

An investigation of three-body effects in intermolecular forces.

III. Far infrared laser vibration-rotation-tunneling spectroscopy of the lowest internal rotor states of Ar₂HCl

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The *c*-type intermolecular out-of-plane bend of Ar₂HCl has been observed at 45.2 cm⁻¹, completing the high resolution far infrared measurements of the three lowest-lying Ar₂HCl bending states which correlate to the *j*=1 internal rotational state of the HCl monomer. The rotational and nuclear quadrupole hyperfine structures indicate the existence of a Coriolis perturbation. The perturbing state is postulated to be a heavy-atom stretching overtone that is very nearly degenerate with the out-of-plane bend. A partial reassignment of the previously reported [J. Chem. Phys. **95**, 3182 (1991)] Ar₂HCl in-plane bend is presented and a treatment of Coriolis effects between the in-plane and Σ bends is discussed. Comparison with dynamically rigorous calculations presented in the accompanying paper [J. Chem. Phys. **98**, 5337 (1993)] indicate substantial three-body contributions to the intermolecular potential, which should be determinable from the data presented in this paper.

INTRODUCTION

The investigation of many-body effects in intermolecular interactions has assumed increasing prominence as modern experimental and computational technology has progressed such that it is now possible to begin to address the details of condensed phases of matter. Although the literature of the last several decades is replete with both experimental and theoretical studies of many-body effects, modern *ab initio* calculations have shown that most such work has seriously underestimated the complexity of the problem. For example, Chalasinski and co-workers have undertaken several *ab initio* (supermolecular Møller-Plesset perturbation theory) studies of three- and four-body effects in several van der Waals clusters and have found that the size and form of many-body terms in the potential are strongly system dependent. These calculations have also shown that hydrogen-bonded systems [such as (H₂O)₃, (HF)₃, (HCl)₃, and (NH₃)₃] display large three-body effects (~10% of pairwise contributions) and that these effects are well approximated by a single term in the perturbation expansion.^{1,2} Conversely, more weakly bound systems (such as Ar₃, Ar₂H₂O, and Ar₂HCl) are expected to show smaller three-body effects that *cannot* be well approximated by single terms in the perturbation expansion,³⁻⁵ thus potentially making such effects more difficult to determine. Cooper and Hutson⁶ have investigated representative models for three-body dispersion, induction, and short-range forces for the Ar₃ system in an effort to determine the effects of these interactions on the molecular energy levels.

The experimental and theoretical techniques presently being used to address many-body forces have been successfully applied to several prototypical binary systems: i.e., ArHCl, ArHF, ArH₂O, and ArNH₃.⁷⁻¹⁰ Such binary van der Waals complexes have been the subject of intense experimental study by high resolution microwave,¹¹ far infrared,¹² and near infrared¹³ spectroscopy. In particular,

the measurement of the low-lying intermolecular vibrations of these complexes has proven to be the most important experimental data, since these motions sample an extensive region of the intermolecular potential energy surface. Therefore, these data, in combination with efficient computational techniques, have permitted the determination of accurate global intermolecular potential surfaces for several of these systems. Although the qualitative details of these surfaces have been firmly established, their quantitative accuracy is critically important for the purpose of the determination of many-body forces, as these effects will be manifested as small deviations from pairwise additivity. Rare-gas dimers clustered with the hydrogen halides are an obvious choice for the study of three-body effects since the rare-gas pair potentials have been well determined by a variety of experimental techniques, and the rare-gas-hydrogen halide systems have been the corresponding prototypes for *anisotropic* pair interactions. Of these systems, the ArHCl potential is one of the most thoroughly characterized. Recently, Hutson,⁷ fit all existing microwave, far infrared, and near infrared data for several ArHCl isotopes to a potential that was explicitly dependent on the HCl monomer vibration. The new potential [denoted H6(4,3,0)] certainly represents one of the most accurate existing anisotropic potential energy surfaces, although the most recent far infrared spectroscopic studies have shown that small, yet significant, inaccuracies may exist in the secondary minimum region of the potential.¹⁴

For the reasons discussed above, recent work concerning the effects of many-body forces in intermolecular forces has largely centered around the Ar₂HX systems,¹⁵⁻¹⁹ with the Ar₂HCl complex receiving the most extensive experimental and theoretical scrutiny. The eventual goal of this work is to measure all spectroscopically accessible states of Ar₂HCl and thus ultimately characterize the full intermolecular potential energy surface, thereby deducing from the form of three-body effects. Towards that end, we have pre-

viously reported the measurement of two intermolecular vibration-rotation bands using far infrared laser spectroscopy.¹⁶⁻¹⁷ These vibrations (and the one reported in the present work) are best understood by considering the HCl subunit as a nearly free rotor. In this case, the lowest-lying intermolecular bending states correlate to the $j=1$ internal rotational state of the HCl monomer. The intermolecular potential serves to split the threefold spatial degeneracy of the HCl $j=1$ rotational state, resulting in three unique bending states. Following the notation of Cooper and Hutson,²⁰ these states are identified as the Σ bend (by analogy to ArHCl) and the in-plane and out-of-plane bends (which correspond to the two components of the Π bend of ArHCl). In order to prevent any possible confusion, it should be noted that in previously reported work, we have referred to the Σ bend as the parallel bend. In the present work, we report a partial reassignment of the in-plane bend, an estimate of the effect of Coriolis mixing between the in-plane bend and the Σ bend, and the measurement and analysis of the third $j=1$ state, the out-of-plane bend.

EXPERIMENT

The far infrared vibration-rotation-tunneling spectra of Ar₂HCl were observed in a continuous supersonic planar jet expansion probed by a tunable far infrared laser spectrometer. The spectrometer has been described in detail previously^{21,22} so only a brief description here will follow. The tunable far infrared radiation is generated by mixing an optically pumped line-tunable far infrared gas laser with continuously tunable frequency modulated microwaves in a Schottky barrier diode to generate light at the sum and difference frequencies ($\nu = \nu_{\text{FIR}} \pm \nu_{\text{MW}}$). The tunable radiation is separated from the much stronger fixed frequency radiation with a Michelson polarizing interferometer and is then directed to multipass optics which encompass the supersonic expansion. After passing ~ 10 times through the expansion, the radiation is detected by a liquid helium cooled Putley-mode InSb detector and the signal is demodulated at $2f$ by a lock-in amplifier. Ar_m[HCl]_n clusters were produced by continuously expanding a 0.5% HCl in argon mixture at a stagnation pressure of 2 atm through a 10 cm by 25 μm slit nozzle planar jet into a vacuum chamber pumped by a 1200 l/s Roots pump. The following far infrared lasers provided the fixed frequency radiation: 1299.9954 GHz CH₃OD, and 1397.1186 GHz CH₂F₂. The unstabilized far infrared laser is typically characterized by a short-term frequency drift of < 100 kHz and a long-term drift of ca. 1 MHz. However, the 1397 GHz CH₂F₂ laser exhibited an unusually large long-term frequency drift (~ 10 MHz) and consequently all absorption features were measured in reference to the $J=1 \rightarrow 2$; $F=3/2 \rightarrow 1/2$ transition of H³⁵Cl (1251.480 94 GHz) (Ref. 23) to yield an absolute frequency accuracy of less than 400 kHz for these transitions (absolute frequencies above 1350 GHz). A representative spectrum is presented in Fig. 1.

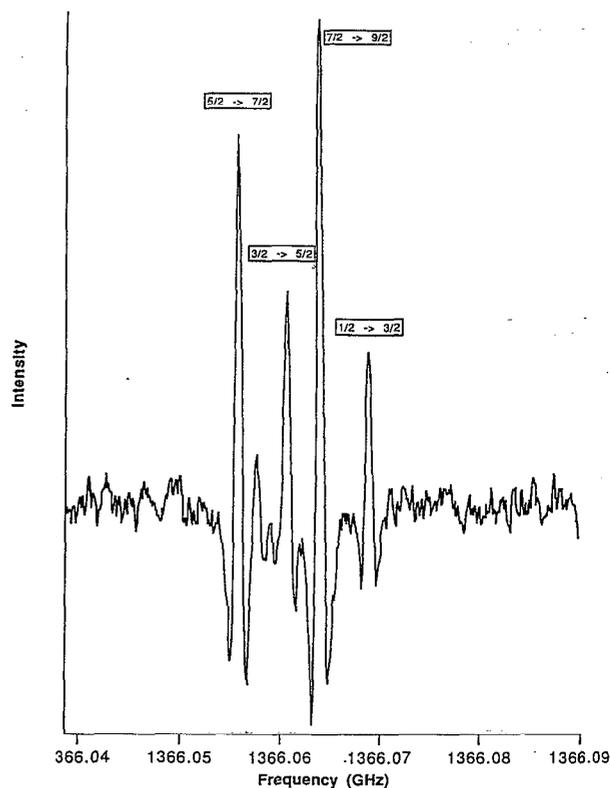


FIG. 1. Experimental trace of the $2_{20} \rightarrow 3_{30}$ transition of the out-of-plane bend of Ar₂H³⁵Cl. The individual nuclear hyperfine components are labeled by their F quantum numbers.

RESULTS AND ANALYSIS

Equilibrium geometry and nuclear spin statistical weights

The Fourier-transform microwave spectroscopy work of Klots *et al.* established the vibrationally averaged ground state geometry of Ar₂HCl as a planar T-shaped asymmetric top of C_{2v} symmetry.^{24,25} Due to the fact that rotation about the C_2 axis involves exchange of identical boson nuclei (⁴⁰Ar; $I=0$) the total wave function must be symmetric with respect to this motion. Because the C_2 axis corresponds to the a inertial axis in the ground state, non-zero nuclear spin statistical weights exist only for even K_p rotational levels.

Assignment techniques

Because of spectral congestion (typically > 400 absorptions/cm⁻¹), varying experimental sensitivity, and the possible existence of perturbations that may destroy ordinarily recognizable features of the spectrum, the task of assigning the observed transitions to their upper and lower state rotational quantum numbers is extremely difficult. We have chosen the common practice of using known ground state energy levels (combination differences) as an assignment technique, while specifically tailoring the details of the method to the characteristics of the experiment and the system under study. As noted in the experiment section, the short-term (several minutes) frequency drift of the unlocked far infrared laser is extremely

small (< 100 kHz) and the long-term (day-to-day) drift is substantially larger (usually ~1 MHz). Therefore, absorption features separated by less than 100 MHz are characterized by a very high relative frequency accuracy. The individual components of the nuclear quadrupole hyperfine structure associated with each rovibrational transition observed for Ar₂HCl therefore possess a very high internal frequency accuracy. In contrast, the rovibrational line centers are often separated by several thousand MHz and therefore possess a lower relative frequency accuracy. Rotational-hyperfine energy levels of the ground state of Ar₂HCl were calculated from the work of Klots *et al.*²⁴ and experimental far infrared combination differences were compared to calculated values to obtain an assignment for the far infrared spectrum. Due to the very high spectral density, many coincidental (and incorrect) assignments may be obtained from rotational combination differences alone. Although increased long-term frequency accuracy (as was obtained by referencing several absorptions to an internal standard for one of the bands) substantially reduces coincidental assignments, the inclusion of the very accurate hyperfine combination differences proved to be crucial in discriminating correct assignments from merely coincidental ones.

Reassignment of the in-plane bend

We previously reported an assignment and the corresponding molecular constants for a vibration (a *b*-type band centered at 37.2 cm⁻¹) we tentatively identified as the in-plane bend.¹⁷ Since that time, Cooper and Hutson²⁰ have carried out more rigorous dynamical calculations on the spectroscopic properties of Ar₂HCl, and these results suggested that some of the experimental conclusions reached for this state may be in error. The observed transitions for that band were subjected to the more rigorous combination difference method outlined above and it was indeed found that a few of the transitions had been misassigned. The properly assigned hyperfine-free line centers (Table I) were fit to a Watson *S*-reduced Hamiltonian²⁶ with the ground state constants held fixed at the values previously determined. In cases where particular distortion constants were not determinable from the data, these parameters were fixed to their ground state values. The nuclear quadrupole hyperfine coupling constants (χ_{xx} , χ_{yy} , and χ_{zz}) were determined in a separate least-squares fit, with the line centers determined from the rotational fit. The first-order matrix elements of the nuclear quadrupole Hamiltonian were calculated in the coupled basis set $|JKIF\rangle$ ($F=I+J$; $I=3/2$ for both ³⁵Cl and ³⁷Cl).²⁷ The upper state coupling constants were fit with the ground state coupling constants held fixed at the values determined by Klots *et al.*^{24,25}

The principal effect of the revised assignments on the previously reported molecular constants¹⁷ is that the fitted values determined from the off-diagonal matrix elements (oblate symmetric top basis) in both the rotational and nuclear quadrupole Hamiltonian matrices are changed. Therefore, ν_0 , B_x+B_y , B_z , and χ_{zz} are essentially unchanged from the previous analysis while B_x-B_y (and

TABLE I. Observed transitions and residuals (MHz) for in-plane bend.

Transition $J''_{K''_a K''_c} \leftarrow J''_{K''_b K''_c}$	Ar ₂ H ³⁵ Cl		Ar ₂ H ³⁷ Cl	
	Frequency	Res.	Frequency	Res.
1 ₁₀ ←2 ₂₁	1 109 016.5	-1.0		
1 ₁₀ ←1 ₀₁	1 115 952.8	0.6		
2 ₁₂ ←3 ₀₃	1 109 071.2	-0.8		
2 ₁₂ ←1 ₀₁	1 119 257.4	-1.9		
3 ₁₂ ←4 ₂₃	1 105 572.7	0.5		
3 ₁₂ ←3 ₀₃	1 119 168.2	-0.9		
3 ₁₂ ←3 ₂₁	1 112 513.3	0.8		
3 ₁₃ ←4 ₀₄	1 107 278.1	-0.1		
3 ₁₃ ←2 ₀₂	1 120 812.0	-1.1		
3 ₃₀ ←3 ₂₁	1 115 937.0	0.4		
3 ₃₀ ←2 ₂₁	1 125 845.6	-0.1	1 125 131.7	1.0
3 ₃₁ ←2 ₂₀	1 124 229.5	-2.4		
4 ₁₃ ←5 ₂₄	1 103 747.1	0.3		
4 ₁₃ ←4 ₀₄	1 120 741.3	-0.5		
4 ₁₃ ←4 ₂₂	1 110 521.2	1.2		
4 ₁₃ ←3 ₂₂	1 124 068.3	-0.7		
4 ₁₄ ←5 ₀₅	1 105 449.9	-0.6	1 105 196.4	0.3
4 ₁₄ ←4 ₂₃	1 108 763.7	0.3		
4 ₁₄ ←3 ₀₃	1 122 359.7	-0.5	1 121 786.7	0.7
4 ₃₁ ←4 ₂₂	1 117 363.6	2.9		
4 ₃₁ ←4 ₄₀	1 113 831.9	3.0		
4 ₃₂ ←4 ₂₃	1 119 035.4	-0.3		
4 ₃₂ ←3 ₂₁	1 125 975.2	-0.9		
5 ₁₄ ←5 ₂₃			1 108 340.6	0.5
5 ₁₄ ←4 ₂₃	1 125 592.0	-1.2	1 124 968.5	0.1
5 ₁₅ ←6 ₀₆	1 103 589.1	-0.5		
5 ₁₅ ←4 ₀₄	1 123 874.6	-0.8	1 123 274.0	-0.4
5 ₃₃ ←5 ₂₄	1 120 574.5	0.8	1 120 044.8	-0.8
5 ₃₃ ←5 ₄₂	1 110 284.2	0.5	1 109 867.2	0.2
5 ₃₃ ←4 ₂₂	1 127 346.9	0.0	1 126 796.1	0.7
5 ₅₀ ←6 ₆₁	1 094 298.3	0.6		
5 ₅₀ ←5 ₄₁	1 115 892.2	1.5		
5 ₅₀ ←4 ₄₁	1 132 086.6	0.8	1 131 113.4	1.0
5 ₅₁ ←5 ₄₂	1 117 132.2	-0.4		
5 ₅₁ ←4 ₄₀	1 130 662.6	-1.4	1 130 268.0	-0.8
6 ₁₅ ←5 ₂₄	1 127 076.5	-0.6	1 126 429.0	-0.8
6 ₁₆ ←5 ₀₅	1 125 357.3	-0.5	1 124 730.2	-1.1
6 ₃₃ ←7 ₄₄	1 096 607.4	0.1		
6 ₃₃ ←6 ₂₄	1 120 377.6	0.1		
6 ₃₃ ←6 ₄₂	1 110 313.1	1.4		
6 ₃₃ ←5 ₄₂			1 129 663.9	0.0
6 ₃₄ ←6 ₂₅	1 122 080.6	0.8		
6 ₃₄ ←6 ₄₃	1 108 419.7	0.6	1 108 152.8	1.1
6 ₃₄ ←5 ₂₃	1 128 800.5	0.3		
6 ₅₁ ←6 ₄₂	1 117 145.1	3.1	1 116 560.4	1.2
6 ₅₁ ←6 ₆₀			1 111 670.6	1.2
6 ₅₂ ←6 ₄₃	1 118 683.6	-1.4		
7 ₁₆ ←8 ₂₇	1 098 074.3	-0.8	1 097 979.8	-0.7
7 ₁₆ ←7 ₀₇	1 125 259.3	-0.9		
7 ₁₆ ←6 ₂₅	1 128 528.9	-0.3	1 127 858.2	-0.1
7 ₁₇ ←6 ₀₆	1 126 807.9	-0.5	1 126 155.8	-1.5
7 ₃₄ ←8 ₄₅	1 094 689.0	0.0	1 094 695.4	-0.2
7 ₃₄ ←7 ₂₅	1 121 852.8	1.0		
7 ₃₄ ←7 ₄₃	1 108 239.1	0.8	1 108 159.6	-0.1
7 ₃₄ ←6 ₄₃	1 131 971.6	0.2	1 131 259.1	-0.3
7 ₃₅ ←8 ₂₆	1 096 380.1	0.0		
7 ₃₅ ←6 ₂₄	1 130 248.8	-1.1	1 129 566.8	0.0
7 ₅₂ ←6 ₆₁	1 134 597.4	-0.6		
7 ₅₃ ←7 ₄₄	1 120 155.5	0.0	1 119 675.2	0.1
7 ₅₃ ←6 ₄₂	1 133 860.3	0.4		
7 ₇₁ ←6 ₆₀	1 136 817.7	1.3	1 136 339.2	2.1
8 ₁₇ ←9 ₂₈	1 096 123.8	-0.2	1 096 070.2	-0.1
8 ₁₇ ←8 ₀₈	1 126 702.3	-1.5		
8 ₁₇ ←7 ₂₆	1 129 950.1	-1.1	1 129 256.4	-0.8
8 ₁₈ ←9 ₀₉	1 097 816.9	-0.2	1 097 717.3	-0.9
8 ₁₈ ←7 ₀₇	1 128 228.0	-0.2	1 127 553.0	-0.4
8 ₃₅ ←9 ₄₆	1 092 743.0	0.3	1 092 790.0	-1.3
8 ₃₅ ←8 ₂₆	1 123 296.5	0.2		
8 ₃₅ ←7 ₄₄	1 133 395.6	-0.3	1 132 681.3	-0.1

TABLE I. (Continued.)

Transition $J''_{K_a K_c} \leftarrow J''_{K_a K_c}$	Ar ₂ H ³⁵ Cl		Ar ₂ H ³⁷ Cl	
	Frequency	Res.	Frequency	Res.
8 ₃₆ ←9 ₂₇	1 094 431.4	-0.6		
8 ₃₆ ←8 ₂₇	1 124 997.9	-0.7	1 124 403.9	1.4
8 ₃₆ ←7 ₂₅	1 131 672.7	0.2	1 130 963.6	-0.8
8 ₅₃ ←8 ₄₄	1 119 913.3	-0.1		
8 ₅₄ ←9 ₄₅	1 091 059.2	-0.4		
8 ₅₄ ←8 ₄₅	1 121 599.9	0.8	1 121 093.1	-1.4
8 ₅₄ ←7 ₄₃	1 135 147.8	-0.6		
8 ₇₁ ←8 ₆₂	1 116 980.0	-3.0		
9 ₁₈ ←10 ₂₉	1 094 144.5	-0.6	1 094 132.3	-0.6
9 ₁₈ ←8 ₂₇	1 131 344.5	0.0	1 130 628.4	0.3
9 ₁₉ ←10 ₁₀	1 095 834.8	0.8	1 095 775.8	-0.2
9 ₁₉ ←8 ₀₈	1 129 618.7	0.0	1 128 920.0	-1.0
9 ₃₆ ←10 ₄₇	1 090 769.3	-0.8		
9 ₃₆ ←9 ₂₇	1 124 711.4	-0.9		
9 ₃₆ ←8 ₄₅	1 134 788.9	-1.1		
9 ₃₇ ←10 ₂₈	1 092 456.1	-0.5	1 092 492.6	-0.8
9 ₃₇ ←9 ₂₈	1 126 413.0	-1.1		
9 ₃₇ ←8 ₂₆	1 133 067.7	0.5	1 132 336.9	0.5
9 ₅₄ ←10 ₆₅	1 087 415.4	0.6		
9 ₅₄ ←9 ₄₅	1 121 325.6	0.8		
9 ₅₄ ←8 ₆₃	1 138 243.6	-0.3		
9 ₅₅ ←10 ₄₆	1 089 087.4	-0.6		
9 ₅₅ ←9 ₄₆	1 123 015.1	0.3		
9 ₅₅ ←8 ₄₄	1 136 520.4	0.0		
9 ₇₃ ←9 ₆₄			1 119 257.4	1.1
9 ₉₁ ←10 ₈₂			1 086 492.6	-0.7
10 ₁₉ ←11 ₂₁₀	1 092 139.5	-0.5	1 092 169.5	-0.3
10 ₁₉ ←9 ₂₈	1 132 711.3	0.7		
10 ₁₁₀ ←11 ₀₁₁	1 093 825.1	0.9	1 093 808.4	0.6
10 ₁₁₀ ←9 ₀₉	1 130 982.1	0.7	1 130 261.2	-0.5
10 ₃₇ ←11 ₄₈	1 088 771.8	-1.0		
10 ₃₇ ←10 ₂₈	1 126 100.3	-1.3		
10 ₃₇ ←9 ₄₆	1 136 157.8	-0.8	1 135 396.4	-2.5
10 ₃₈ ←11 ₂₉	1 090 455.3	-0.5	1 090 534.1	-0.8
10 ₃₈ ←9 ₂₇	1 134 434.8	-0.6	1 133 682.1	-0.8
10 ₅₅ ←11 ₆₆	1 085 419.7	0.2		
10 ₅₅ ←10 ₄₆	1 122 713.2	0.3		
10 ₅₅ ←9 ₄₆	1 139 619.6	-0.5		
10 ₅₆ ←9 ₄₅	1 137 884.0	-0.6		
10 ₇₄ ←10 ₆₅	1 121 032.4	0.0		
10 ₉₂ ←10 ₈₃	1 117 611.9	0.4		
11 ₁₁₀ ←12 ₂₁₁			1 090 182.9	0.0
11 ₁₁₁ ←12 ₀₁₂	1 091 791.9	2.6	1 091 817.3	2.1
11 ₁₁₁ ←10 ₀₁₀	1 132 320.6	2.5	1 131 578.2	1.2
11 ₃₈ ←12 ₄₉	1 086 752.5	-0.2		
11 ₃₈ ←10 ₄₇	1 137 503.3	-0.2		
11 ₃₉ ←12 ₂₁₀	1 088 431.3	-0.2	1 088 552.3	-0.8
11 ₃₉ ←10 ₂₈	1 135 779.0	0.0	1 135 004.4	-0.9
11 ₅₆ ←11 ₄₇	1 124 077.3	-0.2		
11 ₅₆ ←10 ₆₅	1 140 959.4	0.3		
12 ₁₁₁ ←11 ₂₁₀			1 134 589.3	0.8
12 ₁₁₂ ←13 ₀₁₃	1 089 730.9	-0.5	1 089 800.8	0.5
12 ₁₁₂ ←11 ₀₁₁	1 133 631.6	1.0	1 132 871.2	2.4
12 ₃₁₀ ←13 ₂₁₁	1 086 387.6	1.8		
12 ₃₁₀ ←12 ₄₉			1 096 380.1	-0.2
12 ₃₁₀ ←11 ₂₉	1 137 101.4	1.4		
12 ₅₇ ←12 ₄₈	1 125 420.8	0.4		
12 ₅₇ ←11 ₆₆	1 142 279.9	0.8		
13 ₁₁₂ ←14 ₂₁₃			1 086 147.4	1.6
13 ₁₁₂ ←12 ₂₁₁			1 135 865.1	1.0
13 ₁₁₃ ←14 ₀₁₄	1 087 652.1	-0.5		
13 ₁₁₃ ←12 ₀₁₂	1 134 920.4	-0.7	1 134 139.2	0.1
13 ₃₁₀ ←13 ₂₁₁			1 129 474.6	-0.1
13 ₃₁₀ ←12 ₄₉			1 139 304.8	-0.1
13 ₃₁₁ ←12 ₂₁₀			1 137 585.8	1.0
14 ₁₁₄ ←15 ₀₁₅	1 085 554.4	-0.9		
14 ₁₁₄ ←13 ₀₁₃	1 136 190.7	-0.9	1 135 389.5	-0.7
15 ₁₁₅ ←14 ₀₁₄	1 137 443.8	-1.5	1 136 621.9	-2.4
16 ₁₁₆ ←15 ₀₁₅	1 138 686.6	2.3		

TABLE II. Molecular constants (MHz) for in-plane bend (1σ uncertainties).

	Ar ₂ H ³⁵ Cl	Ar ₂ H ³⁷ Cl
ν_0	1 115 098.6(3)	1 114 654.1(5)
B_x	1 683.61(2)	1 683.98(3)
B_y	1 682.42(2)	1 621.21(2)
B_z	826.702(9)	811.215(9)
D_J	0.014 07(13)	0.014 74(19)
D_{JK}	-0.041 8(3)	-0.040 7(4)
D_K	0.022 47(19)	0.020 7(2)
d_1	0.002 479(fixed)	0.002 927(fixed)
d_2	-0.0034(3)	-0.000 456(fixed)
rms error	1.0	1.0

thus the individual values of B_x and B_y) and $\chi_{xx} - \chi_{yy}$ have now been correctly determined. Due to the possibility of rotational axis switching, the molecular constants are expressed in a molecule-fixed axis system as explained in Ref. 17, rather than the conventional principal axis system. The rotational parameters are reported in Table II and the hyperfine coupling constants are reported in Table V for both

Ar₃H ³⁵Cl and Ar₂H ³⁷Cl. In order to compare the experimental coupling constants to theoretical values, the following equations provide the relation between these constants and the relevant angular expectation values:

$$\chi_{xx} = \chi_{\text{HCl}} \langle P_2(\cos \theta) \rangle, \quad (1)$$

$$\chi_{yy} - \chi_{zz} = \frac{2}{3} \chi_{\text{HCl}} \langle \Delta(\theta, \phi) \rangle. \quad (2)$$

Here χ_{HCl} is the nuclear quadrupole coupling constant of the uncomplexed HCl monomer and $\langle \Delta(\theta, \phi) \rangle = \sin^2 \theta \cos 2\phi$. The deviation of $\langle P_2(\cos \theta) \rangle$ from unity is a measure of the bending amplitude of the HCl monomer, whereas the deviation of $\langle \Delta(\theta, \phi) \rangle$ from zero characterizes the anisotropy of the torsional motion (positive values indicating in-plane localization and negative values indicating out-of-plane localization). The positive sign of the corrected $\langle \Delta(\theta, \phi) \rangle$ value (Table V) indicates that this state is indeed the in-plane bend.

The out-of-plane bend

The out-of-plane bend of Ar₂HCl is characterized by very dense Q -branch structure (indicative of a c -type transition) and was observed around 45.2 cm⁻¹. Due to the values of the upper state nuclear quadrupole coupling constants, it was possible to resolve all four of the strong $\Delta F = \Delta J$ hyperfine components for a large number of the rovibrational transitions. These transitions were assigned according to the method outlined above and are recorded in Table III. Once again hyperfine-free line centers were fitted to a Watson S -reduced Hamiltonian and the nuclear quadrupole structure was separately fitted as previously discussed for the in-plane bend. The results of the rotational fit are contained in Table IV for both the Ar₂H ³⁵Cl and Ar₂H ³⁷Cl isotopes. The results of the nuclear quadrupole hyperfine fit are compiled in Table V.

TABLE III. Observed transitions and residuals (MHz) for out-of-plane bend.

Transition $J''_{K_p K_o} \leftarrow J''_{K_p K_o}$	Ar ₂ H ³⁵ Cl		Ar ₂ H ³⁷ Cl	
	Frequency	Res.	Frequency	Res.
2 ₁₁ ←3 ₂₁	1 345 392.1	-30.9		
2 ₁₁ ←2 ₂₁	1 355 300.5	-31.6		
2 ₁₁ ←1 ₀₁	1 362 233.4	-33.5		
3 ₁₂ ←4 ₂₂	1 342 111.4	-17.8	1 342 367.3	-24.8
3 ₁₂ ←3 ₂₂	1 355 661.6	-16.7		
3 ₁₂ ←2 ₀₂	1 365 869.3	-16.5	1 365 568.6	-23.8
3 ₃₀ ←4 ₄₀	1 342 205.2	-25.9	1 342 232.4	-14.4
3 ₃₀ ←2 ₂₀	1 366 062.1	-24.8	1 365 798.8	-15.8
3 ₃₁ ←4 ₄₁	1 341 942.3	-18.6		
3 ₃₁ ←2 ₂₁	1 365 987.5	-17.0		
4 ₁₃ ←5 ₂₃			1 339 188.2	3.7
4 ₁₃ ←3 ₀₃			1 369 151.1	3.3
4 ₁₄ ←5 ₂₄	1 338 562.3	0.0		
4 ₁₄ ←4 ₀₄	1 355 555.5	-1.8		
4 ₃₁ ←5 ₄₁	1 339 651.8	-32.7	1 339 887.9	-6.9
4 ₃₁ ←3 ₂₁	1 369 982.0	-32.1	1 369 473.0	-7.0
4 ₃₂ ←5 ₄₂	1 339 137.0	-26.3	1 339 303.2	4.7
4 ₃₂ ←4 ₂₂	1 356 200.3	-26.2		
4 ₃₂ ←3 ₂₂	1 369 749.3	-26.3	1 369 397.2	4.3
5 ₁₄ ←6 ₂₄	1 335 797.9	-1.5	1 336 084.6	12.0
5 ₁₄ ←5 ₂₄	1 356 180.9	-3.2		
5 ₁₄ ←4 ₀₄	1 373 175.9	-3.2	1 372 732.2	11.8
5 ₁₅ ←6 ₂₅	1 335 349.8	30.5		
5 ₁₅ ←5 ₀₅	1 355 742.7	30.8		
5 ₃₂ ←6 ₄₂	1 336.604.3	6.9		
5 ₃₂ ←4 ₂₂	1 373 828.6	7.5		
5 ₃₃ ←6 ₄₃	1 336 163.3	-8.7	1 336 443.8	23.6
5 ₃₃ ←5 ₂₃	1 356 543.9	-9.2	1 356 447.8	24.6
5 ₃₃ ←4 ₂₃	1 373 528.9	-9.2	1 373 076.0	24.0
5 ₅₀ ←6 ₆₀	1 336 343.8	-14.6		
5 ₅₀ ←4 ₄₀	1 373 922.7	-13.5		
5 ₅₁ ←6 ₆₁	1 335 972.8	5.1		
5 ₅₁ ←4 ₄₁	1 373 759.6	3.8		
6 ₁₅ ←7 ₂₅	1 332 693.8	11.0		
6 ₁₅ ←6 ₂₅	1 356 471.7	8.7		
6 ₁₅ ←5 ₀₅	1 376 864.6	9.0		
6 ₁₆ ←7 ₂₆	1 332 195.2	97.8		
6 ₁₆ ←6 ₀₆	1 355 984.3	97.5		
6 ₃₃ ←7 ₄₃	1 333 686.8	129.5		
6 ₃₃ ←6 ₄₃	1 357 421.0	130.6		
6 ₃₃ ←5 ₂₃	1 377 801.8	130.3		
6 ₃₄ ←7 ₄₄	1 333 038.6	-120.6		
6 ₃₄ ←6 ₂₄	1 356 808.7	-120.7		
6 ₃₄ ←5 ₂₄	1 377 193.2	-120.9		
6 ₅₁ ←7 ₆₁	1 334 415.4	-31.0	1 334 536.4	10.6
6 ₅₁ ←5 ₄₁	1 378 254.3	-30.9	1 377 482.3	9.8
6 ₅₂ ←7 ₆₂	1 333 638.5	-29.0		
6 ₅₂ ←6 ₄₂	1 357 696.5	-30.4		
6 ₅₂ ←5 ₄₂	1 377 857.1	-30.3		
7 ₁₆ ←8 ₂₆	1 329 618.4	30.2		
7 ₁₆ ←7 ₂₆	1 356 791.0	28.6	1 356 648.5	11.8
7 ₁₆ ←6 ₀₆	1 380 580.1	28.4	1 379 980.8	11.4
7 ₁₇ ←8 ₂₇	1 329 144.4	247.5		
7 ₁₇ ←7 ₀₇	1 356 331.0	248.9		
7 ₃₄ ←8 ₄₄	1 330 610.7	-30.2		
7 ₃₄ ←6 ₂₄	1 381 528.6	-30.0		
7 ₃₅ ←8 ₄₅	1 330 155.4	-9.9	1 330 548.1	-1.8

TABLE III. (Continued.)

Transition $J''_{K_p K_o} \leftarrow J''_{K_p K_o}$	Ar ₂ H ³⁵ Cl		Ar ₂ H ³⁷ Cl	
	Frequency	Res.	Frequency	Res.
7 ₃₅ ←7 ₂₅	1 357 317.2	-11.5	1 357 173.4	-0.9
7 ₃₅ ←6 ₂₅	1 381 097.0	-11.0	1 380 488.0	-2.1
7 ₅₂ ←8 ₆₂	1 331 747.0	58.3		
7 ₅₂ ←7 ₆₂	1 358 290.4	58.8		
7 ₅₂ ←6 ₄₂	1 382 349.5	58.6		
7 ₅₃ ←8 ₆₃	1 331 000.4	-3.7	1 331 352.8	9.1
7 ₅₃ ←7 ₄₃	1 358 170.1	-3.7	1 358 160.6	8.9
7 ₅₃ ←6 ₄₃	1 381 903.5	-3.5	1 381 260.5	9.1
7 ₇₀ ←8 ₈₀	1 330 762.6	24.7		
7 ₇₀ ←6 ₆₀	1 382 127.7	25.1		
8 ₁₇ ←9 ₂₇	1 326 560.9	45.1		
8 ₁₇ ←8 ₂₇	1 357 126.2	43.8		
8 ₁₇ ←7 ₀₇	1 384 311.2	43.7		
8 ₃₅ ←9 ₄₅	1 327 576.1	-186.7	1 328 240.2	-17.0
8 ₃₅ ←8 ₄₅	1 358 115.8	-186.5	1 358 160.6	-17.0
8 ₃₅ ←7 ₂₅	1 385 278.6	-186.6	1 384 785.7	-16.3
8 ₃₆ ←9 ₄₆	1 327 188.1	-5.8	1 327 638.4	-40.2
8 ₃₆ ←8 ₂₆	1 357 740.1	-7.3	1 357 592.0	-39.7
8 ₃₆ ←7 ₂₆	1 384 914.4	-7.4		
8 ₅₃ ←9 ₆₃	1 328 922.0	216.7		
8 ₅₃ ←7 ₄₃	1 386 492.5	217.9		
8 ₅₄ ←9 ₆₄	1 328 323.2	89.2	1 328 722.8	-25.3
8 ₅₄ ←8 ₄₄	1 358 850.2	91.0	1 358 642.0	-25.7
8 ₅₄ ←7 ₄₄	1 385 996.6	89.9	1 385 210.6	-24.9
8 ₇₁ ←9 ₈₁	1 329 603.6	-4.6		
8 ₇₁ ←7 ₆₁	1 386 995.1	-4.6		
8 ₇₂ ←9 ₈₂	1 328 537.5	-18.3		
8 ₇₂ ←7 ₆₂	1 386 366.5	-17.0		
9 ₁₈ ←9 ₂₈	1 357 475.5	52.4		
9 ₁₈ ←8 ₀₈	1 388 055.7	52.8		
9 ₁₉ ←10 ₂₉	1 322 378.3	-181.5		
9 ₁₉ ←9 ₀₉	1 356 352.1	-181.2		
9 ₃₆ ←10 ₄₆	1 324 877.7	-31.5		
9 ₃₆ ←9 ₄₆	1 358 803.7	-32.3		
9 ₃₆ ←8 ₂₆	1 389 357.0	-32.6		
9 ₃₇ ←10 ₄₇	1 324 244.9	-0.2		
9 ₃₇ ←9 ₂₇	1 358 184.8	-2.0		
9 ₃₇ ←8 ₂₇	1 388 751.9	-2.5		
9 ₅₄ ←10 ₆₄	1 325 888.8	-62.6		
9 ₅₄ ←9 ₆₄			1 359 791.0	-15.5
9 ₅₄ ←8 ₄₄	1 390 292.4	-62.3	1 389 710.3	-15.8
9 ₅₅ ←10 ₆₅	1 325 401.1	-68.5	1 326 179.0	43.8
9 ₅₅ ←9 ₄₅	1 359 310.4	-69.3	1 359 395.4	43.7
9 ₅₅ ←8 ₄₅			1 389 315.8	43.7
10 ₁₉ ←10 ₂₉	1 357 836.5	52.0		
10 ₁₉ ←9 ₀₉	1 391 810.1	52.2		
10 ₁₁₀ ←11 ₂₁₀	1 319 260.6	-162.1		
10 ₁₁₀ ←10 ₀₁₀	1 356 627.1	-161.9		
10 ₃₇ ←11 ₄₇	1 322 048.2	-30.1		
10 ₃₇ ←10 ₄₇	1 359 359.8	-29.8		
10 ₃₇ ←9 ₂₇	1 393 300.8	-31.0		
11 ₁₁₀ ←12 ₂₁₀	1 317 478.8	46.6		
11 ₁₁₀ ←11 ₂₁₀	1 358 210.2	43.6		
12 ₁₁₁ ←12 ₂₁₁	1 358 600.7	31.1		
13 ₁₁₂ ←13 ₂₁₂	1 359 011.3	18.1		
14 ₁₁₃ ←14 ₂₁₃	1 359 445.2	7.6		
15 ₁₁₄ ←15 ₂₁₄	1 359 903.8	1.1		

TABLE IV. Molecular constants (MHz) for out-of-plane bend of Ar₂HCl.

	Ar ₂ H ³⁵ Cl	Ar ₂ H ³⁷ Cl
ν_0	1 355 140.(31.0)	1 355 130.(16.0)
B_x	1 774.(2.0)	1 767.3(1.9)
B_y	1 752.(2.0)	1 679.9(1.3)
B_z	854.6(6)	835.1(7)
D_J	0.06(2)	-0.031 8(7)
D_{JK}	-0.12(5)	-0.039 33(fixed)
D_K	-0.07(3)	0.017 83(fixed)
d_1	0.002 479(fixed)	0.002 927(fixed)
d_2	-0.000 406 6(fixed)	-0.000 456(fixed)
rms error	77.3	21.0

DISCUSSION

Coriolis coupling: General considerations

It may be seen from Table IV that the rms errors from the rotational fits for the out-of-plane bend of Ar₂HCl are substantially larger than would be expected from the experimental uncertainties. This effect is the signature of a strong heterogeneous perturbation, which is most likely due to a Coriolis interaction. In addition, the in-plane and Σ bends are also *expected* to interact via a Coriolis mechanism, although the perturbation is not apparent simply from the residuals resulting from the zero-order rotational fit. We therefore turn to a general discussion of the possible and observed effects of Coriolis coupling in the Ar₂HCl system.

The standard vibration-rotation Hamiltonian used for the fitting of spectra usually neglects the Coriolis cross terms in the full Hamiltonian because such effects are often too small to be determined from experimental data. Although it is possible to treat these effects perturbatively, it is often desirable, especially in the case of fitting to high resolution data and/or strong mixing between states, to explicitly form the full Hamiltonian matrix and diagonalize to obtain energies. The exact form of the Coriolis operator depends on the form of the Hamiltonian used—which in turn is often determined by the most appropriate basis set—but it can be expressed generally as βJ_i , where $i=a, b, c$ (corresponding to the principal axes) and β is a constant. The molecule-fixed axes for Ar₂HCl (Ref. 17) correspond to the principal axes in the following manner for the states of relevance: $x \leftrightarrow a$, $y \leftrightarrow b$, and $z \leftrightarrow c$. In the case

TABLE V. Nuclear quadrupole coupling constants and angular expectation values.

	Out-of-plane bend		In-plane-bend	
	Ar ₂ H ³⁵ Cl	Ar ₂ H ³⁷ Cl	Ar ₂ H ³⁵ Cl	Ar ₂ H ³⁷ Cl
χ_{xx} (MHz)	1.72(15)	0.9(5)	0.0(2)	0.0(2)
χ_{yy} (MHz)	14.08(15)	11.5(5)	-17.2(2)	-13.2(2)
χ_{zz} (MHz)	-15.81(6)	-12.1(2)	17.29(7)	13.3(2)
$\langle P_2(\cos \theta) \rangle$	-0.025(2)	-0.017(9)	0.000(3)	0.000(4)
$\langle \Delta(\theta, \phi) \rangle$	-0.295(2)	-0.309(7)	0.340(3)	0.331(5)

of Ar₂HCl, Cooper and Hutson²⁰ have used a diatom-diatom Hamiltonian, which results in two Coriolis operators: $\mathbf{J} \cdot \mathbf{j}_{\text{Ar-Ar}}$ and $\mathbf{J} \cdot \mathbf{j}_{\text{HCl}}$. Because \mathbf{j}_{HCl} and especially $\mathbf{j}_{\text{Ar-Ar}}$ are only approximate quantum numbers, essentially all states can couple through these operators. In order to determine the appropriate matrix element for any two interaction Ar₂HCl vibrational states, the transformation properties of J_i in the molecular symmetry group $C_{2v}(M)$ must be considered. Because it can be shown that the J_i transform the same as the rotations,²⁸ reference to the $C_{2v}(M)$ character table reveals J_a , J_b , and J_c transform as A_2 , B_1 , and B_2 , respectively. Therefore, in order to ensure a totally symmetric direct product ($\Gamma_1 \times \Gamma_{\text{Coriolis}} \times \Gamma_2 = A_1$), the direct product of the two interacting states ($\Gamma_1 \times \Gamma_2 = \Gamma_{\text{Coriolis}}$) indicates the nonvanishing βJ_i .²⁸ The symmetries of the 10-lowest-lying vibrational states of Ar₂HCl, the nonvanishing Coriolis interactions, and the associated matrix elements (calculated in the oblate symmetric top basis) are presented in Table VI.

Coriolis coupling: The in-plane and Σ bends

The in-plane and Σ bends¹⁶ are coupled by a c -type Coriolis interaction, although the coupling is apparently relatively weak since both bands can be fit with good residuals to the zero-order rotational Hamiltonian parameters. An explicit deperturbation was attempted, using the appropriate form of the matrix element from Table VI, but the multiplying coefficient β could not be determined from the data. Nevertheless, even in the limit of weak coupling, the rotational constants can be substantially affected by such an interaction by as much as a few percent. Because the calculations of Cooper and Hutson yield *structural* rotational constants,²⁰ it is desirable to recover the structural contributions to the experimental rotational constants (which also include any dynamical effects) in order to make the comparison between theory and experiment.

The $\mathbf{J} \cdot \mathbf{j}_{\text{HCl}}$ contribution to the Coriolis coupling constant β can be estimated in the limit of free internal rotation of the HCl monomer (characterized by the angular momentum quantum number \mathbf{j}_{HCl}). At this point, it is not possible to reasonably estimate the magnitude of the $\mathbf{J} \cdot \mathbf{j}_{\text{Ar-Ar}}$ coupling, therefore, it is arbitrarily set to zero (although there is no real justification for this choice). Estimating β from the $\mathbf{J} \cdot \mathbf{j}_{\text{HCl}}$ interaction alone yields $\beta = B_c [2j_{\text{HCl}}(j_{\text{HCl}} + 1)]^{1/2}$. For the particular case of coupling under consideration here, B_c was chosen to be the approximate *structural* rotational constant along the c axis (B_z). Since the Ar₂HCl bending states of interest correlate to the $j=1$ rotational state of the HCl monomer, β is simple two times the rotational constant. In direct fits to experimental data for the ArHCl system, the coupling constant between the Σ and Π bends (to which the in- and out-of-plane bends of Ar₂HCl correlate) has been determined to be 2833 MHz or 1.6 times the rotational constant.²⁹ The deviation of β from $2B$ results from the breakdown of \mathbf{j}_{HCl} as a rigorously good quantum number, which is a consequence of the anisotropic potential. In an attempt to remove the effects of Coriolis coupling from the experimental rotational constants, we have refit the data with

TABLE VI. Symmetries of relevant vibrational states and Coriolis coupling matrix elements.

State ^a	Symmetries			Coriolis types and matrix elements	
	Γ	$\Gamma_1 \times \Gamma_2$			Matrix element ^b
ground state	A_1	$A_2(a \text{ type})$			$\beta[J(J+1) - K(K \pm 1)]^{1/2} \Delta K', K \pm 1$
wagging stretch	A_1	$B_1(b \text{ type})$			$\mp \beta[J(J+1) - K(K \pm 1)]^{1/2} \delta K', K \pm 1$
χ bend	B_2	$B_2(c \text{ type})$			$\beta K \delta_{K', K}$
breathing stretch	A_1				
in-plane bend	B_2				
parallel bend	A_1				
out-of-plane bend	B_1				
wag. stretch ($\nu=2$)	A_1				
χ bend + wag. stretch	B_2				
χ bend ($\nu=2$)	A_1				

^aStates listed in estimated ascending energy order.

^bMatrix elements calculated in oblate symmetric top basis.

assumed values for β [and using a structural value of $B_z(s) = 850$ MHz]. The results for the in-plane bend in Table II and the parameters reported for the Σ bend in Ref. 16 then correspond to an assumed value of $\beta=0$. Fits for assumed values for β of $2B_z$ (free rotor value), $1.6B_z$ (ArHCl value), and $1.3B_z$ (an educated guess for the more anisotropic Ar₂HCl) were performed and the results are contained in Table VII. Because the B_x and B_y rotational constants did not vary with different assumed values for β , only the values for B_z are reported. Although the structural rotational constants calculated by Cooper and Hutson are not in absolute quantitative agreement with experiment (Table VIII),²⁰ it is interesting to note that the calculated difference between the in-plane and Σ bend B_z constants (21 MHz) is in much better agreement with the experimental difference for an assumed value of $\beta=1.3B_z$ (22 MHz) than for any of the other assumed values of β . In addition, in order to appreciate the small magnitude of this interaction, the sum-of-squares wave-function amplitudes recovered from the matrix diagonalization for three rotational levels of the in-plane bend are also reported in Table VII. The small degree of mixing in the $J=5$ rotational level is particularly significant since the nuclear hyperfine quadrupole coupling constants for the in-plane and Σ bends were fitted from similar low- J rovibrational transitions. Therefore, the fact that the hyperfine structure could be accurately fitted without explicitly treating the Coriolis interaction is consistent with the notion

TABLE VII. Results of in-plane and parallel bend Coriolis analysis.

	$\beta=2B_z(s)$	$\beta=1.6B_z(s)$	$\beta=1.3B_z \text{ s}(s)$	$\beta=0$
in-plane bend B_z (MHz)	867.44	852.72	843.85	826.70
parallel bend B_z (MHz)	842.24	856.96	865.83	883.04
In-plane bend contribution to the square modulus of the wave function for a number of individual rotational states				
$ \psi_{\text{in-plane}}(5_{15}) ^2$	0.98	0.99	0.99	1.00
$ \psi_{\text{in-plane}}(10_{110}) ^2$	0.95	0.97	0.98	1.00
$ \psi_{\text{in-plane}}(15_{115}) ^2$	0.91	0.94	0.96	1.00

that the perturbation is quite weak. Nevertheless, we again note that even this weak perturbation causes changes of $\sim 2\%$ in the effective rotational constants determined from a fit of the data to a pure rotational Hamiltonian ($\beta=0$). For the purposes of comparing experimental and theoretical rotational constants in an effort to determine possible three-body effects in Ar₂-HCl, neglecting Coriolis effects to the rotational constants that result in deviations as much as 2% from the corresponding "structural" values is an unacceptable approximation.

Coriolis coupling: The out-of-plane bend

The out-of-plane bend of Ar₂HCl appears to be much more strongly perturbed, as is evidenced by the large residuals resulting from the zero-order rotational fit. In fact, the rms error is more than two orders of magnitude larger than the experimental uncertainties. In addition, although the uncertainties in the rotational constants reflect the poor fit, it should be noted that the results for the Ar₂H³⁷Cl isotope cannot be obtained by simply mass scaling the Ar₂H³⁵Cl results, indicating that the fitted constants may be less reliable than the stated uncertainties reveal.

Unfortunately, the perturbing state is almost definitely one that carries little transition intensity of its own (a "dark" state). The calculations of Cooper and Hutson indicate that the first overtone of the "wagging stretch" (see Cooper and Hutson²⁰ for an explanation of the heavy-atom vibrational modes) is the most likely candidate for the identity of the dark state.³⁰ In fact, all possible perturbing states are heavy-atom vibrations whose motions do not result in an appreciable change in the dipole moment of the complex and are therefore "dark." Although there are many unassigned lines in the spectral region around the out-of-plane bend, it was not possible to definitively assign any of these lines to a possible perturbing state, and therefore it is not currently possible to perform a rigorous deperturbation of the spectra. In addition, it is difficult to provide an estimate for β , since the coupling of the end-over-end rotation to these motions is not easily represented in the otherwise-convenient free-rotor basis. However, it is worth noting that the β parameter for the Π bend-stretch

TABLE VIII. Comparison of experimental and theoretical results for Ar₂H ³⁵Cl.

	Observed (1σ)	Calc. 1 ^a	Calc. 2 ^b	Calc. 3 ^c
Ground state ^d				
<i>B_x</i> (MHz)	1733.8560(4)	...	1757.19	1756.99
<i>B_y</i> (MHz)	1667.921 40(4)	1702.4	1671.10	1668.24
<i>B_z</i> (MHz)	844.444 87(16)	857.6	849.53	848.73
$\langle P_2(\cos \theta) \rangle$	0.4165(4)	0.4540	0.4472	0.4429
$\langle \Delta(\theta, \phi) \rangle$	0.0313(2)	0.02179	0.0222	0.0255
In-plane bend ^e				
$\nu_0(\text{cm}^{-1})$	37.195 426(10)	40.315	39.587	39.190
<i>B_x</i> (MHz)	1683.61(2)	...	1744.23	1744.98
<i>B_y</i> (MHz)	1682.42(2)	1730.8	1694.27	1686.04
<i>B_z</i> (MHz)	826.702(9)	864.8	851.25	849.22
$\langle P_2(\cos \theta) \rangle$	0.000(3)	-0.0330	-0.0191	-0.0031
$\langle \Delta(\theta, \phi) \rangle$	0.340(3)	0.3673	0.3531	0.3441
Σ bend ^f				
$\nu_0(\text{cm}^{-1})$	39.554 709(10)	42.589	40.734	41.325
<i>B_x</i> (MHz)	1733.70(4)	...	1753.23	1753.72
<i>B_y</i> (MHz)	1720.89(3)	1793.4	1758.94	1766.59
<i>B_z</i> (MHz)	883.040(13)	879.2	868.55	870.47
$\langle P_2(\cos \theta) \rangle$	0.291(3)	0.2943	0.2772	0.2752
$\langle \Delta(\theta, \phi) \rangle$	0.062(7)	0.04296	0.0474	0.0591
Out-of-plane bend ^g				
$\nu_0(\text{cm}^{-1})$	45.2026(10)	47.236	46.686	46.542
<i>B_x</i> (MHz)	1774.0(2.0) ^h	...	1750.15	1749.94
<i>B_y</i> (MHz)	1752.0(2.0) ^h	1740.8	1706.72	1705.52
<i>B_z</i> (MHz)	854.6(6) ^h	867.1	856.59	856.21
$\langle P_2(\cos \theta) \rangle$	-0.025(2)	-0.0030	-0.0140	-0.0224
$\langle \Delta(\theta, \phi) \rangle$	-0.295(2)	-0.3098	-0.3146	-0.3197

^aCalc. 1 refers to the dynamically approximate clamped-Ar₂ calculations on the H6(3)+HFD-C pairwise-additive surface (Ref. 15).

^bCalc. 2 refers to the full five-dimensional dynamical calculation on the H6(3)+HFD-C pairwise-additive surface (Ref. 20).

^cCalc. 3 refers to the full five-dimensional dynamical calculation on the H6(4,3,0)+HFD-C pairwise additive surface (Ref. 20).

^dReferences 16 and 24.

^eReference 17 and this work.

^fReference 16.

^gThis work.

^hSee text for discussion of reliability of these fitted constants.

interaction in ArHCl was experimentally determined to be about one-third of the value determined for the Σ -II bend interaction.²⁹ Because of the smaller coupling coefficient, one would expect a bend-stretch interaction to be more *localized* (more dependent on near resonance) than a similar bend-bend interaction.

It is of considerable interest to determine the probable energy separation of the two interacting states for the purpose of roughly locating the position of the "dark" state. By using features of the spectra to determine where the two interacting states "cross" (become resonant) one can obtain a qualitative estimate of the desired energy difference. Clearly, large residuals in the zero-order rotational fit indicate states which are more nearly resonant than states with smaller residuals. In addition, the observed nuclear quadrupole hyperfine structures are also determined by a linear combination of the pure "bright" and "dark" state

hyperfine contributions. Consequently, large rotational residuals should correlate with large hyperfine residuals. It should be noted that the *relative* measured accuracy for the hyperfine energies (1 to 10²) is much less than the *relative* measured accuracy for rotational energies (10⁴ to 10⁵). Therefore, the hyperfine structure is not as sensitive to perturbations as are the rotational energies.

Unfortunately, only four transitions with exceptionally large rotational residuals (> 60 MHz) have fully resolved (and therefore more accurately measured) hyperfine structure. By reference to Table I, it may be seen that the transitions which involve the 6₁₆, 7₁₇, 9₁₉, and 10₁₁₀ upper state levels possess very large rotational residuals and it is these transitions for which fully resolved hyperfine structure has been measured. It is also of interest to note that the 6₁₆ and 7₁₇ levels are characterized by large *positive* residuals while the 9₁₉ and 10₁₁₀ levels are characterized by large *negative* residuals. This is suggestive of a "crossing" occurring around the 8₁₈ level, which has thus far eluded assignment. The nuclear quadrupole structure also shows evidence for strong mixing; these transitions are the only fully resolved hyperfine spectra which, upon inclusion in the hyperfine fit, did not yield residuals consistent with expected experimental uncertainties. In an attempt to further quantify the correlation between the rotational and hyperfine residuals, the upper state hyperfine coupling constants associated with these transitions were assumed to be the result of the following linear combination:

$$\chi_{ii}(\text{observed}) = c^2 \chi_{ii}(\text{dark state}) + (1 - c^2) \chi_{ii}(\text{out-of-plane bend}). \quad (3)$$

The χ_{ii} for the out-of-plane bend were fixed at the experimentally determined values and the χ_{ii} for the dark state were assumed to be the same as for the ground state (a good approximation for the heavy-atom vibrational states in the limit of weak potential coupling to the HCl bending states). The hyperfine structure for each transition was subsequently fit, with *c* as the variable parameter. The determined *c* coefficients did indeed correlate with the rotational residuals, yielding values (rotational residuals in parentheses) of 0.27 (98 MHz), 0.55 (248 MHz), 0.36 (-181 MHz), and 0.34 (-162 MHz) for the 6₁₆, 7₁₇, 9₁₉, and 10₁₁₀ levels, respectively. As a caveat, it should be noted that the quality of the fit was not sensitive to the χ_{ii} values assumed for the dark state. However, this information is strong support for a fairly localized perturbation that is near resonant around the 8₁₈ rotational level of the out-of-plane bend. Because the "crossing" occurs at a relatively low total rotational energy (about 4 cm⁻¹), it is likely that the separation of the two interacting vibrational states is 1 cm⁻¹ or less.

Coriolis coupling: General conclusions

From the arguments presented above, it is apparent that Coriolis mixing in the Ar₂HCl system can lead to substantial effects in the spectra through a subtle interaction (the in-plane-bend- Σ -bend interaction) or more obviously, through a strong perturbation (the out-of-plane-

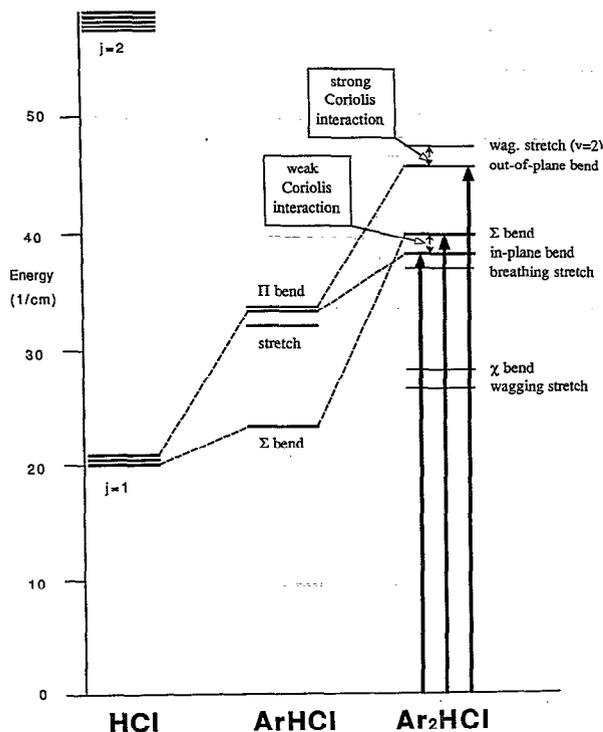


FIG. 2. Energy level correlation diagram for the Ar_nHCl ($n=0,1,2$) systems. Measured far infrared transitions for Ar₂HCl are denoted by solid arrows. States whose energies have been experimentally determined are represented by thick lines and calculated states (thin lines) are from the results of Cooper and Hutson (Ref. 20).

$\nu=2$ wagging stretch interaction). Although these instances should become more ubiquitous as the cluster size increases (due to an increase in the density of states), these interactions have been shown to have important effects on the spectra of all four prototypical binary systems mentioned in the introduction (ArHCl, ArHF, ArH₂O, and ArNH₃).⁷⁻¹⁰ Weak Coriolis interactions are particularly troublesome since it is often not possible to detect the existence of such coupling from fits to a purely rotational Hamiltonian, although the effects on the rotational constants can still be substantial. Accurate vibrational calculations for Ar₂HCl have made an approximate understanding of these effects possible, although full rovibrational calculations will be needed to fully account for these interactions. We emphasize that similar considerations should be expected to be important for similar and larger systems and that these effects will likely *often* compromise a “structural” interpretation of experimental rotational constants.

Comparison of experiment and theory

Since all three Ar₂HCl bending vibrations that correlate to the $j=1$ internal rotational state of the HCl monomer (see Fig. 2) have now been measured, the experimental data set is sufficient to warrant a meaningful comparison with theoretical results. For the purposes of exploring the capabilities and limitations of various theoretical efforts, we have included comparisons with three

different pairwise-additive calculations (Table VIII). The three-dimensional (Ar₂ clamped) dynamical calculations of Hutson, Beswick, and Halberstadt¹⁵ using the H6(3) potential³¹ are expected to be the least accurate results because of the dynamically approximate nature of the method and the use of the now-superseded H6(3) ArHCl pair potential. Also included for comparison are the recent calculations of Cooper and Hutson²⁰ which fully treat the five-dimensional dynamical problem. They have used a variational method with both the H6(3) and the more reliable H6(4,3,0) ArHCl pair potentials in order to determine the sensitivity of the molecular parameters to the ArHCl pair potential. Therefore, comparison between columns 2 and 3 in Table VIII indicate separately the effects of the dynamical approximation of Hutson, Beswick, and Halberstadt [for both calculations use the H6(3) ArHCl pair potential] and comparison between columns 3 and 4 indicate separately the effects of the different pair potentials on the molecular parameters (for both calculations are dynamically rigorous).

It may be seen that there are fairly substantial differences between the dynamically approximate and the full five-dimensional calculation, thus demonstrating the necessity of the computationally expensive calculation. In our previous analysis of the in-plane bend,¹⁷ we concluded that the experimental rotational constants indicated substantial potential coupling between the Ar₂ coordinates and the HCl bending motions and that for this reason more rigorous dynamical calculations were needed. The reassignment of the in-plane bend and the resulting molecular constants in this work does not compromise the logic of those conclusions, which were based on changes in the experimental rotational constants on the order of a few percent. However, the full dynamical calculations actually reveal very small *potential* mixing of these states.²⁰ We have shown in this work that even weak Coriolis perturbations can lead to significant changes in the experimental rotational constants and that “structural” conclusions based on small changes in the experimental rotational constants are, in fact, extremely tenuous. Indeed, inspection of the experimental and calculated rotational constants for all three excited bending states reveals some very substantial discrepancies, indicating the probable effects of Coriolis coupling. In order to allow comparison between experiment and theory for these very valuable parameters, it will be necessary to explicitly treat these Coriolis effect effects in future calculations.

The agreement between calculated and observed band origins and angular expectation values is qualitatively good. However, in the instance of agreement between the measured and calculated band origins, it should be noted that experimental uncertainties are on the order of less than 0.001 cm⁻¹ and the level of convergence for these calculated quantities²⁰ is about 0.01 cm⁻¹, whereas the discrepancies *between* the measured and calculated values are larger than 1 cm⁻¹. Therefore, it must be concluded that the pairwise-additive potential energy surface is not sufficiently accurate to obtain agreement with experiment. The comparison between calculations using the two differ-

ent ArHCl potentials provides some measure of the possible discrepancies introduced by slight inaccuracies in the pair potentials. Although the differences resulting from the two calculations are non-negligible, it may be noted that the discrepancies between the two theoretical values are substantially less than the discrepancy between experimental and theoretical values. In addition, the results from the more accurate potential do not necessarily correspond with better agreement with experiment. Therefore, it may be concluded that potential inadequacies in the ArHCl pair potential *cannot* be entirely responsible for the theoretical-experimental inconsistencies. However, the results of Cooper and Hutson²⁰ indicate that the effects of three-body forces can indeed be of the same magnitude as the current disagreement between experiment and theory and that it should be possible to directly determine these forces from the spectra reported in this work. Such efforts are in progress.

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