

Rotational spectrum and structure of the Ar₃-HCl symmetric top

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The Ar₃-HCl tetramer has been identified via the observation of its microwave rotational spectrum using the pulsed nozzle Fourier transform technique. The rotational spectroscopic constants of the ground vibrational state have been obtained for the ³⁵Cl/³⁷Cl isotopes from measurements of the $J = 1 \rightarrow 2$ to $J = 4 \rightarrow 5$ transitions and their hyperfine structure. For Ar₃-H³⁵Cl, the values found for B_0 , D_J , D_{JK} , and χ_{aa} are 843.8974(1) MHz, 2.333(2) and 1.818(6) kHz, and 31.006(5) MHz, respectively, and for Ar₃-H³⁷Cl, 825.9811(2) MHz, 2.211(5) and 1.940(12) kHz, and 24.481(8) MHz. The cluster is a symmetric top with the HCl along the C_3 axis, its H end directed towards the Ar₃ trimer. In its torsional oscillations, the HCl makes an average angle of 36.91° with the symmetry axis. The chlorine isotopic substitution leads to values of 3.8510 and 4.0024 Å for the Ar-Ar and Ar-Cl distances. The results of the present study are compared with those reported earlier for the Ar_{*m*}-HF ($m = 1, 2, 3$) and Ar_{*m*}-HCl ($m = 1, 2$) clusters.

INTRODUCTION

There are some 200 reports of rotational spectra for weak, bimolecular complexes, most of them in the past decade. Many of the dimers have been identified and characterized using high resolution microwave techniques such as the pulsed nozzle, Fourier transform microwave (FTMW), and the molecular beam electric resonance (MBER) experiments.¹ The resolution of rotational structure has also been demonstrated in the IR,² and most recently in the far IR.³ In addition, UV electronic absorption spectra have been obtained for dimeric complexes with rotational resolution.⁴

Of late there are reports characterizing larger complexes, in particular trimers and tetramers. FTMW spectroscopy has enabled the detailed study of small, noble gas-hydrogen halide clusters such as Ar₂-HF/HCl⁵⁻⁷ and Ar₃-HF^{8,9} in the ground vibrational state. Also, 13 trimers incorporating the linear HCN-HCN dimer have been observed using the Fourier transform technique, most notably the linear trimer (HCN)₃,¹⁰ Several cyclic trimers have been investigated: (HF)₃ using IR vibrational predissociation spectroscopy,¹¹ an IR study with partial rotational resolution of acetylene trimer,¹² and a near IR observation of rotational fine structure for both the linear and cyclic forms of (HCN)₃.¹³

Presently, we wish to report microwave rotational spectra of the Ar₃-H^{35/37}Cl tetramers observed with a Balle-Flygare spectrometer. Ar₃-HCl is the HCl analog of the previously reported Ar₃-HF, but it has the advantage of there being two naturally abundant isotopes of Cl. This is helpful because a minimum of two structural parameters is needed to fully characterize the symmetric top. Deuterium substitution was used in the Ar₃-HF study to establish that the hydrogen is towards the Ar₃ group. The deuterium results also could be used in the moment of inertia expressions to approximate the two structural parameters. However, because of the large difference in torsional amplitudes for the HF and DF species, ³⁵Cl/³⁷Cl isotopic substitution in Ar₃-HCl should give more reliable distances. Moreover, the chlorine nuclear quadrupole coupling constant can also be used to

determine the torsional amplitude of the HCl subunit.

All complexes of the type Ar_{*m*}-HF/HCl ($m = 1, 2, 3$) have now been investigated^{5-9, 14, 15} and with these results at hand, substantial opportunity exists for comparison. The comparative results should aid our present understanding of small, weakly bound clusters.

EXPERIMENTAL

The spectrometer synchronizes microwave pulses with an expanding gas pulse, inside of an evacuated Fabry-Perot cavity. The pulsed gas cools during the supersonic expansion, generating weak molecular complexes and giving final rotational temperatures of ~5 K.¹⁶ Initially, the Ar₃-HCl complex was observed with 1% HCl (Linde) seeded in Ar at a backing pressure of 0.9 atm behind the 1.0 mm diam nozzle. Later, in order to increase the signal strength, neon "first run" (Airco)—a mix of 70% Ne and 30% He—was employed as the carrier gas, seeded with only ~10% Ar and 0.5% HCl.⁷ The backing pressure was boosted to about 2 atm, with a larger pulse of gas required for optimum complex generation. Generally a fourfold increase in signal strength was obtained over that with an Ar carrier. A slight drawback is that linewidths are some 30% to 40% greater with first run. Doppler doubling was not observed with the neon/helium carrier. The increased signal was sufficient for detection of even the weaker hyperfine components.

Spectra were taken in the 3-9 GHz range of the $J = 1 \rightarrow 2$ to $J = 5 \rightarrow 6$ transitions. A given hyperfine component, or set of them, was averaged at an overall rate of 8 Hz on an LSI-11. After suitable accumulation of free induction decay signal (usually for 2 or 3 min), a Fourier transform routine was used to calculate the power spectrum. This was repeated several times so that an average line frequency and standard deviation could be determined. The standard deviations obtained were typically 2 kHz for individual lines of the hyperfine structure (hfs). The accuracy for the ³⁵Cl species is a bit better than for ³⁷Cl because of the latter's poorer signal-to-noise.

RESULTS AND ANALYSIS

Search, hfs, and rotational constants

The search for the Ar₃-HCl tetramer relied on the Ar₃-HF^{8,9} and Ar₂-HCl⁷ findings as guides. In the latter, Ar₃-HF was shown rigorously to be a symmetric top with the HF along the C₃ axis and the H nearest the Ar₃ group. The interatomic distances, namely Ar-Ar (*r*) and Ar-Cl (*d*₀), were transferred from those found in Ar₂-HCl, 3.832 and 4.019 Å, respectively, neglecting torsional effects. This approach predicted a *B*₀ of ~835 MHz, the values differing by about 20 MHz for the two chlorine isotopes. Also, it showed that the Ar₃-HCl symmetric top would be very close to a spherical top. The initial search was for the *J* = 2 → 3 transition for either ³⁵Cl or ³⁷Cl, predicted to be around 5.0 GHz. For this Δ*J* manifold, only the *K* = 0 transition with its set of hyperfine structure was expected to show up,^{8,9} which would simplify assignment and analysis of the chlorine quadrupole hfs. The first set of transitions found was at 4956 MHz. Adjustments in composition of the gas mixture readily established that the transitions need Ar and HCl only. Also, the hfs was fitted by a single quadrupolar nucleus, with *I* = 3/2 and a *χ*_{aa} of ~ -24.5 MHz, as expected for H³⁷Cl. Observation of a transition at (4/3) × 4956 MHz along with additional hfs attributable to *K* = ± 3 was indicative of a symmetric top ladder. A similar set of transitions, approximately three times stronger was found at slightly higher frequencies

TABLE I. Observed and calculated frequencies of the hyperfine components for *J* = 1 → 2 to *J* = 4 → 5 transitions of Ar₃-H³⁵Cl.^a

Component <i>J, K, F</i> → <i>J', K', F'</i>	Obs. (MHz)	Diff. (kHz)	<i>χ</i> _{aa} (MHz)	
1,0,1/2	2,0,3/2	3367.7757	0.6	- 31.003(9)
1/2	1/2	3375.5158	1.8	
3/2	5/2	3376.1816	- 0.2	
5/2	7/2	3376.1816	- 3.4	
3/2	3/2	3381.7302	1.2	
2,0,7/2	3,0,7/2	5055.7546	0.2	- 31.006(6)
1/2	3/2	5061.5785	- 3.4	
3/2	5/2	5061.5785	0	
5/2	7/2	5063.5067	2.8	
7/2	9/2	5063.5067	0.7	
5/2	5/2	5067.1300	8.7	- 31.006(6)
3/2	3/2	5069.3246	- 9.0	
3,0,5/2	4,0,7/2	6749.9174	- 2.6	
9/2	11/2	6750.8194	2.6	
± 3,7/2	± 3,9/2	6745.7239	1.9	
5/2	7/2	6749.2976	- 5.2	
9/2	11/2	6752.6691	0.8	
3/2	5/2	6756.2727	2.5	
4,0,7/2	5,0,9/2	8437.4361	0.9	- 31.006(6)
11/2	13/2	8437.9693	- 0.9	
± 3,9/2	± 3,11/2	8435.4374	1.7	- 31.021(17)
7/2	9/2	8436.6149	- 1.9	
11/2	13/2	8438.9327	- 1.5	
5/2	7/2	8440.0977	1.7	

^a Best fit values for line centers are given in Table III. Transitions with the same best fit value of *χ*_{aa} were fitted simultaneously.

(2.17%) indicating that the ³⁷Cl species was found first. The observations were extended to higher and lower *J*, giving the hyperfine frequencies summarized in Tables I and II.

The Hamiltonian used in the analysis consists of rotational, *H*_r, and chlorine nuclear quadrupole, *H*_q, terms:

$$H = H_r + H_q. \quad (1)$$

Spin rotation and the HCl dipole-dipole interactions are small and were not considered. The matrix elements were calculated in the coupled basis set *F* = *J* + *I*, where *I* = 3/2 for both chlorine isotopes. The *J* = 2 → 3 hfs was fitted to get an initial value of *χ*_{gg} since the transitions for higher *J* were a messy mix of *K* = 0 and ± 3 hfs. Correct assignment of the hyperfine components to *K* and *F* state was then possible and enabled fitting of all hfs. The chlorine quadrupole interaction is large enough for the second order corrections to be appreciable (up to ~15 kHz); they were included in the fitting program employed.

The results of the fit are also listed in Tables I and II, in terms of a difference frequency and a single quadrupole coupling constant. For their fitting, several transitions were grouped together and fitted simultaneously as shown in the tables. In addition, the fit determines the unperturbed line centers *ν*₀ which are listed in Table III for *J* → *J'*. In turn, the centers were fitted to the symmetric top expression¹⁷:

TABLE II. Observed and calculated frequencies of the hyperfine components of *J* = 2 → 3 to *J* = 4 → 5 transitions of Ar₃-H³⁷Cl.^a

Component <i>J, K, F</i> → <i>J', K', F'</i>	Obs. (MHz)	Diff. (kHz)	<i>χ</i> _{aa} (MHz)	
2,0,7/2	3,0,7/2	4949.818	- 4	- 24.476(6)
1/2	3/2	4954.425	2	
3/2	5/2	4954.425	2	
5/2	7/2	4955.940	0	
7/2	9/2	4955.940	- 1	
5/2	5/2	4958.802	6	
3/2	3/2	4960.537	- 5	- 24.476(6)
3,0,9/2	4,0,9/2	6601.352	2	
3/2	5/2	6606.758	- 4	
5/2	7/2	6606.758	- 2	
7/2	9/2	6607.471	2	
9/2	11/2	6607.471	2	
7/2	7/2	6609.618	0	- 24.476(6)
5/2	5/2	6612.880	0	
± 3,7/2	± 3,7/2	6602.657	0	
7/2	9/2	6603.412	1	
5/2	7/2	6606.231	0	
9/2	11/2	6608.917	0	
9/2	9/2	6611.053	- 9	- 24.486(12)
3/2	5/2	6611.745	8	
4,0,7/2	5,0,9/2	8258.412	- 1	
5/2	7/2	8258.412	- 1	
11/2	13/2	8258.834	1	- 24.486(12)
9/2	11/2	8258.834	1	
± 3,9/2	± 3,11/2	8256.791	0	- 24.486(12)
11/2	13/2	8259.547	- 1	
5/2	7/2	8260.469	1	

^a Best fit values for line centers are given in Table III. Transitions with the same best fit value of *χ*_{aa} were fitted simultaneously.

TABLE III. Fit of the line centers determined^a for the $J = 1 \rightarrow 2$ to $J = 4 \rightarrow 5$ transitions of Ar₃-H³⁵Cl/³⁷Cl.^a

Transition		Ar ₃ -H ³⁵ Cl		Ar ₃ -H ³⁷ Cl	
J, K	$\rightarrow J', K'$	Obs. (MHz)	Diff. (kHz)	Obs. (MHz)	Diff. (kHz)
1,0	2,0	3375.5140	-0.7	...	
2,0	3,0	5063.1322	0.1	4955.6469	-0.7
3,0	4,0	6750.5819	0.5	6607.2836	1.1
3, ± 3	4, ± 3	6750.4507	0.2	6607.1426	-0.2
4,0	5,0	8437.8066	-0.2	8258.7047	-0.5
4, ± 3	5, ± 3	8437.6430	-0.1	8258.5308	0.2

^a Obtained by fitting of hfs reported in Tables I and II.

$$v_0 = 2B_0J' - 4D_JJ'^3 - 2D_{JK}J'K^2. \quad (2)$$

Final values for the parameters B_0, D_J, D_{JK} , and χ_{aa} are listed in Table IV for both isotopes.

Molecular geometry

As in the case of Ar₃-HF, the Ar₃-HCl tetramer is a symmetric top best thought of as an equilateral trio of argons with the HCl lying along the symmetry axis, the H inwards (Fig. 1). The main observations supporting this geometry are the symmetric top spectra, indicating C₃ or higher symmetry, and the absence of certain K states. We noted above that only $K = 0$ and ± 3 states were found. This is readily seen in the summary of line centers in Table III. It corresponds to the requirements of the Bose-Einstein statistics for three identical $I = 0$ nuclei (⁴⁰Ar) off the C₃ axis.¹⁷ Higher K states which are multiples of three are allowed for $J > 6$ but we did not attempt to observe them. The geometry of Fig. 1 is supported also by the close agreement between predicted and observed B_0 's, a point which is considered in more detail in the inertial analysis.

HCl torsion

The nuclear quadrupole hfs is also indicative of cylindrical symmetry at the Cl nucleus. Unlike Ar₂-HCl, only a single coupling constant vibrationally averaged over the

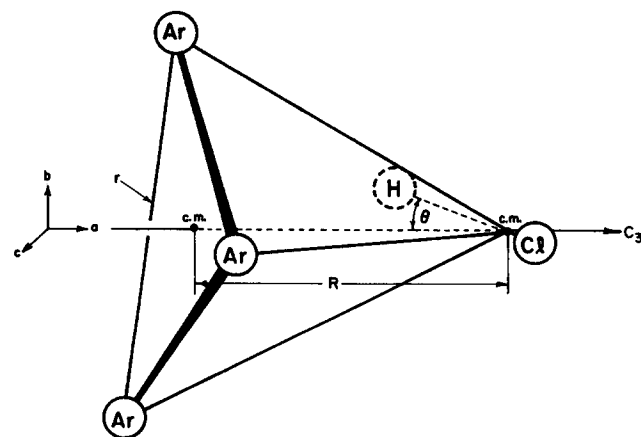


FIG. 1. Geometrical structure and inertial axes of the Ar₃-HCl cluster. The atomic positions in the prolate symmetric top are drawn to scale; θ is the "average" angle between the C₃ axis and the HCl direction.

ground-state isotropic torsion of the HCl in Ar₃-HCl is needed to account for the hfs. We proceed in the usual manner by assuming the electrical properties of HCl to be unchanged by cluster formation. The quadrupole coupling constant χ_0 of the free molecule is projected onto the inertial axes of the cluster, giving its observed hyperfine interaction constant to be¹⁸

$$\chi_{gg} = (1/2)\chi_0\langle 3 \cos^2 \theta - 1 \rangle. \quad (3)$$

In this expression, θ is the angle between the HCl bond vector and the symmetry/inertial axis (Fig. 1), and the brackets indicate an average over the torsional oscillations. Equation (3) may be used as an operational definition for an average torsional angle,

$$\theta = \arccos \left[\left\{ (2\chi_{gg}/\chi_0) + 1 \right\} / 3 \right]^{1/2}. \quad (4)$$

With the reported χ_0 values for free HCl (see Table V in Ref. 7) the above analysis yields 36.917(5) and 36.900(6) deg for the ³⁵Cl and ³⁷Cl isotopic species, respectively.

Inertial analysis

By treating the complex as pseudodiatom with Ar₃ and HCl subunits, and neglecting vibrational effects except those of the HCl torsion, we can describe its moment of inertia with the expression¹⁸

$$I_b = \mu_c R^2 + I_b(\text{Ar}_3) + (1/2)\langle 1 + \cos^2 \theta \rangle I_0(\text{HCl}). \quad (5)$$

Here, μ_c is the reduced mass of the pseudodiatom complex, R is the separation between the centers of mass for the two subunits, and $I_b(\text{Ar}_3)$ is the moment of inertia of the Ar₃ about the b axis of the complex. For the geometry of Fig. 1, $I_b(\text{Ar}_3)$ is simply $2m_{\text{Ar}}(r/2)^2$, where r is the Ar-Ar distance. The angle θ is taken as that from the chlorine hfs analysis (36.91°). This leaves two unknowns, R and r , and also the orientation of the HCl to be determined. The values obtained for R and r from the two observed B_0 's depend upon the orientation assumed for HCl. The value of r found with the H closest to the Ar₃ is more consistent with other determinations of the Ar-Ar distance, as described below.

The B_0 's in Table IV for the two isotopic complexes may be combined by subtracting Eq. (5) for ³⁵Cl from that for ³⁷Cl. (This approach is equivalent to the substitution method.) The resulting expression, Eq. (5'), includes the R 's for the two isotopic species, $R(35)$ and $R(37)$. If we make the reasonable assumption that the distance between the Ar₃ center of mass (c.m.) and the projection of the Cl on the a axis is the same for both isotopes, the two R 's are related by

$$R(37) = R(35) \pm \delta R(\text{HCl}) \cos \theta = R(35) \pm 0.00152 \text{ \AA}. \quad (6)$$

Here, $\delta R(\text{HCl})$ is the difference (0.001 90 Å) in location of the c.m. for free H³⁵Cl and H³⁷Cl.⁷ The plus sign is for the H end closest to Ar₃ and the minus sign for the Cl end closest. Use of Eq. (6) to eliminate $R(37)$ from Eq. (5') leads to two possible values for $R(35)$, 3.2992 and 3.3744 Å for Ar₃-HCl and -ClH, respectively. In turn, their substitution in Eq. (5) for Ar₃-H³⁵Cl gives corresponding values of 3.8510 and

3.7597 Å for the Ar-Ar distance r and 4.0024 and 3.9881 Å for the Ar to Cl distance d_0 .

Of these, the 3.8510 and 4.0024 Å pair of values is strongly favored by several lines of evidence, confirming that the H end of the HCl is closest to the Ar₃, as expected from the results for Ar_{*m*}-HF^{5,6,14} and Ar_{*m*}-HCl ($m = 1,2$).^{7,15} A high resolution UV absorption study of Ar₂ gives 3.821 Å for r_0 .¹⁹ Also, the value found in Ar₂-HCl was 3.8297 Å.⁷ The Ar-Cl distance (d_0) for the Ar₃-HCl orientation is also more compatible with those observed in Ar-HCl¹⁵ and Ar₂-HCl.⁷ The structural parameters obtained for the Ar₃-HCl configuration, averaged over the HCl torsion are summarized in Table V. The results for the three species Ar_{*m*}-H³⁵Cl ($m = 1,2,3$) are compared in Table VI, also averaged over the HCl torsion only. In the calculations, a conversion factor of 505 379.07 amu Å² was used for $I \times B$.

Mainly as an exercise, we calculated the moment of inertia about the symmetry axis. One would expect there to be appreciable torsional "tilt" of the Ar₃ group,⁹ but in the absence of evidence about its magnitude, we neglect it. With inclusion of the HCl torsion, we have

$$I_a = 3m_{\text{Ar}}(r/3)^2 + (\sin^2 \theta)I_{\text{HCl}}. \quad (7)$$

This gives $I_a = 593.2115$ amu Å² ($A = 851.938$ MHz) and 593.2124 amu Å² ($A = 851.937$ MHz) for the ³⁵Cl and ³⁷Cl species, respectively. Therefore, the Ar₃-H³⁵Cl complex is within 1% of being a spherical top and Ar₃-H³⁷Cl is within 3%. However, the symmetry axis is definitely the *a* axis.

DISCUSSION

In terms of its mass distribution the Ar₃-HCl cluster is practically a spherical top, particularly the ³⁵Cl species. Of course, if it were a spherical top, it would be an accidental one, but upon closer examination one sees that the similarity is not so accidental. Ar and HCl are isoelectronic, with similar polarizability, van der Waals radius, and mass. Therefore, as shown in Table VI, the Ar-Cl distance in the cluster (4.002 Å) is close to that for Ar-Ar (3.851 Å). At the limit for true spherical tops, $D_J = D_{JK} = D$, which is the single first-order centrifugal distortion constant and which must be positive.²⁰ For the near spherical top Ar₃-HCl, D_J and D_{JK} are quite close in magnitude and have the same sign (Table IV, ~ 2 kHz). So it appears that the cluster is closer in nature to a true spherical top like P_4 with a symmetrical force field than to a pyramidal XY₃ (e.g., NH₃, NF₃). In the latter, D_{JK} is almost always negative. For Ar₃-HF, which is an oblate top with B_0 and C_0 of about 1188 and 850 MHz, $D_J = 6.85$ MHz and $D_{JK} = -5.76$ kHz.^{8,9}

TABLE IV. Spectroscopic constants determined for the Ar₃-HCl tetramers.^a

Isotopic species	B_0 (MHz)	D_J (kHz)	D_{JK} (kHz)	χ_{aa} (Cl) (MHz)
Ar ₃ -H ³⁵ Cl	843.8974(1)	2.333(2)	1.818(6)	-31.008(8)
Ar ₃ -H ³⁷ Cl	825.9811(2)	2.211(5)	1.940(12)	-24.481(8)

^a Obtained by fitting the data in Tables I-III.

TABLE V. Torsionally averaged structural parameters determined for Ar₃-HCl.^a

Isotopic species	R^b (Å)	R_0 (Å)	d_0 (Å)	r (Å)	θ (deg)
Ar ₃ -H ³⁵ Cl	3.2992	3.3280	4.0024	3.8510	36.92
Ar ₃ -H ³⁷ Cl	3.3007	3.3280	4.0024	3.8510	36.90

^a The distances are: R , Ar₃ c.m. to HCl c.m.; R_0 , Ar₃ c.m. to Cl; r , Ar-Ar; d_0 , Ar-Cl; averaging is over the HCl torsion.

^b The difference between the ³⁵Cl and ³⁷Cl species was imposed.

A related interesting point is that $(D_J + D_{JK}) = 4.151$ kHz for both Ar₃-HCl clusters. This implies that D_K must be identical for both species. For any C_{3v} top,²⁰

$$D_K = -(D_J + D_{JK}) - h^4 \tau_{zzzz} / 4. \quad (8)$$

The distortion constant τ_{zzzz} depends entirely on angular momentum about the symmetry axis and associated changes in the moment of inertia, I_{zz} (I_{aa}). For Ar₃-HCl this is dependent only on the masses off axis (m_{Ar}) and force constants which must be the same for both isotopic species, so τ_{zzzz} remains unchanged and D_K is the same for ³⁵Cl and ³⁷Cl.

The Ar₃-HCl results are consistent with and complement those of the previously studied noble gas-hydrogen halide clusters. Ar₃-HCl is like Ar₃-HF in having C_{3v} symmetry as established by the spin statistics of the rotational levels. The HX subunit is directed along the symmetry axis towards the Ar₃ group in both complexes. Moreover, the relative intensities of Ar-HCl/Ar₂-HCl/Ar₃-HCl are in rough agreement with the concentrations (4:2:1) found in mass spectra of supersonic jets.²¹ In particular the Ar₃-HCl transition intensities were observed to be approximately 1/4 of Ar₂-HCl.

The internuclear distances appear to be reasonable. Table VI lists the structural and torsional results for the complexes Ar_{*m*}-HCl ($m = 1,2,3$). For instance, the Ar to Cl distance remains remarkably constant at around 4.010 Å in dimer, trimer, and tetramer, especially in view of the different symmetries and Ar_{*m*} motions involved. For Ar-HCl dimer a single radial parameter R_m is evaluated from a single rotational constant. R is of course easily converted to the Ar to Cl distance d_0 . In the asymmetric top Ar₂-HCl there was more than enough information to evaluate r and R from the three rotational constants. The results for ³⁵Cl and ³⁷Cl

TABLE VI. Comparison of structural parameters found for Ar_{*m*}-H³⁵Cl ($m = 1,2,3$)^a averaged over the HCl torsion.

Species	R (Å)	d_0 (Å)	r (Å)	θ (deg)
Ar-HCl ^b	3.9787	4.0056	...	41.53
Ar ₂ -HCl ^c	3.5013	4.0223	3.8296	38.60 ^d
Ar ₃ -HCl	3.2992	4.0024	3.8510	36.91

^a The distances are: R , Ar_{*m*} c.m. to HCl c.m.; d_0 , Ar-Cl; r , Ar-Ar.

^b Reference 15.

^c Reference 7.

^d Torsion is anisotropic with $\theta_{ab} = 30.40^\circ$ and $\theta_{ac} = 28.43^\circ$.

could be combined to determine the effects of the Ar₂ "torsion" on r and R by using a pseudotriatomic model which excludes out-of-plane motions of the heavy nuclei.⁷ The large, positive inertial defect of Ar₂-HCl was indicative of the complex's bent XY₂ nature with no out-of-plane motion possible. It is worth noting again the slight asymmetry found in the torsional oscillations of the HCl in the trimer. The average in-plane torsion was about 2° greater than the out-of-plane. Finally, in the case of Ar₃-HCl, the two isotopic constants were combined to determine r and R and from them, an Ar to Cl distance d_0 of 4.0024 Å. However, the tilt of the Ar₃ could not be obtained from the data available, so all of the R and d_0 values summarized in Table VI include only the effects of the HCl torsion. This applies to the Ar-Ar distance as well, which was found to be 3.8297 and 3.8510 Å in Ar₂- and Ar₃-HCl, respectively. This difference may or may not be significant. Inclusion of the Ar₂ torsion (β) in the Ar₂-HCl analysis has a substantial effect. It lengthens r by 0.032 Å and shortens d_0 by 0.017 Å making both more compatible with the other two complexes. Even without it, the values are sufficiently longer than in free Ar₂ ($r = 3.821$ Å) to indicate a slight lengthening, and weakening of the Ar-Ar interaction, upon cluster formation with HCl. A force constant analysis of Ar₂-HCl supports this view, giving a slightly smaller Ar-Ar "force" constant than in free Ar₂.¹⁹ The model used, however, is simplistic. For Ar₃-HCl, attempts to estimate the stretching force constant k_R from D_J with a pseudodiatomic approximation gave an unrealistically low result (1.87×10^{-3} mdyn/Å), as found for Ar₃-H/DF.⁹

An interesting trend among the three Ar_{*m*}-HCl complexes is the increase observed in χ_{aa} on going from Ar-HCl to Ar₃-HCl. This may be interpreted through Eq. (3) as a decrease from 41.5° to 36.9° in the "average" torsional oscillation which the HCl makes with the symmetry axis of the complexes (Table VI). Another possibility is that each additional argon perturbs the electric field gradient at the Cl nucleus, increasing it. Generally, however, complexes of a noble gas with any covalent subunit are too weak to perturb appreciably the field gradients in the subunit. The only counter example appears to be the T-shaped Ar-ClCN, in which χ_{cc} for ³⁵Cl was found to be 0.15% less than in free HCl.²² This is much too small and in the wrong direction to account for the 25% change found in Ar_{*m*}-HCl. Most likely, the observed increase in χ reflects decreased torsional amplitudes of the HCl.

In contrast, the torsional amplitudes for H/DF in Ar_{*m*}-H/DF ($m = 1,2,3$) are virtually independent of m . The angles are 41.6°, 40.7°, and 41.0° for the HF species with $m = 1,2,3$ and 33.5°, 35.0°, and 35.6° for the DF. The differences between the HF and HCl amplitudes no doubt reflect

differences in the potential functions generated by the multi-body interactions in the Ar₂-HX and Ar₃-HX clusters. We have not found a physical rationale for the difference. But it is noteworthy that the M5 potential function reported for the Ar-HF dimer²³ has a deeper, narrower angular well than that for Ar₃-HCl.²⁴

ACKNOWLEDGMENTS

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