with this study. A mass spectrum of the region  $m/e = 160$  to 180 is shown in Fig. 1.

The spectroscopic techniques have been used extensively on other molecular beam spectrometers and have been described previously. In this study, microwave ( $\Delta J = 1$ ) and radio frequency ( $\Delta J = 0$ ,  $\Delta M_J = 1$ ) transitions for  $^{132}\text{XeH}^{35}\text{Cl}$  have been measured. Linewidths for the radio frequency transitions are typically 10 kHz. Linewidths for microwave transitions varied from 10 to 40 kHz. The larger linewidths are probably due to microwave radiation causing transitions in non-field-free portions of the spectrometer. Typical spectra are shown in Figs. 2 and 3.

## RESULTS

The transitions observed (see Tables I and II) are well fitted by an almost rigid rotor model with zero angular momentum about the  $a$  inertial axis. The Stark effects were second order and well fitted by standard linear molecule formulas. The measured quantities, listed in Table III, are the rotational constant  $B$ , the centrifugal distortion constant  $D_J$ , the component of the dipole moment along the  $a$  inertial axis  $\mu_a$ , and the chlorine nuclear quadrupole coupling constant component along the  $a$  axis  $(eqQ)_a$ . Only one isotope,  $^{132}\text{XeH}^{35}\text{Cl}$ , is presently studied. We assume the atomic arrangement in XeHCl is the same as in ArHCl, where it has been shown to be as written.<sup>9</sup>

The average structure of XeHCl is obtained by assuming that the chlorine quadrupole coupling tensor is identical in magnitude and orientation to that in free HCl. The observed hyperfine structure is then given by  $(eqQ)_a = (eqQ)_0 \langle P_2(\cos\theta) \rangle$  where  $\theta$  is the angle between the  $a$  axis and the HCl axis.

The ratio found for  $(eqQ)_a/(eqQ)_0$ ,  $-34.640/-67.618 = 0.51229$ , defines an average angle  $\theta = 34.77^\circ$  from  $P_2(\cos\theta) = 0.51229$ . This angle is appreciably less than  $41.5^\circ$  found for ArHCl. In the absence of spectra for XeDCl, we assume that, as for ArHCl, a linear equilibrium configuration is most likely. The observed angle of  $34.77^\circ$  is then a consequence of zero point oscillation. This angle is determined by the anisotropy of the intermolecular potential. In the present experiment, this is the only datum which is strongly affected by the anisotropy. We choose to convert this into an effective harmonic bending force constant.

We do not use the dipole moment of XeHCl for geometric purposes. Although  $\mu_a$  is determined with high precision, it is clear that in order to use it meaningfully, (i.e., to determine  $\theta$  to 1%) from an expression such as  $\mu_a = \mu_0 \cos\theta + \mu_{\text{ind}}$ ,  $\mu_{\text{ind}}$  must be estimable to about 5%. It seems unlikely that this is realistically possible. Thus, it does not appear useful to use the

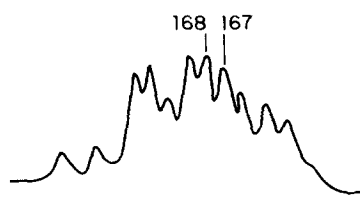


FIG. 1. Mass spectrum of the region  $m/e = 160-180$  containing the various isotopic species of XeHCl and ArXe. The source pressure is 2.5 atm of 5% HCl, 10% Xe, 85% Ar mixture at 25°C.

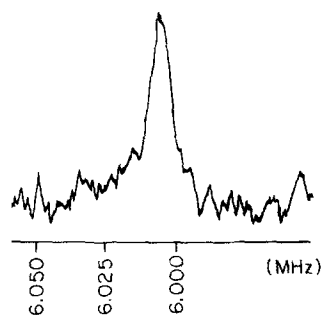


FIG. 2. Radio frequency rf spectrum of the  $J = 3$ ,  $F = \frac{3}{2} \rightarrow F = \frac{5}{2}$   $M_F = \frac{1}{2} \leftarrow F = \frac{3}{2}$ ,  $M_F = \frac{3}{2}$  resonance in  $^{132}\text{XeH}^{35}\text{Cl}$ .  $E = 996.71$  V/cm. Time constant = 10 sec.

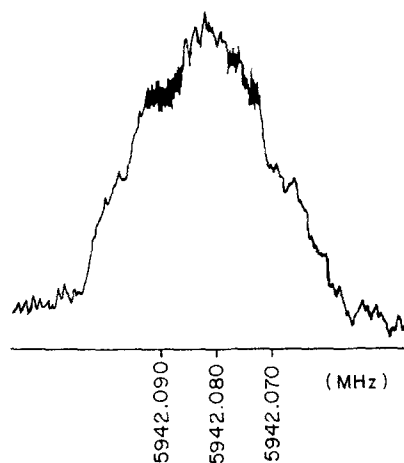


FIG. 3. Zero field microwave spectrum of the  $J = 3$   $F = \frac{3}{2} \rightarrow J = 2$   $F = \frac{3}{2}$  transition in  $^{132}\text{XeH}^{35}\text{Cl}$ . Time constant = 10 sec.

TABLE I. Observed radio frequency transitions of  $^{132}\text{Xe}^{35}\text{HCl}$ .

Frequency (MHz)	$J$	$F$	$M_F \rightarrow F'$	$M_{F'}$	Electric field (V/cm)
8.5190	3	$\frac{3}{2}$	$\frac{1}{2} \rightarrow \frac{3}{2}$	$\frac{3}{2}$	199.34
8.1048	3	$\frac{3}{2}$	$\frac{3}{2} \rightarrow \frac{3}{2}$	$\frac{3}{2}$	398.68
7.4735	3	$\frac{3}{2}$	$\frac{5}{2} \rightarrow \frac{3}{2}$	$\frac{3}{2}$	598.03
6.7283	3	$\frac{3}{2}$	$\frac{7}{2} \rightarrow \frac{3}{2}$	$\frac{3}{2}$	797.37
6.0144	3	$\frac{3}{2}$	$\frac{9}{2} \rightarrow \frac{3}{2}$	$\frac{3}{2}$	996.71

TABLE II. Observed microwave transitions in  $^{132}\text{XeH}^{35}\text{Cl}$  at zero electric field.

Frequency (MHz)	$J$	$F \rightarrow J'$	$F'$
1980.24(7)	1	$\frac{5}{2} \rightarrow 0$	$\frac{3}{2}$
1987.20(10)	1	$\frac{3}{2} \rightarrow 0$	$\frac{3}{2}$
3956.923(5)	2	$\frac{5}{2} \rightarrow 1$	$\frac{3}{2}$
3972.530(40)	2	$\frac{7}{2} \rightarrow 1$	$\frac{3}{2}$
5933.425(20)	3	$\frac{5}{2} \rightarrow 2$	$\frac{3}{2}$
5942.082(5)	3	$\frac{7}{2} \rightarrow 2$	$\frac{3}{2}$

TABLE III.  $^{132}\text{XeH}^{35}\text{Cl}$  spectroscopic constants.

$B = 989.262(5)$ MHz
$D_J = 3.84(32)$ kHz
$(eqQ)_a = -34.640(20)$ MHz
$\mu_a = 1.0901(30)$ D
$\omega_s = 33.5(1.5)$ $\text{cm}^{-1}$
$k_s = 0.0187(17)$ mdyn/ $\text{\AA}$
$k_b = 0.0017$ mdyn $\cdot\text{\AA}$

present data in an attempt to refine our knowledge about the angular distribution of HCl in XeHCl beyond that obtained from quadrupolar hyperfine structure.

In analogy to ArHCl, it appears likely that XeHCl has a linear equilibrium structure and that the observed average value of  $\theta$  is the result of zero point vibration. Using the coordinates of Fig. 4, the angle  $\phi$  is used to obtain the effective harmonic bending constant,

$$k_b = \frac{\hbar^2}{m_b \phi^4},$$

where  $m_b$  is the appropriate bending moment of inertia. For XeHCl,  $k_b = 0.0017$  mdyn $\cdot\text{\AA}$ .

The rotational constant  $B$  provides the average distance of the weak bond, chosen to be the Xe-Cl length. The HCl unit is taken to be at its average angular position. The Xe-Cl distance is 4.258  $\text{\AA}$ . The centrifugal distortion constant is related to the effective harmonic stretching frequency by  $D_J = 4B^3/\omega_s^2$ . The effective force constant for radial motion is  $k_s = 4\pi^2\omega_s^2\mu$ , where  $\mu = 28.46$  a. m. u. These relations give  $\omega_s = 33.5$   $\text{cm}^{-1}$  and  $k_s = 0.0187$  mdyn/ $\text{\AA}$ .

## DISCUSSION

The spectroscopic and structural parameters for the complexes of HCl with the rare gases Ne through Xe are listed in Table IV. These results permit a qualitative comparison of the binding in these systems. There are essentially three quantities which may be compared: the anisotropy of the intermolecular potential as exhibited by the average angle, the bond length, and the bond stretching force constant.

An examination of  $\theta$  values in Table IV clearly shows that the anisotropy of the intermolecular potential in-

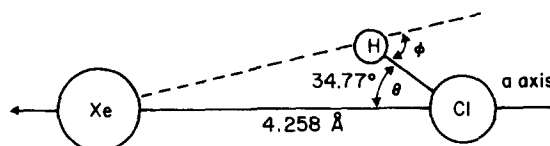


FIG. 4. The vibrationally averaged structure of XeHCl.

creases from ArHCl to XeHCl. Examination of NeHCl by Novick *et al.*<sup>11</sup> showed this species to behave as a nonpolar molecule in electric deflection. An estimate of the upper limit of the dipole moment is  $0.2D$ . This may be interpreted to mean that  $\langle \cos\theta \rangle < 0.2/\mu_{\text{HCl}} = 0.2$  or  $80^\circ \leq \theta \leq 90^\circ$ . Since  $\theta = 90^\circ$  for free rotor HCl, it is clear that we presently cannot tell how far NeHCl deviates from a free rotor. The lack of observable polarity of NeHCl appears to preclude the possibility of determining structural parameters by electric resonance spectroscopy. The species ArHCl and XeHCl show a strong increase in anisotropy as measured by the effective harmonic bending force constant. The value for XeHCl is twice that of ArHCl. It is expected that this will be roughly the ratio of the anisotropic parts of the intermolecular potential energy. The increase in stretching force constant from ArHCl to XeHCl is quite appreciable. This is certainly expected.

As mentioned earlier, line broadening studies of HCl by Xe show large vibrational effects, making comparison with the present essentially rotational results extremely difficult. Vapor pressure measurements of Xe-HCl systems<sup>12,13</sup> have been interpreted in terms of the Xe-HCl intermolecular potential. We find it difficult to compare the present spectroscopic results with the results from the liquid studies since the distance between the H nucleus and Xe is less than a factor of 3 different from its distance to Cl; an exact specification of the coordinate system is required. It is clear from the potential deduced for ArHCl that many features of it cannot be reproduced by the assumed potential forms used for XeHCl. For example, the minimum in the anisotropic part of the potential of ArHCl is located at 0.4  $\text{\AA}$  larger distance than that of the spherical term. It is not clear how unique the intermolecular pair potential deduced from fitting vapor pressures of liquid is.

The present results for the rare gas-HCl system may be compared with the more complete results available for the rare gas-H<sub>2</sub> system. The latter subject is well discussed by LeRoy and van Kranendonk<sup>14</sup> and by Dunker and Gordon,<sup>15</sup> who fit the infrared absorption spectra of

TABLE IV. Comparison of spectroscopic and structural parameters of NeHCl, ArHCl, KrHCl, and XeHCl.

Complex	$B$ (MHz)	$D_J$ (kHz)	$(eqQ)_a\text{Cl}^{35}$ (MHz)	$\mu_a$ (D)	$\omega_s$ ( $\text{cm}^{-1}$ )	$k_s$ (mdyn/ $\text{\AA}$ )	$k_b$ (mdyn $\cdot\text{\AA}$ )	$\theta$	$R$ ( $\text{\AA}$ )
NeHCl <sup>a</sup>	"Free rotor HCl"							80°-90°	
ArHCl <sup>b</sup>	1678.511	20.33	-23.027	0.81144	32.2	0.0115	0.0009	41.5°	4.006
KrHCl <sup>c</sup>	1205	...	...	...	...	...	...	...	4.078
XeHCl <sup>d</sup>	989.262	3.84	-34.640	1.0901	33.5	0.0187	0.0017	34.77°	4.258

<sup>a</sup>See Ref. 10.<sup>b</sup>See Ref. 9.<sup>c</sup>See Ref. 14.<sup>d</sup>This work.

TABLE V. Hydrogen-inert gas distances at the potential minimum.

	H <sub>2</sub> (Å) <sup>a</sup>	HCl(Å)
Ne	2.94	
Ar	3.22	2.73
Kr	3.39	2.80
Xe	3.59	2.98

<sup>a</sup>A. Dunker and R. G. Gordon, Ref. 15.

Welsh and McKellar<sup>16-18</sup> and by Zandee, Verberne, and Reuss<sup>19,20</sup> in the analysis of their scattering experiments.

Qualitatively, the two systems are different. For example, the spherical well depth of the ArHCl is near 133 cm<sup>-1</sup>, while that of ArH<sub>2</sub> is 55 cm<sup>-1</sup>. Secondly, ArHCl is fitted by an anisotropic term consisting of both  $P_1$  and  $P_2$  Legendre polynomials, while the H<sub>2</sub> complexes have only a  $P_2$  term. The magnitudes of the anisotropy are considerably greater in ArHCl, 70 cm<sup>-1</sup>, than in ArH<sub>2</sub>, 8 cm<sup>-1</sup>.

Perhaps the most readily seen difference between the rare gas-HCl and the rare gas-H<sub>2</sub> systems is the rare gas-H distance. These are listed in Table V. For the rare gas-H<sub>2</sub> system the distance minimum of the anisotropic term occurs very close to that of the isotropic term. The minimum energy configuration for both rare gas-H<sub>2</sub> and rare gas-HCl are linear. The rare gas-H distance in rare gas-H<sub>2</sub> is then  $R_m - 0.37$  Å. For the rare gas-HCl system less detailed information exists. We use the observed rare gas-Cl distance to calculate the rare gas-H distance. For ArHCl this gives an ArH distance of 2.73 Å, while using the minimum in the intermolecular potential gives an ArH distance of 2.71 Å. This agreement results from several compensating factors, but for the present qualitative comparison is quite adequate.

It is clear that a van der Waals radius for hydrogen is not a well defined quantity. The rare gas-hydrogen distances are about 0.5 Å shorter for HCl than for H<sub>2</sub>. Furthermore, the difference between the two systems is not constant but varies with inert gas. The difference is greatest in the Xe complexes. This behavior is reminiscent of hydrogen bonding.

The present results, on one isotope only, must be re-

garded as preliminary. The results show clearly that a considerable variation in binding of HCl to the inert gases exists. The XeHCl system, with a large number of isotopes available, should permit detailed evaluation of many of the intermolecular potential parameters by spectroscopic study.

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