Tunable far infrared laser spectroscopy of a ternary van der Waals cluster Ar_2HCl: A sensitive probe of three-body forces

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The first far infrared intermolecular vibration–rotation spectrum of a ternary van der Waals cluster has been measured near 39.5 cm^{-1} and assigned to an *a*-type Σ bending vibration of Ar_2HCl. Spectra of both chlorine isotopes were observed and nuclear quadrupole hyperfine structure was resolved. Values of the fitted constants (rotational constants, hyperfine projections) evidence large amplitude out-of-plane motion, and demonstrate the sensitivity of spectroscopic observables to the three body forces operative in the Ar_2HCl system. Spectroscopic predictions calculated by Hutson *et al.* from pairwise-additive and "three-body" corrected potential energy surfaces [J. Chem. Phys. **90**, 1337 (1989)] are compared to experimental results.

INTRODUCTION

The subject of many-body effects in intermolecular forces is becoming an increasingly prominent one, as numerous investigators turn to exploration of the detailed behavior of condensed matter with both theory and experiment. While the nature of three-body and higher order corrections to the well-known isotropic pair potentials of rare gases has received considerable attention, substantial ambiguities remain to be resolved even for these relatively simple systems. In particular, most treatments of nonpairwise additivity simply involve the incorporation of the Axilrod–Teller (AT) triple-dipole correction of the dispersion energy,[1] assuming a cancellation of higher order dispersion terms and neglecting many-body exchange contributions entirely. Recent *ab initio* calculations have shown, however, that many-body exchange and charge overlap effects are important,[2] and that the agreement of calculations employing only the AT correction with experimental results is due to a "fortuitous compensation of errors."[3] Studies of many-body effects on the crystal binding energies and third virial coefficients of rare gases also indicate the need for corrections beyond the AT term.[4] The principal reason for the current reign of speculation in this field is that the existing experimental data available are obtained exclusively from imprecise, classical experiments (transport properties, etc.). Many-body interactions in systems exhibiting *anisotropic* forces are even more poorly understood, due to a similar lack of high quality experimental data.

High resolution infrared (IR)[5] and far infrared (FIR) laser spectroscopies have recently been shown to be extremely sensitive probes of intermolecular forces and associated intramolecular dynamics. In particular, precise FIR spectroscopic measurements of the van der Waals stretching and bending vibrations [referred to as vibration–rotation–tunneling (VRT) spectra] in the ArHCl complex have been used to determine an accurate and detailed anisotropic potential energy surface for this system.[6–11] Similarly, recent tunable FIR measurements of VRT spectra of ArH_2O have been fit directly to an accurate three-dimensional potential energy surface using modern many-body dynamics theory.[12] It seems logical, therefore, to extend the application of this method to the study of three-body forces by measuring FIR-VRT spectra of ternary complexes, such as Ar_2HCl and Ar_2H_2O.

Recently, Gutowsky and co-workers investigated the Ar_mHF ($m = 1$–4)[13–16] and Ar_mHCl ($m = 1$–3)[17,18] systems with Fourier transform (FT) microwave spectroscopy, providing detailed information on the ground states of these larger van der Waals clusters. Hutson *et al.*[19] calculated pairwise additive and "adjusted" (adjusted empirically to account for nonadditive effects in the ground state) potential energy surfaces for Ar_2HCl in an effort to determine whether high resolution spectroscopy could, in principle, characterize the nature of three-body forces. Ar_2HCl was chosen as the ideal system for study because both the Ar–Ar and Ar–HCl pair potentials are very accurately known, thus potentially allowing the quantification of deviations from the pairwise-additive potential. Although they found that the microwave data were relatively insensitive to the nonadditive forces—because the ground state wave functions probe only a small region of the potential near the van der Waals minimum—Hutson *et al.* noted the considerable sensitivity of the frequencies and properties of the van der Waals *vibrational* modes to the three-body corrections employed.[19]

In this context, we report the first far infrared vibration–rotation spectrum of a van der Waals trimer, viz. Ar_2HCl. We have measured and assigned more than two hundred vibration–rotation transitions, including the resolution of nuclear quadrupole hyperfine structure. Transitions arising from both $Ar_2H^{35}Cl$ and $Ar_2H^{37}Cl$ were observed.

EXPERIMENTAL

The spectrum of Ar_2HCl was observed with a recently constructed tunable far infrared laser spectrometer, which is

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essentially identical to the existing Berkeley spectrometer already described in the literature.[10,20] Consequently, only those details relevant to this particular study will be presented here. The fixed frequency FIR radiation is provided by the 1193.7273 GHz CH_3OH laser line. The tunable radiation is detected by an InSb hot electron bolometer configured in the "Putley mode," with a fixed magnetic field of 5 kG employed to achieve maximum responsivity at ~ 40 cm^{-1}. Atmospheric water absorptions in the scanning region require that the entire beam path be purged with dry nitrogen. The laser beam is passed in front of the planar jet ten times with a multipass cell. The multipass cell system, based on the design of Perry and co-workers,[21] provides a fivefold improvement in sensitivity when used in the configuration described by Schmuttenmaer *et al.*[22]

The clusters were generated by continuously expanding a mass flow-controlled (MKS Instruments) mixture of HCl (Matheson, technical grade) and argon through a 10 $cm \times 25$ μm planar supersonic jet into a chamber pumped by a 2800 cfm Roots blower (Edwards). The production of Ar_2HCl was found to be quite sensitive to the HCl/Ar ratio and to the total chamber pressure. Maximum signal strength was realized with a 0.5% HCl/Ar mixture and a total chamber pressure of ~ 300 mTorr. This compares to an optimum mix of 1.0% for ArHCl and $> 5.0\%$ for $(HCl)_2$ under similar conditions. It was possible to completely suppress the Ar_2HCl signal by increasing the HCl concentration. In addition, cooling the jet with a dry ice/methanol bath (-78.5 °C) resulted in a twofold increase in signal, presumably due to additional clustering. This effect was not observed for the ArHCl and $(HCl)_2$ systems. The best spectra of Ar_2HCl exhibited signal-to-noise ratios near 30:1.

RESULTS AND ANALYSIS

The search for Ar_2HCl was guided by the predictions of Hutson, *et al.*[19] (all van der Waals modes were predicted to be within the range 35–45 cm^{-1}). An extremely dense spectrum was observed immediately upon scanning with the 251 μm CH_3OH laser line. The spectrum exhibited the gross features characteristic of P, Q, and R branches, and also revealed hyperfine splittings consistent with existence of one chlorine nucleus within the absorbing molecule.

Rotational assignment

The particular selection rules for Ar_2HCl are dictated by the existence of two identical nuclei (^{40}Ar) within the molecule. Because ^{40}Ar ($I = 0$) is a boson, the total wave function for the complex must be symmetric with respect to rotation about the C_{2v} axis. This, in turn, requires the K_p quantum number to be even in the ground state, effectively halving the number of allowed asymmetric rotor transitions.

The rotational structure was assigned with the aid of ground state combination differences from the FT-microwave measurements of Klots *et al.*[17] No two transitions corresponding to combination differences were observed for the chlorine-37 isotope, but the relative intensities ($^{35}Cl/^{37}Cl$:3/1) and spectral splittings ($^{35}Cl/^{37}Cl$:5/4) of the hyperfine components facilitated the assignment. In all, 168 intermolecular vibration–rotation transitions were assigned to $Ar_2H^{35}Cl$ and 66 transitions were assigned to $Ar_2H^{37}Cl$ (Table I and Fig. 2).

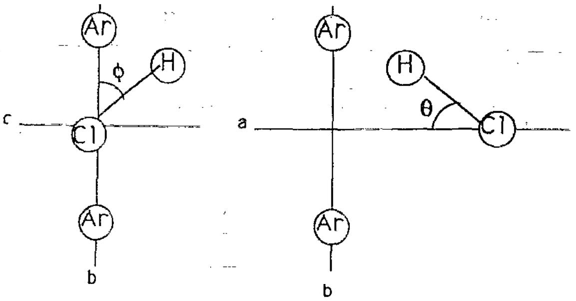

FIG. 1. Coordinate system for Ar_2HCl.

The observed intermolecular vibrational band was found to be of a-type symmetry with the following selection rule: $ee \leftrightarrow eo$ (where even and odd refer to the parity of the K_p, K_o quantum numbers). This assignment was confirmed by the presence of all lines in the $K_p = 0 \leftarrow 0$ subband as evident in Fig. 3, whereas b- or c-type transitions would be characterized by a missing $P(1)$ or $R(0)$ line. The observed Q branches and the general congestion of the spectrum are due to the existence of several $K_p = n \leftarrow n$ ($n = 2,4,6,8,10$) subbands. In addition, several weakly allowed transitions of the type $K_p = n \leftarrow n + 2$ or $n - 2$ were also observed.

The far infrared data were simultaneously fit with the ground state microwave data of Klots *et al.*[17] to a Watson S-reduced Hamiltonian.[23] The results of the fit are contained in Table II. Most of the lines observed were doublets (due to nuclear quadrupole interactions), and the line centers used for the rotational fit were calculated by simply averaging the two lines of each doublet. Rotational constants and all five quartic centrifugal distortion constants were determined for both the lower and upper vibrational states of both isotopes. Sextic distortion constants (H_J and H_K) were needed to accurately fit the upper state of $Ar_2H^{35}Cl$.

Vibrational assignment

Through consideration of the dynamics of Ar_2HCl, it is found that there are two possible intermolecular vibrational transitions of a-type symmetry: the van der Waals stretch and the motion that correlates in the HCl hindered-rotor picture to a Σ bending vibration ($j = 1$ $m_j = 0$). Hutson *et al.*[19] refer to this motion in normal coordinate language as the parallel bend. Based on the fact that the B and C rotational constants are larger in the upper state, we dismiss the van der Waals stretch as a possible assignment for the observed band. We therefore assign the band observed at 39.55 cm^{-1} to the parallel bend. Analysis of the parameters extracted from this spectrum confirm this assignment, as presented in the discussion.

TABLE I. Observed transitions for $Ar_2H^{35}Cl/^{37}Cl$ (MHz).

v'	v''	$J'_{K_pK_o}$	$J''_{K_pK_o}$	$\nu(Ar_2H^{35}Cl)$	O − C	$\nu(Ar_2H^{37}Cl)$	O − C
1	0	14_{014}	15_{015}	1 167 278.1	−0.4		
1	0	13_{013}	14_{014}	1 167 965.7	−0.3	1 168 252.4	−0.1
1	0	12_{012}	13_{013}	1 168 718.5	−0.4	1 168 958.2	0.0
1	0	11_{011}	12_{012}	1 169 537.8	−0.4	1 169 730.5	−0.4
1	0	10_{010}	11_{011}	1 170 424.4	−0.8	1 170 571.1	−0.7
1	0	9_{09}	10_{010}	1 171 380.0	−1.2	1 171 481.9	−0.5
1	0	8_{08}	9_{09}	1 172 407.6	0.2	1 172 463.2	−0.8
1	0	7_{07}	8_{08}	1 173 505.0	−0.2	1 173 517.9	0.0
1	0	6_{06}	7_{07}	1 174 674.7	−0.9	1 174 645.0	−0.4
1	0	5_{05}	6_{06}	1 175 919.9	0.0	1 175 847.8	0.2
1	0	4_{04}	5_{05}	1 177 238.6	−0.2	1 177 125.9	0.3
1	0	3_{03}	4_{04}	1 178 633.0	−0.4	1 178 481.1	0.7
1	0	2_{02}	3_{03}	1 180 104.0	−0.2	1 179 911.5	0.4
1	0	1_{01}	2_{02}	1 181 648.1	−0.9		
1	0	0_{00}	1_{01}	1 183 308.5	0.2	1 183 070.9	−0.7
1	0	1_{01}	0_{00}	1 188 426.4	1.9		
1	0	2_{02}	1_{01}	1 190 292.1	0.6		
1	0	5_{05}	4_{04}	1 196 205.9	0.2		
1	0	6_{06}	5_{05}	1 198 338.4	1.2		
1	0	7_{07}	6_{06}	1 200 540.0	−1.9	1 200 041.4	−1.2
1	0	8_{08}	7_{07}	1 202 819.7	1.3	1 202 301.5	2.3
1	0	9_{09}	8_{08}	1 205 165.6	−0.1	1 204 627.8	0.4
1	0	10_{010}	9_{09}	1 207 582.3	0.0		
1	0	11_{011}	10_{010}	1 210 067.6	0.8		
1	0	12_{012}	11_{011}	1 212 618.1	0.2		
1	0	13_{013}	12_{012}	1 215 234.9	0.7		
1	0	14_{014}	13_{013}	1 217 914.6	0.0		
1	0	14_{213}	15_{214}	1 165 231.3	1.4		
1	0	12_{210}	13_{211}	1 164 776.1	3.8		
1	0	12_{211}	13_{212}	1 166 721.9	−0.6		
1	0	11_{29}	12_{210}	1 165 638.5	−0.4		
1	0	11_{210}	12_{211}	1 167 566.9	−0.2	1 167 847.1	0.9
1	0	10_{28}	11_{29}	1 166 572.8	−0.1		
1	0	10_{29}	11_{210}	1 168 478.0	−1.0	1 168 708.1	0.6
1	0	9_{27}	10_{28}	1 167 575.4	−0.4	1 167 830.1	−0.0
1	0	9_{28}	10_{29}	1 169 458.5	−1.2	1 169 638.2	−0.0
1	0	8_{26}	9_{27}	1 168 648.6	−0.6	1 168 849.6	−0.3
1	0	8_{27}	9_{28}	1 170 509.5	−1.0	1 170 639.3	−0.5
1	0	7_{25}	8_{26}	1 169 793.6	−0.8	1 169 941.7	−0.6
1	0	7_{26}	8_{27}	1 171 632.1	−0.7	1 171 712.6	−1.0
1	0	6_{24}	7_{25}	1 171 012.0	−0.8		
1	0	6_{25}	7_{26}	1 172 827.5	−0.4	1 172 861.0	−0.1
1	0	5_{23}	6_{24}	1 172 306.0	0.0	1 172 349.2	−0.4
1	0	5_{24}	6_{25}	1 174 096.7	−0.2		
1	0	4_{22}	5_{23}	1 173 673 3	−2.4	1 173 651.2	−0.4
1	0	4_{23}	5_{24}	1 175 440.1	−0.8	1 175 381.3	−0.6
1	0	3_{21}	4_{22}			1 175 002.6	−0.9
1	0	3_{22}	4_{23}	1 176 861.1	0.2	1 176 764.9	1.1
1	0	2_{20}	3_{21}	1 176 816.0	−2.7		
1	0	2_{21}	3_{22}	1 178 363.9	0.1		
1	0	2_{20}	2_{21}	1 186 728.1	0.3		
1	0	2_{21}	2_{20}	1 185 140.5	1.9	1 184 926.6	−0.7
1	0	3_{21}	3_{22}	1 188 672.5	0.2		
1	0	3_{22}	3_{21}	1 183 800.5	−0.7		
1	0	4_{22}	4_{23}	1 190 662.2	1.4		
1	0	4_{23}	4_{22}			1 182 131.3	−0.5
1	0	5_{24}	5_{23}	1 180 820.4	3.2		
1	0	6_{25}	6_{24}	1 179 522.6	−0.8		
1	0	7_{25}	7_{26}	1 196 971.2	2.7		
1	0	8_{26}	8_{27}	1 199 218.8	3.0		
1	0	9_{27}	9_{28}	1 201 535.2	1.9		
1	0	10_{28}	10_{29}	1 203 920.6	0.9		

TABLE I. (*continued*).

v'	v''	$J'_{K_pK_o}$	$J''_{K_pK_o}$	$\nu(Ar_2H^{35}Cl)$	O − C	$\nu(Ar_2H^{37}Cl)$	O − C
1	0	11_{29}	11_{210}	1 206 374.5	1.1		
1	0	12_{210}	12_{211}	1 208 892.9	0.2		
1	0	14_{212}	14_{213}	1 214 123.3	1.4		
1	0	15_{213}	15_{214}	1 216 827.5	− 1.2		
1	0	4_{23}	3_{22}	1 195 765.0	1.9		
1	0	4_{22}	3_{21}	1 197 601.3	0.2		
1	0	5_{23}	4_{22}	1 199 463.9	0.0	1 199 083.0	2.4
1	0	5_{24}	4_{23}	1 197 802.4	0.1		
1	0	6_{24}	5_{23}	1 201 514.2	0.8	1 201 050.7	− 0.5
1	0	6_{25}	5_{24}	1 199 907.2	− 0.9	1 199 429.7	0.8
1	0	7_{25}	6_{24}	1 203 663.3	− 0.8		
1	0	7_{26}	6_{25}			1 201 591.2	− 0.2
1	0	8_{26}	7_{25}			1 205 387.5	0.0
1	0	8_{27}	7_{26}	1 204 335.5	− 2.1	1 203 826.5	− 0.1
1	0	9_{27}	8_{26}	1 208 186.2	− 0.1		
1	0	9_{28}	8_{27}	1 206 659.3	0.3		
1	0	10_{29}	9_{28}	1 209 049.1	− 0.4		
1	0	11_{29}	10_{28}	1 212 986.2	− 0.2		
1	0	11_{210}	10_{29}	1 211 508.1	0.5		
1	0	12_{210}	11_{29}	1 215 486.2	− 0.3		
1	0	12_{211}	11_{210}	1 214 032.9	1.0		
1	0	13_{211}	12_{210}	1 218 050.2	− 0.8		
1	0	13_{212}	12_{211}	1 216 621.3	0.4		
1	0	14_{212}	13_{211}	1 220 677.9	− 0.6		
1	0	14_{213}	13_{212}	1 219 272.4	− 0.7		
1	0	15_{214}	14_{213}	1 221 987.2	0.1		
1	0	14_{410}	15_{411}	1 159 386.8	1.2		
1	0	14_{411}	15_{412}	1 161 287.8	− 0.9		
1	0	13_{49}	14_{410}	1 160 153.9	− 3.3		
1	0	12_{49}	13_{410}	1 162 864.7	0.8		
1	0	11_{47}	12_{48}	1 161 897.9	0.5		
1	0	8_{45}	9_{46}	1 166 821.7	− 0.1		
1	0	7_{43}	8_{44}	1 166 222.0	1.1	1 166 504.8	− 3.0
1	0	7_{44}	8_{45}	1 167 988.8	− 0.4	1 168 205.1	− 0.9
1	0	6_{42}	7_{43}	1 167 496.3	− 2.6		
1	0	6_{43}	7_{44}			1 169.394.0	− 1.1
1	0	5_{41}	6_{42}	1 168 906.6	0.8	1 169 069.2	− 0.9
1	0	5_{42}	6_{43}	1 170 548.9	0.4		
1	0	4_{40}	5_{41}	1 170 646.9	1.8		
1	0	4_{41}	5_{42}	1 171 942.4	0.7		
1	0	4_{40}	4_{41}	1 186 837.6	− 2.7	1 186 282.3	− 2.5
1	0	4_{41}	4_{40}	1 185 473.9	0.9		
1	0	5_{41}	5_{42}	1 189 067.5	1.2		
1	0	5_{42}	5_{41}	1 184 523.7	− 1.6		
1	0	6_{42}	6_{43}	1 191 231.4	− 0.6		
1	0	6_{43}	6_{42}	1 182 934.9	− 0.5		
1	0	9_{45}	9_{46}	1 197 842.0	2.2		
1	0	10_{46}	10_{47}	1 200 181.4	0.3	1 199 915.6	0.2
1	0	11_{47}	11_{48}	1 202 591.6	1.0		
1	0	12_{48}	12_{49}	1 205 064.1	− 2.2		
1	0	5_{41}	4_{40}	1 202 598.9	1.2	1 201 510.3	− 0.9
1	0	5_{42}	4_{41}	1 200 717.4	− 3.1		
1	0	6_{42}	5_{41}	1 205 208.1	− 0.7	1 204 799.6	2.7
1	0	6_{43}	5_{42}	1 203 096.6	0.7	1 202 494.4	0.3
1	0	7_{43}	6_{42}	1 207 073.9	1.1		
1	0	7_{44}	6_{43}	1 205 271.3	− 0.3	1 204 771.0	1.1
1	0	8_{44}	7_{43}	1 209 118.2	0.6		
1	0	8_{45}	7_{44}	1 207 474.3	− 0.5	1 206 984.3	− 0.7
1	0	9_{45}	8_{44}	1 211 346.1	0.9		
1	0	9_{46}	8_{45}	1 209 746.4	− 0.5	1 209 250.9	0.6
1	0	10_{46}	9_{45}	1 213 660.6	− 0.8	1 213 187.3	− 0.4
1	0	10_{47}	9_{46}	1 212 088.7	− 0.8		

TABLE I. (*continued*).

v'	v''	$J'_{K_pK_o}$	$J''_{K_pK_o}$	$\nu(\mathrm{Ar_2H^{35}Cl})$	O − C	$\nu(\mathrm{Ar_2H^{37}Cl})$	O − C
1	0	11_{47}	10_{46}	1 216 047.9	− 1.5	1 215 567.3	− 0.6
1	0	11_{48}	10_{47}	1 214 500.0	− 0.6		
1	0	12_{48}	11_{47}	1 218 503.1	− 2.5		
1	0	11_{65}	12_{66}	1 158 299.4	0.2		
1	0	9_{63}	10_{64}	1 160 409.1	1.1		
1	0	8_{62}	9_{63}	1 161 625.2	− 1.3		
1	0	6_{60}	6_{61}	1 186 998.0	− 2.9	1 186 257.0	− 2.8
1	0	6_{61}	6_{60}	1 185 899.7	2.9	1 185 761.6	− 0.8
1	0	8_{63}	8_{62}	1 184 047.1	− 2.0		
1	0	10_{64}	10_{65}	1 196 585.1	1.3		
1	0	11_{65}	11_{66}	1 198 950.4	− 1.3		
1	0	7_{62}	6_{61}	1 207 771.9	0.7		
1	0	8_{62}	7_{61}	1 213 066.7	− 0.3		
1	0	9_{63}	8_{62}	1 215 064.5	3.6		
1	0	9_{64}	8_{63}			1 212 424.3	− 2.1
1	0	10_{64}	9_{63}	1 217 012.1	− 1.1		
1	0	11_{66}	10_{65}	1 217 632.0	− 3.0		
1	0	14_{87}	15_{88}	1 153 907.3	2.1		
1	0	10_{82}	11_{83}	1 156 132.7	0.1		
1	0	10_{83}	11_{84}	1 157 594.8	− 1.5		
1	0	9_{82}	10_{83}	1 158 682.6	− 0.2		
1	0	10_{82}	9_{81}	1 221 099.7	1.0		
1	0	10_{83}	9_{82}	1 218 224.4	− 2.3		
1	0	13_{85}	12_{84}	1 227 492.8	3.9		
1	0	10_{100}	10_{101}	1 187 427.7	− 2.0	1 186 301.8	− 0.2
1	0	10_{101}	10_{100}	1 186 747.2	0.5		
1	0	11_{102}	11_{101}			1 188 085.9	0.4
1	0	14_{104}	14_{105}	1 199 429.7	− 1.3		
1	0	2_{02}	2_{21}	1 183 358.3	1.5		
1	0	3_{03}	3_{22}	1 181 958.7	− 1.9		
1	0	4_{04}	4_{23}	1 180 552.6	1.0		
1	0	8_{27}	8_{08}	1 201 090.9	0.5		
1	0	9_{28}	9_{09}	1 203 433.5	0.4	1 202 963.4	1.0
1	0	4_{22}	3_{03}			1 203 615.4	0.5
1	0	5_{23}	5_{42}	1 182 400.0	− 0.6		
1	0	6_{24}	6_{43}	1 181 131.1	− 1.3		
1	0	4_{41}	4_{22}	1 189 004.0	− 0.9		
1	0	9_{46}	9_{27}	1 199 671.8	2.4		
1	0	10_{47}	10_{28}	1 202 034.8	2.2	1 201 697.6	2.0
1	0	11_{48}	11_{29}	1 204 463.3	0.0	1 204 122.2	0.0
1	0	12_{49}	12_{210}	1 206 960.9	1.2		
1	0	14_{411}	14_{212}			1 211 794.4	− 0.2
1	0	4_{40}	3_{21}	1 200 972.5	− 2.2	1 200 682.5	1.8
1	0	5_{41}	4_{22}	1 206 131.0	1.5		
1	0	6_{42}	6_{61}			1 182 437.1	2.9
1	0	7_{43}	7_{62}	1 183 013.3	− 0.2		
1	0	9_{64}	9_{45}	1 196 047.2	2.3		
1	0	10_{65}	10_{46}	1 198 365.8	1.5		
1	0	11_{65}	11_{47}	1 200 751.8	− 1.6	1 200 563.1	− 1.1
1	0	6_{60}	5_{41}	1 208 596.1	2.2		
1	0	8_{62}	7_{43}	1 219 195.1	− 0.7		
1	0	8_{63}	7_{44}	1 220 948.2	1.2		
1	0	8_{62}	8_{81}	1 183 781.7	− 0.1		
1	0	12_{85}	12_{66}			1 199 595.3	0.8
1	0	11_{83}	11_{102}	1 184 661.3	− 1.6		
0^{a}	0	1_{01}	0_{00}	2 512.344	0.001		
0	0	2_{02}	1_{01}	4 263.277	0.007	4 204.727	0.000
0	0	2_{20}	1_{01}	7 695.914	− 0.001	7 600.216	0.000
0	0	3_{22}	3_{03}	4 283.470	0.000		
0	0	3_{03}	2_{02}	5 924.082	− 0.004	5 817.047	0.001
0	0	3_{22}	2_{21}	7 536.064	0.003	7 304.977	0.001
0	0	3_{21}	2_{02}	12 580.642	0.000		

TABLE I. (*continued*).

v'	v''	$J'_{K_pK_o}$	$J''_{K_pK_o}$	$\nu(Ar_2H^{35}Cl)$	O − C	$\nu(Ar_2H^{37}Cl)$	O − C
0	0	3_{21}	2_{20}	9 147.947	0.001	8 792.848	− 0.001
0	0	4_{04}	3_{03}	7 610.706	− 0.001	7 467.052	− 0.004
0	0	4_{23}	3_{22}	9 313.367	− 0.002	9 117.129	0.001
0	0	4_{22}	3_{21}	11 175.955	− 0.005		
0	0	4_{40}	3_{21}	14 707.822	0.000	14 772.203	0.001
0	0	5_{05}	4_{04}	9 298.901	0.001	9 122.837	0.002
0	0	5_{23}	4_{22}	12 749.386	0.005	12 579.497	0.000
0	0	5_{42}	4_{41}	14 104.776	− 0.004		
0	0	5_{41}	4_{40}	15 621.761	0.002		
0	0	6_{25}	5_{24}			12 456.355	− 0.001

[a] Microwave transitions are from Ref. 17.

Hyperfine analysis

The nuclear quadrupole coupling constants were determined in a separate least-squares fit. The line centers used for the fit were determined from the constants obtained in the rotational analysis. Only a small number of hyperfine multiplets were used in the fit, as the hyperfine structure collapses to a doublet for $J > 4$. The matrix elements[24] for the nuclear quadrupole Hamiltonian were calculated in a space-fixed coupled basis set $|J\,K\,I\,F\rangle$ ($F = I + J$; $I = 3/2$ for both ^{35}Cl and ^{37}Cl). Because Ar_2HCl possesses C_{2v} symmetry, only terms of the form eqQ_{ii} ($i = a,b,c$) are nonvanishing. Only first order terms (matrix elements diagonal in J) were used, as this level of calculations was entirely satisfactory for fitting the ground state hyperfine constants. Although the long-term drift of the FIR laser is about 1 MHz, as evidenced by a standard deviation of 1.3 MHz in the rotational fit, the short term drift is less than 100 kHz. We weighted the hyperfine transitions accordingly, fixed the ground state hyperfine parameters at the microwave values obtained by Klots *et al.*,[17] and fitted the upper state nuclear quadrupole coupling constants (Table III).

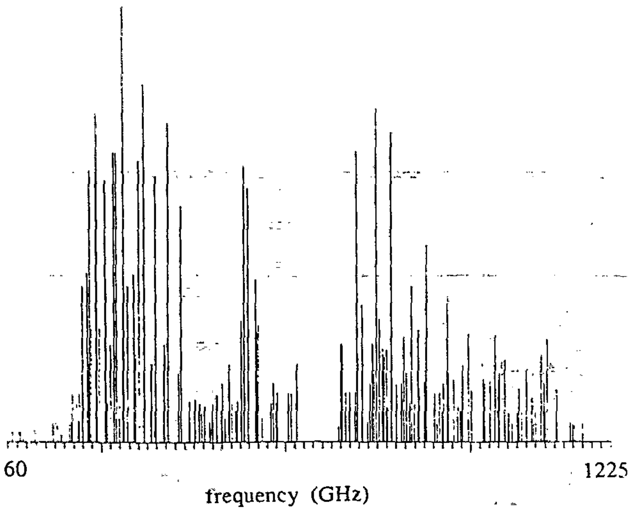

FIG. 2. Observed vibration–rotation spectrum of the parallel bend for $Ar_2H^{35}Cl$.

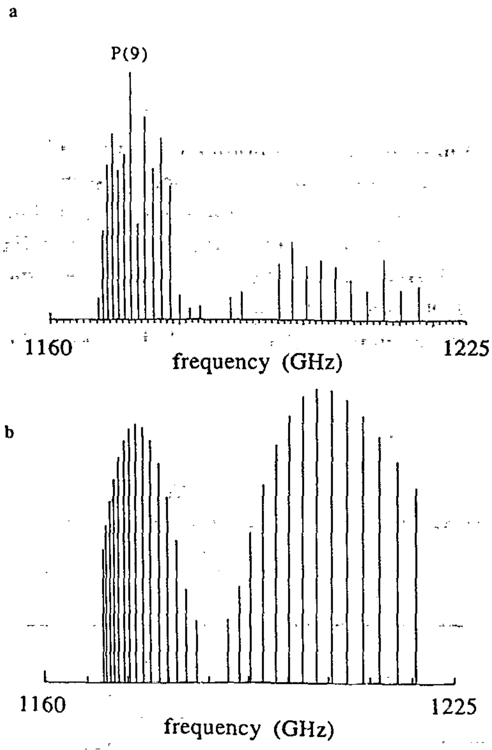

FIG. 3. (a) Observed $K_p = 0 \leftarrow 0$ subband for $Ar_2H^{35}Cl$. $R(2)$ and $R(3)$ were not observed because of the scanning coverage of the FIR sideband spectrometer. (b) Calculated $K_p = 0 \leftarrow 0$ subband for $Ar_2H^{35}Cl$ for $T_r = 5$ K. Note: The discrepancy between observed and calculated intensities is most likely an experimental artifact (e.g., atmospheric water absorptions and detector rolloff).

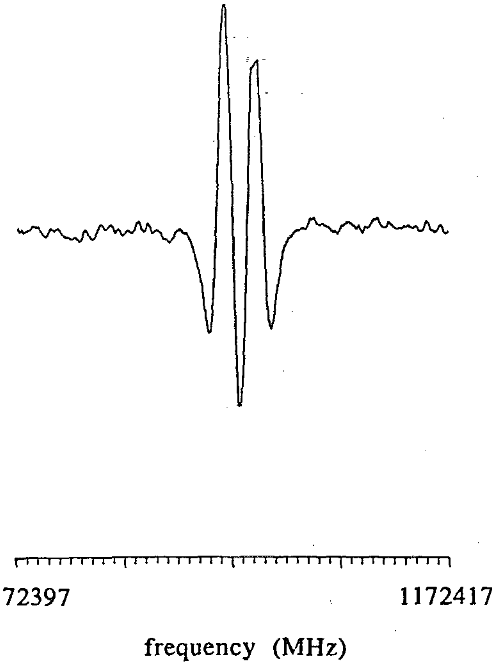

FIG. 4. $P(9)$ of the $K_p = 0 \leftarrow 0$ subband. This line shape is characteristic of the hyperfine doublets observed and represents the maximum signal-to-noise ratio realized ($\sim$30:1).

TABLE III. Nuclear quadrupole coupling constants (MHz).[a]

	$Ar_2H^{35}Cl$		$Ar_2H^{37}Cl$	
	$v=0$	$v=1$	$v=0$	$v=1$
eqQ_{aa}	−28.123(14)	−19.69(19)	−22.201(5)	−14.9(5)
eqQ_{bb}	12.471(13)	6.72(19)	9.844(21)	5.3(5)
eqQ_{cc}	15.658(13)	12.97(19)	12.356(21)	9.7(2)

[a] Ground state constants are from Ref. 17.

DISCUSSION

The orientation of the HCl monomer within the vibrationally excited complex is an important property to characterize, as it reveals the nature of the vibrational motion. The existence of a secondary minimum for ArHCl at the ArClH geometry was conclusively established by the spectroscopic measurements of Robinson *et al.*[7–9] and the resulting potential energy surface calculated by Hutson.[11] The potential energy surface calculated by Hutson *et al.*[19] for Ar_2HCl also indicates the existence of a double minimum, with the secondary minimum (Ar_2ClH) located 60 cm^{-1} above the absolute minimum. Since both isotopes of Ar_2HCl were measured in this work, an inertial analysis of the complex in the vibrationally excited state could be performed using the procedure given by Klots *et al.*[17] in their analysis of the ground state. The inertial defect is found to be large and negative ($\Delta = -13.36$ amu Å^2 for the excited vibrational state and 3.9682 amu Å^2 for the ground state of $Ar_2H^{35}Cl$), indicating that the vibrational amplitude is very large, and that there is significant out-of-plane motion. Using the planar moments

$$P_A = 1/2(I_B + I_C - I_A), \tag{1}$$

and with P_B and P_C defined by cyclic permutation, and neglecting torsional oscillations, the following relation is obtained:

$$P_A = \mu R^2 + I_{HCl}, \tag{2}$$

where μ is the reduced mass of the complex, and R is the distance between the Ar_2 and HCl centers of mass. In the ground state, R is 3.4969(1) and 3.4975(1) Å for $Ar_2H^{35}Cl$ and $Ar_2H^{37}Cl$, respectively. Since the center of mass separation is smaller for the ^{35}Cl isotope, the HCl monomer must be oriented with the hydrogen atom pointing toward the two argon atoms in this state. However, in the upper state, R is

TABLE II. Molecular constants (MHz) for $Ar_2H^{35}Cl/^{37}Cl$.[a)]

	$Ar_2H^{35}Cl$		$Ar_2H^{37}Cl$	
	$v=0$	$v=1$	$v=0$	$v=1$
ν_0	···	1185 820.7(3)	···	1185 506.9(4)
A	1733.856 0(4)	1 730.70(4)	1733.824 7(4)	1 731.33(4)
B	1667.921 40(18)	1 720.89(3)	1606.865 1(5)	1 663.62(4)
C	844.444 87(16)	883.040(13)	828.453 42(16)	867.73(2)
D_J	0.024 201(7)	0.017 47(13)	0.023 369(14)	0.019 5(2)
D_{JK}	−0.040 915(18)	−0.010 44(10)	−0.039 33(4)	−0.010 6(3)
D_K	0.018 679(14)	0.002 74(19)	0.017 83(3)	0.001 5(2)
d_1	0.002 479(6)	−0.001 98(17)	0.002 927(17)	0.004 6(2)
d_2	−0.000 406 6(18)	−0.002 18(5)	−0.000 456(6)	−0.003 55(7)
H_J	···	0.000 001 9(4)	···	···
H_K	···	0.000 003 2(7)	···	···

[a] Uncertainties represent one standard deviation. Least-squares fit includes hyperfine-corrected line centers from Ref. 17.

3.3915(4) and 3.3882(4) Å for $Ar_2H^{35}Cl$ and $Ar_2H^{37}Cl$, respectively. This calculation not only indicates that the HCl monomer is closer to the argon atoms in the vibrationally excited state, but it also reveals that the HCl monomer is now oriented with the hydrogen atom pointing away from the two argon atoms, as in the Σ bending state of ArHCl. This confirms the assignment of the observed vibration–rotation band to the parallel bend.

The nuclear quadrupole coupling constants can provide information pertaining to the vibrational dynamics of the complex. Using the relations

$$eqQ_{aa} = eqQ_{\rm HCl} \langle P_2(\cos\theta)\rangle, \tag{3}$$

$$eqQ_{bb} - eqQ_{cc} = (3/2) eqQ_{\rm HCl} \langle \Delta(\theta,\phi)\rangle, \tag{4}$$

where $\Delta(\theta,\phi) = \sin^2\theta\cos 2\phi$ and $eqQ_{\rm HCl}$ is the quadrupole coupling constant of the uncomplexed monomer, one can obtain additional information about the angular orientation of HCl monomer within the complex. Figure 1 depicts the axis system used to describe the dynamics of Ar_2HCl in this study. The deviation of $\langle P_2(\cos\theta)\rangle$ from unity is a measure of the bending amplitude of the HCl monomer, while the deviation of $\langle\Delta(\theta,\phi)\rangle$ from zero characterizes the anisotropy of the torsional motion of the HCl monomer. Table IV contains the expectation values for Ar_2HCl as well as similar results for the Σ bending vibration of ArHCl. It is seen that Ar_2HCl exhibits a larger bending amplitude than ArHCl in their respective excited vibrational states. The torsional motion of the HCl monomer in Ar_2HCl seems to be largely unhindered.

Some insight into the nature of the three-body forces operating in Ar_2HCl can be gained by comparing the properties of the excited Σ bending state calculated by Hutson *et al.* with those extracted in the present study. However, Hutson has noted that the severe dynamical constraints imposed in their model require that such comparisons be made with considerable caution.[25] Within their somewhat limited model, Hutson *et al.* found that the pairwise-additive potential predicts an HCl bending motion which is too isotropic and which is too small in amplitude to account for the experimental results for $\langle P_2(\cos\theta)\rangle$ and $\langle\Delta(\phi,\theta)\rangle$ in the ground state of the complex. Moreover, the pair potential yielded *B* and *C* rotational constants which were considerably larger than the experimental values, implying the existence of a repulsive three-body contribution to the intermolecular potential.

The addition of a three-body dipole–dipole induction term was attempted to correct for the angular dependent discrepancies. The incorporation of this term produced changes in the angular expectation values, which brought them in closer agreement with their experimental values. However, the magnitudes of these changes induced by three-body induction term were much too small. By multiplying this term by an empirical factor of 25, good agreement with experiment was obtained. This adjustment produced only a small effect on the rotational constants.

The term included to correct the rotational constants for three-body effects was not of any physically relevant form. The overall repulsive three-body form used by Hutson *et al.* empirically represents the net isotropic contribution of the three-body exchange and dispersion forces. The AT term is expected to contribute repulsively to the total potential, given the triangular geometry of Ar_2HCl,[1] while *ab initio* theory predicts that the three-body exchange contribution is attractive.[2] The incorporation of this empirical factor brought the rotational constants into agreement with experiment. Satisfactory agreement among all calculated and measured properties for the Ar_2HCl ground state was achieved by incorporating both of these corrections to the pairwise-additive potential. With this "adjusted" potential, Hutson *et al.* predicted the spectroscopic properties of four intermolecular vibrational modes of the complex, and compared these predictions with calculations performed with the pairwise-additive potential. From the calculations described above (Table VI in Ref. 19), it may be noted that the parallel bend and the in-plane bend are most strongly affected by the differences in the pairwise-additive and the adjusted potentials.

In Table V we compare our results with the predictions for the parallel bend. The vibrational frequency increases by 3.0 $\rm cm^{-1}$ in going from the pairwise-additive potential to the adjusted potential, whereas the observed frequency is actually 3.1 $\rm cm^{-1}$ *lower* than the pairwise-additive result. Similarly the experimental values for *C* and $\langle P_2(\cos\theta)\rangle$ in the vibrationally excited state agree better with the predictions from the pairwise-additive potential, while *B* and $\langle\Delta(\theta,\phi)\rangle$ agree well with the adjusted potential calculations. It thus appears that the three-body induction term required to produce agreement with the ground state measurements is indeed much too large, as Hutson *et al.* have already suggested.[19] The effects of this term on the ground state are principally to slightly reduce (~7%) the magnitude of $\langle P_2(\cos\theta)\rangle$, while increasing that of $\langle\Delta(\theta,\phi)\rangle$ by 50%. In the excited parallel bending state, the effect on $\langle P_2(\cos\theta)\rangle$ is much larger (41%), while that on $\langle\Delta(\theta,\phi)\rangle$ is about the same. Hence, the size of this correction required to force agreement with experiment for the ground state

TABLE IV. Comparison of angular expectation values for excited parallel bending states of ArHCl and Ar_2HCl.

Molecule	$\langle P_2(\cos\theta)\rangle$	$\langle\Delta(\theta,\phi)\rangle$
$ArH^{35}Cl^a$	0.341(2)	···
$ArH^{37}Cl$	0.3417(6)	···
$Ar_2H^{35}Cl$	0.291(3)	0.062(7)
$Ar_2H^{37}Cl$	0.280(10)	0.055(15)

[a] ArHCl data from Ref. 10.

TABLE V. Spectroscopic properties of parallel bend of Ar_2HCl.

ν_0 ($\rm cm^{-1}$)	*B* (MHz)	*C*(MHz)	$\langle P_2(\cos\theta)\rangle$	$\langle\Delta(\theta,\phi)\rangle$
Calculated from pairwise additive potential (Ref. 19)				
42.589	1793.4	879.2	0.2943	0.04296
Calculated from adjusted potential (Ref. 19)				
45.595	1721.2	861.9	0.1687	0.07713
Experimental				
39.555	1720.9	883.0	0.291	0.062

overcorrects for the excited bending state, implying that this form of the correction is inadequate. Higher order induction terms may be important, but the inclusion of analytical expressions for the exchange and dispersion three-body contributions is more likely to produce an accurate total intermolecular potential.

In any case, it is clear that additional experiments and more elaborate calculations are necessary to further elucidate the nature of the nonpairwise-additive forces operating in the Ar_2HCl system. From this work, it is clear that FIR-VRT spectroscopy of ternary complexes does provide a viable new route for the study of three-body contributions to intermolecular forces. We also note that near-IR laser spectroscopy has recently been utilized successfully in the study of Ar_nHF ($n = 2$–4) by Nesbitt and co-workers.[26]

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