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High resolution infrared spectra of H_2 -Ar, HD-Ar, and D_2 -Ar van der Waals complexes between 160 and 8620 cm⁻¹

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Spectra of weakly bound hydrogen–argon complexes have been studied at high spectral resolution $(0.04-0.10 \text{ cm}^{-1})$ using a long-path (154 m), low-temperature (77 K) absorption cell and a Fourier transform infrared spectrometer. The observations cover a wide spectral range from the far-infrared D_2 –Ar $S_0(0)$ band at 180 cm⁻¹ to the near-infrared H_2 –Ar $S_2(1)$ band at 8600 cm⁻¹. Compared to earlier studies, the new results have considerably improved resolution and accuracy. They also extend to new regions, namely the first overtone band of H_2 and the pure rotational band of H_2 and D_2 , and they include weak transitions involving excitation of the van der Waals stretching motion. These data serve as a basis for determining a greatly improved three-dimensional intermolecular potential energy surface for the hydrogen–argon system in the following paper. [S0021-9606(96)00231-0]

I. INTRODUCTION

The detection of rotational structure due to the H₂-Ar complex in the H₂-stretching region near 4500 cm⁻¹ (2.2 μ m) by Kudian *et al.*¹ in 1966 was one of the very first spectroscopic observations of a van der Waals molecule. Since that time, there has been a series^{2–8} of refinements of the original IR experiment, involving improved spectral resolution, extended wavelength coverage, and the study of other hydrogen isotopes (HD, D₂) and other rare gas atoms (Ne, Kr, Xe). Radio frequency hyperfine spectra of hydrogen–rare gas complexes have also been reported.⁹

The original observation¹ stimulated the first theoretical study of the H₂-Ar spectrum, which was made by Cashion¹⁰ in 1966. Subsequently, large scale analyses of the IR spectra have been made by Le Roy and Van Kranendonk,¹¹ Dunker and Gordon,¹² Le Roy and Carley,¹³ and, most recently, by Le Roy and Hutson.¹⁴ These workers determined anisotropic intermolecular potential surfaces for hydrogen-rare gas systems by directly fitting the observed IR spectra, sometimes in combination with other experimental data. In two cases, an induced dipole moment surface was also derived for H₂-Ar.^{12,15} The hydrogen-argon system has become a popular benchmark for theory,¹⁶ especially for calculations of rotational and vibrational predissociation effects.¹⁷⁻²⁶ This popularity can be ascribed to the fundamental nature of the H₂-Ar system, to the relatively weak anisotropy of the intermolecular forces, and to the availability of high-quality experimentally based potential energy surfaces.

A new and much more complete set of experimental IR spectra of the hydrogen–argon complex has now been obtained. These data, which were obtained using a cooled (77 K) long-path absorption cell and a Fourier transform spectrometer, exhibit significantly improved resolution and wave number accuracy compared to the best previous results.⁷ Equally important is that they extend the coverage of the spectra to include far-IR pure rotational transitions of H₂ and D₂ (160–610 cm⁻¹), vibrational overtone transitions of H₂

(8050–8620 cm⁻¹), and excited van der Waals stretch (n = 1) transitions of H₂–Ar and D₂–Ar. This extended coverage means that the hydrogen–argon potential energy surface is more fully probed, especially in terms of its dependence on the hydrogen stretching coordinate.

In the present paper, these new hydrogen-argon IR spectra are presented, discussed, and compared with theory. In the following paper,²⁷ the IR data are used, together with other experimental input and appropriate theoretical constraints, to determine a definitive new potential surface. This new exchange-coulomb (XC) surface fits the present data about 7 times better than the best previous empirical surface, TT₃ of Le Roy and Hutson.¹⁴

The hydrogen molecule (H₂, D₂, or HD) within a hydrogen-argon complex exhibits almost completely free rotation and vibration, because its rotational and vibrational level spacings are very much larger than any hindering terms in the intermolecular potential. The consequences of this freedom are that the hydrogen vibrational and rotational quantum numbers (denoted here by v and $j_{\rm H}$) remain good labels in the complex, and the spectra due to the complex occur as rotational bands, each of which is approximately centered around a hydrogen vibration–rotation transition. These hydrogen transitions, and hence hydrogen–argon "bands," are labeled here as $S_0(0)$, $Q_1(1)$, etc., where the Q or S denotes $\Delta j_{\rm H}=0$ or 2, respectively, the subscript 0, 1, or 2 denotes $v=0 \leftarrow 0$, $1 \leftarrow 0$, or $2 \leftarrow 0$, respectively, and the number 0 or 1 in parentheses denotes the initial value of $j_{\rm H}$.

For a given H₂ state (v and $j_{\rm H}$) the energy levels of a complex may be characterized by an end-over-end rotational quantum number, l, and a van der Waals stretching quantum number, n. The total angular momentum of the complex, J, is the vector sum of $j_{\rm H}$ and l. The rovibrational energy of the complex is then given, to a first approximation, by the internal rovibrational energy of its constituent hydrogen minus the complex binding energy (which is a function of n) plus its end-over-end rotational energy, $B_{\rm complex}l(l+1)$. Values of



FIG. 1. Approximate radial potential energy curve for hydrogen-argon, showing the locations of the ground (n=0) and excited (n=1) van der Waals stretching states for the l=0 levels of H₂-Ar and D₂-Ar. Note the large zero-point energy, and the wide radial extent of the states, especially n=1.

the rotational constant, B_{complex} , are about 0.57, 0.39, and 0.31 cm⁻¹ for H₂-Ar, HD-År, and D₂-Ar, respectively.

On closer examination, each *l* level is split by the anisotropy of the intermolecular potential into $2j_{\rm H}+1$ sublevels with different values of J (or 2l+1 sublevels for $l < j_{\rm H}$). Transitions involving the ground intermolecular stretch levels (n=0) predominate in the observed spectra of hydrogen-rare gas complexes. As noted previously,^{5,10} this is because the induced dipole moment depends very strongly on intermolecular separation, being weaker for larger separations, and levels with higher *n*-values have larger separations due to the considerable anharmonicity of the potential. Weak transitions involving n=1 levels are reported for the first time in the present paper.

Figure 1 shows an approximate radial potential energy curve for hydrogen-argon, based on TT₃.¹⁴ The actual TT₃ potential is, of course, angle dependent and also changes slightly depending on the hydrogen isotope and the value of v. Also indicated in Fig. 1 are the positions of the n=0 and 1 van der Waals stretching states for both H₂-Ar and D₂-Ar. These serve to indicate which regions are sampled by transitions involving these states, and to emphasize the much wider probing of the potential afforded by n = 1. Note that the zero-point energy is more than half the well depth for H₂-Ar, and almost half for D₂-Ar. Figure 1 applies to l=0levels; those with larger values of l tend to probe larger values of the intermolecular separation.

II. EXPERIMENTAL DETAILS

The 5.5 m long-path cell used here has been described previously.7,28 It is vacuum insulated and was cooled to 77 K by means of liquid nitrogen contained in a concentric jacket surrounding the inner sample tube, which has a diameter of 12 cm. The total absorption path was 154 m, obtained with 28 traversals of the cell.

TABLE I. Experimental conditions for the present measurements. In all cases, the absorption path was 154 m and the temperature was 77 K.ª

Transition	Region (cm ⁻¹)	Resolution (cm ⁻¹)	H ₂ /HD/D ₂ pressure (Torr)	Ar pressure (Torr)
$H_2 - Ar S_0(0)$	350	0.06	56	44
H_2 -Ar $S_0(1)$	590	0.10	72	70
H_2 -Ar $Q_1(0)/S_1(0)$	4160/4500	0.04	22	20
H_2 -Ar $Q_1(1)/S_1(1)$	4150/4710	0.04	30	30
$H_2 - Ar S_2(0)$	8400	0.10	208	195
H_2 -Ar $Q_2(1)/S_2(1)$	8070/8600	0.15	208	195
$D_2 - Ar S_0(0)$	180	0.10	80	80
D_2 -Ar $Q_1(0)/S_1(0)$	2990/3170	0.05	49	62
$D_2 - Ar Q_1(1)$	2990	0.07	73	77
HD–Ar $Q_1(0)/S_1(0)$	3630/3890	0.08	59	79

^aAdditionally, weak $Q_1(0)$ n=1 features were studied with total pressures of 260 Torr for H₂-Ar (as used for Fig. 2) and 223 Torr for D₂-Ar.

The spectra were recorded with a Bomem DA3.02 Fourier transform spectrometer at spectral resolutions varying from 0.04 to 0.10 cm⁻¹. Modulated IR radiation was passed by transfer optics from the spectrometer to the cell and then to an IR detector, such that the entire IR radiation path outside of the cell was evacuated. For the mid-IR spectra, 2900–8620 cm⁻¹, a CaF₂ beamsplitter, quartz-halogen tungsten filament source, and fused silica cell windows were used. The liquid nitrogen cooled photovoltaic detector was InSb $(2900-5000 \text{ cm}^{-1})$ or Ge $(8050-8620 \text{ cm}^{-1})$. For the far-IR spectra, 160–610 cm⁻¹, a mylar beamsplitter, ceramic glower source, and CsI cell windows were used. The liquid helium cooled detector was a Si bolometer $(160-190 \text{ cm}^{-1})$ or a Ge:Cu photoconductor (340-610 cm⁻¹). Data acquisition times were typically 5-15 h per spectrum. Details of the various spectral resolutions and gas pressures used are summarized in Table I.

The low temperature equilibrium species, para-hydrogen and ortho-deuterium, were produced in the conventional manner by liquefying H_2 or D_2 for about 15 min in the presence of a chrome-alumina catalyst. Each H2-Ar run was performed using either *para*-H₂, which is virtually all in the $j_{\rm H}$ =0 rotational state at 77 K, or with normal H₂, composed of 25% $j_{\rm H}$ =0 and 75% $j_{\rm H}$ =1. In the case of low temperature D_2 , the normal species is 67% $j_H=0$ and 33% $j_H=1$; most experiments were performed with ortho- D_2 ($j_H=0$), and only one, to examine the $Q_1(1)$ transition, with normal D₂ (see Table I). For HD, with its inequivalent nuclei, there is no possibility of separating states of different $j_{\rm H}$, and only the HD-Ar bands with an initial value of $j_{\rm H}$ =0 could be probed at 77 K.

III. RESULTS

A. The H₂–Ar spectrum

The overall appearance of the H₂-Ar absorption over a wide range of 670 cm^{-1} in the region of the fundamental band of H_2 ($v = 1 \leftarrow 0$) is illustrated in Fig. 2. This result was obtained using a mixture of para-H2 and Ar at a total pressure of 260 Torr, and it shows two H2-Ar bands, corre-



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FIG. 2. An overview of the absorption induced by argon (120 Torr) in *para*-hydrogen (140 Torr) at 77 K in the region of the H₂ fundamental band. The path was 154 m and the spectral resolution was 0.10 cm⁻¹. Note the broad lines due to collision-induced absorption with superimposed sharp structure due to H₂-Ar complexes. The inset shows the simple *P*- and *R*-branch structure of the $Q_1(0)$ band of H₂-Ar.



FIG. 3. The S(0) bands of the H₂-Ar complex accompanying the pure rotational band (top trace), the fundamental band (middle trace), and the first overtone band (lower trace) of H₂. Experimental conditions are given in Table I. The structure of the three bands is very similar (apart from effects due to the different pressures used), but the slight differences between them directly probe the dependence of the intermolecular potential on the H₂ stretching state, v.



FIG. 4. Expanded views of the central portions of the $S_0(0)$ and $S_1(0)$ bands of the H₂-Ar complex. Experimental conditions are given in Table I.

sponding to the transitions $Q_1(0)$ near 4161 cm⁻¹ and $S_1(0)$ near 4498 cm⁻¹. Each band, consisting of a number of sharp lines arising from bound H₂–Ar complexes, sits on top of a much broader ($\approx 100 \text{ cm}^{-1}$) continuous absorption feature which is due to collision-induced absorption²⁹ (CIA) arising from transient H₂–Ar collision events. Figure 2 helps to illustrate a close connection between the CIA and complex spectra in this system.³⁰ These two parts of the spectrum are aspects of the same absorption process, governed by the same induced dipole moment and intermolecular potential surface, but distinguished from each other mainly by the duration of the relevant molecular interaction.

The simplest H₂-Ar band is $Q_1(0)$, as shown in the inset of Fig. 2. Since the H₂ is in its spherically symmetric $j_{\rm H}=0$ level for both the initial and final states of this transition, the end-over-end rotational levels of the complex have l=J and only P(l) and R(l) transitions ($\Delta l = \pm 1$) are possible. Note that transitions higher than R(6) and P(7) are not present, indicating that only levels with l < 8 are bound.

The $S_1(0)$ band, for which $j_H=2\leftarrow 0$, is considerably more complicated than $Q_1(0)$, as shown in the central trace of Fig. 3. The angular dependence of the induced dipole moment of the complex results in strong N(l) and T(l) (Δl $= \mp 3$) transitions, and there are also splittings and shifts of the P(l) and R(l) transitions. Also shown in Fig. 3 are the bands $S_0(0)$ near 350 cm⁻¹ and $S_2(0)$ near 8410 cm⁻¹; these have very similar structures to $S_1(0)$, differing only because of effects due to the dependence of the H₂–Ar potential on the H₂ vibrational state (or, equivalently, on the H₂



FIG. 5. The Q(1) bands of H₂-Ar accompanying the fundamental band (center trace) and first overtone band (lower trace) of H2. Also shown in the short upper trace is the $Q_1(0)$ band (measured using pure para-H₂), the lines of which are also present in the $Q_1(1)$ spectrum (measured using normal H₂).

bond length). Figure 4 shows the central portions of $S_0(0)$ and $S_1(0)$ in detail.

The strong lines near the center of $S_1(0)$ and $S_2(0)$ which go off the scale in Fig. 3 are not part of the spectrum of the H₂-Ar complex, but rather are the quadrupole transitions of the H₂ monomer. There is also a $S_0(0)$ quadrupole transition located at the position indicated by the arrow in the top trace of Fig. 3, but it is too weak to be observed due to the frequency cubed dependence of the quadrupole absorption strength. Note that in Fig. 3, and elsewhere in this paper, arrows connected to the band labels [like $S_1(0)$] indicate the positions of the unperturbed hydrogen transition frequencies. This position corresponds to a quadrupole line except for the far IR, where they are too weak, and for $Q_1(0)$, where a quadrupole transition is forbidden. Any shift between the arrow and the apparent center of the complex band is a reflection of the small vibrational (and, to a lesser extent, rotational) frequency shift induced in the hydrogen by the presence of the nearby argon.

 $S_1(0)$ is the best resolved of the three S(0) bands in Fig. 3. In comparison, the $S_0(0)$ band is inherently stronger, but this advantage is outweighed by reduced experimental sensitivity in the far-IR (350 cm^{-1}) region compared to the mid-IR (4500 cm⁻¹). And the $S_2(0)$ band is inherently much



FIG. 6. The S(1) bands of the H₂-Ar complex accompanying the pure rotational band (top trace), the fundamental band (middle trace), and the first overtone band (lower trace) of H2. Experimental conditions are given in Table L

weaker than $S_1(0)$, requiring higher sample pressures and hence showing larger pressure broadening effects.

Using normal H₂, the Q(1) $(j_{H}=1\leftarrow 1)$ and S(1) $(j_{\rm H}=3\leftarrow1)$ bands of H₂-Ar were observed, as shown in Fig. 5 $[Q_1(1) \text{ and } Q_2(1)]$ and Fig. 6 $[S_0(1), S_1(1), \text{ and } S_2(1)]$. At the top of Fig. 5 is a high-resolution trace of $Q_1(0)$, to illustrate that some of the weaker lines in the $Q_1(1)$ spectrum are due to $Q_1(0)$ lines since there is 25% para-H₂ in normal H₂. Interestingly, it was not possible to detect any trace of a $Q_2(0)$ band for H₂-Ar. This failure is consistent with the previously observed³¹ absence of $Q_2(0)$ in CIA spectra of hydrogen, ascribed to the weakness of the "overlap induced" component of the transition dipole moment for the $v = 2 \leftarrow 0$ overtone band. The S(1) bands (Fig. 6) are the most complicated of those studied here. Not only P(l) and R(l), but also N(l) and T(l) lines, are split into a number of components by anisotropic intermolecular interactions. This larger number of individual transitions means that the $S_0(1)$ and, especially, $S_2(1)$ bands are only partially resolved in Fig. 6.

The measured positions of the observed H₂-Ar lines are listed in Tables II-V, together with estimates of their uncertainties and comparisons with the new calculations²⁷ based on the XC(fit) potential surface (see below). In the case of $Q_1(0)$, some weak lines due to transitions with $n=1 \leftarrow 0$

TABLE II. Observed transitions in the $Q_1(0)$ band of H₂-Ar.^a

<i>l'</i>	J'	<u> </u>	<i>l</i> "	J''	Observed ^b (cm ⁻¹)	Obs-calc XC ^c (cm ⁻¹)	Obs-calc TT3 ^d (cm ⁻¹)
5	5		6	6	4153.926(4)	0.003	-0.005
4	4		5	5	4154.762(4)	0.001	-0.010
3	3		4	4	4155.734(4)	-0.001	-0.014
2	2		3	3	4156.778(4)	-0.004	-0.019
1	1		2	2	4157.869(4)	-0.004	-0.021
0	0		1	1	4158.985(7)	-0.001	-0.019
1	1		0	0	4161.220(7)	-0.002	-0.019
2	2		1	1	4162.317(4)	-0.002	-0.019
3	3		2	2	4163.384(4)	-0.002	-0.018
4	4		3	3	4164.407(4)	0.000	-0.015
5	5		4	4	4165.362(4)	0.001	-0.013
6	6		5	5	4166.211(4)	0.003	-0.012
1	1		2	2	4179.550(20) ^e	-0.043	-0.174
0	0		1	1	4181.400(20) ^e	-0.048	-0.167

^aIn all cases, $v = 1 \leftarrow 0$ and $j_{\rm H} = 0 \leftarrow 0$. Unless otherwise indicated, $n = 0 \leftarrow 0$.

^bEstimated line position uncertainties in units of the last quoted digit are given in parentheses.

^cCalculation based on the XC(fit) potential surface of Bissonette et al. (Ref. 27).

^dCalculation (Ref. 33) based on the TT₃ potential surface of Le Roy and Hutson (Ref. 14).

^eFor these two weak transitions, $n = 1 \leftarrow 0$.

were observed, two of which are reported in Table II. Such transitions were relatively more prominent in the D_2 -Ar spectrum, as discussed below. Most of the transitions included in Tables II–V are "uniquely assigned" ones which are reasonably sharp and unblended, and therefore suitable for direct comparison with theoretical line positions.

B. The D₂–Ar spectrum

Due to its greater reduced mass, the D₂-Ar complex has more bound states than H₂-Ar (up to about l=11 as compared to l=7), and it therefore exhibits more extensive rotational structure. Figure 7 illustrates the Q_1 region near 3000 cm⁻¹ for mixtures of argon with *ortho*-D₂ (upper trace) and normal D₂ (lower trace). Since the *ortho*-D₂ concentration was actually somewhat less than 100%, some $Q_1(1)$ lines are visible in the upper trace along with the expected $Q_1(0)$ ones. Measured positions for uniquely assigned lines of $Q_1(0)$ and $Q_1(1)$ are given in Tables VI and VII. Overviews of the $S_0(0)$ and $S_1(0)$ bands are shown in Fig. 8, and more detailed views of their crowded central portions are shown in Fig. 9. The line positions for these bands are given in Table VIII. The S(1) bands and the D₂ overtone ($\nu=2\leftarrow0$) region were not studied.

By using a higher sample-pressure, it was possible to observe some weak transitions involving the excited intermolecular stretching state, n=1, in the regions of $Q_1(0)$ and $S_1(0)$. These are illustrated in Fig. 10. The top and center traces of Fig. 10 show structure just below and above the main region of the $Q_1(0)$ band which can be assigned to combination bands with $\Delta n = -1$ and +1. Measured positions for the more well-defined transitions in these subbands are given in Table VI. In addition to these lines, there is also

TABLE III. Observed transitions in the $Q_1(1)$ and $Q_2(1)$ bands of H₂- Ar.^a

		←		J''	Q_1	1)	$Q_2(1)$		
l'	J'		<i>l</i> "		Observed ^b (cm ⁻¹)	Obs-calc XC ^c (cm ⁻¹)	Observed ^b (cm ⁻¹)	Obs-Calc XC ^c (cm ⁻¹)	
4	5		7	6	4135.969(10)	0.019	8054.910(40)	-0.015	
3	4		6	5	4138.319(4)	0.000	8057.330(20)	0.015	
2	3		5	4	4141.175(4)	0.000	8060.195(20)	0.006	
1	2		4	3	4144.270(4)	0.001	8063.295(20)	0.000	
0	1		3	2	4147.500(7)	0.000			
3	2		0	1	4160.778(7)	-0.004			
4	3		1	2	4163.998(4)	0.000	8082.998(20)	0.008	
5	4		2	3	4167.076(4)	0.002	8086.065(20)	0.019	
6	5		3	4	4169.932(4)	0.004	8088.917(20)	0.020	
7	5		4	5	4172.354(8)	-0.007	8091.395(20)	0.012	
8	6		5	4			8093.38(20)	0.030	

^aIn all cases, $j_{\rm H}=1\leftarrow 1$ and $n=0\leftarrow 0$. For $Q_1(1)$, $v=1\leftarrow 0$; and for $Q_2(1)$, $v=2\leftarrow 0$.

^bEstimated line position uncertainties in units of the last quoted digit are given in parentheses.

^cCalculation based on the XC(fit) potential surface of Bissonette et al. (Ref. 27).

TABLE IV. Observed transitions in the $S_0(0)$, $S_1(0)$, and $S_2(0)$ bands of H₂-Ar.^a

					S_0	(0)	$S_1($	0)	$S_2(0)$	
<i>l'</i>	J'	\leftarrow	l''	J″	Observed ^b (cm ⁻¹)	Obs-calc XC ^c (cm ⁻¹)	Observed ^b (cm ⁻¹)	Obs-calc XC ^c (cm ⁻¹)	Observed ^b (cm ⁻¹)	Obs-calc XC ^c (cm ⁻¹)
4	6		7	7	335.812(8)	0.011	4478.108(10)	-0.020	8385.560(30)	-0.028
3	5		6	6	338.135(3)	0.001	4480.476(3)	-0.002	8387.960(20)	-0.003
2	4		5	5	340.993(3)	0.003	4483.349(3)	-0.002	8390.859(20)	0.002
1	3		4	4	344.118(3)	0.000	4486.489(3)	-0.004	8394.008(20)	-0.005
0	2		3	3	347.454(5)	0.001	4489.832(5)	-0.003		
1	2		2	2	352.689(8)	-0.007	4495.126(7)	-0.011		
2	1		1	1	356.033(8)	0.000	4498.376(5)	-0.003		
3	1		2	2			4499.130(7)	-0.001		
3	2		2	2	357.483(8)	-0.004	4499.857(5)	-0.003		
4	2		3	3			4500.258(7)	0.001		
3	3		2	2			4500.463(6)	-0.006		
4	3		3	3	358.635(8)	-0.002	4500.999(5)	-0.007		
5	3		4	4			4501.265(7)	-0.003		
4	4		3	3			4501.507(5)	-0.005		
5	4		4	4	359.661(8)	0.004	4502.025(7)	0.002		
6	5		5	5	360.521(8)	0.000	4502.907(5)	0.000		
6	6		5	5	360.877(10)	0.003	4503.312(5)	0.006		
3	1		0	0			4502.476(7)	-0.004		
4	2		1	1	363.484(3)	-0.002	4505.791(3)	-0.003	8413.240(20)	-0.005
5	3		2	2	366.618(3)	-0.004	4508.916(3)	-0.003	8416.350(20)	0.001
6	4		3	3	369.501(3)	-0.004	4511.810(3)	-0.001	8419.235(20)	0.003
7	5		4	4	371.884(6)	-0.024	4514.289(4)	-0.005	8421.760(20)	0.000
8	6		5	5					8423.80(10)	0.049

^aIn all cases, $j_H=2\leftarrow 0$ and $n=0\leftarrow 0$. For $S_0(0)$, $v=0\leftarrow 0$; for $S_1(0)$, $v=1\leftarrow 0$; and for $S_2(0)$, $v=2\leftarrow 0$.

^bEstimated line position uncertainties in units of the last quoted digit are given in parentheses.

^cCalculation based on the XC(fit) potential surface of Bissonette et al. (Ref. 27).

some structure, indicated on Fig. 10, due to CH₄ impurity in the gas sample. Another weak structure is due to D₂–Ar $Q_1(1)$ transitions, though the *ortho*-D₂ purity is better here than in Fig. 7. Still other structure may be due to the $Q_1(2)$ band, which can arise from the equilibrium population of D₂ (15%) in the $j_{\rm H}$ =2 state at 77 K. Some lines due to $S_1(0)$ transitions with Δn =+1 are shown in the lower trace of

Fig. 10 and listed in Table VIII; although some $\Delta n = -1$ structure was also noted at lower wave numbers, below $S_1(0)$, it was too weak to be reliably measured.

C. The HD-Ar spectrum

The $Q_1(0)$ and $S_1(0)$ bands of the HD–Ar complex are shown in Fig. 11. The $Q_1(0)$ band appears rather similar to

TABLE V. Observed transitions in the $S_0(1)$, $S_1(1)$, and $S_2(1)$ bands of H₂-Ar.^a

				S_0	$S_0(1)$		$S_{1}(1)$		
<i>l'</i>	$J' \leftarrow$	- 1"	J''	Observed ^b (cm ⁻¹)	Obs-calc XC ^c (cm ⁻¹)	Observed ^b (cm ⁻¹)	Obs-calc XC ^c (cm ⁻¹)	Observed ^b (cm ⁻¹)	
4		7		568.633(9)		4693.365(10)		8583.640(30)	
3		6				4695.635(10)			
3		6		571.015(6)		4695.764(8)		8586.060(20)	
2		5				4698.529(10)			
2		5		573.899(6)		4698.666(8)		8588.970(20)	
1		4		577.050(6)		4701.829(8)		8592.170(20)	
0		3		580.432(8)		4705.212(10)		8595.570(50)	
4	2	1	1	595.593(10)	0.006	4720.321(8)	0.001		
5	3	2	2	598.793(8)	0.005	4723.524(8)	0.003		
5	2	2	1	599.457(8)	0.001	4724.147(8)	-0.002		
6	4	3	3	601.706(8)	0.000	4726.456(8)	0.001		
6	3	3	2	602.347(8)	0.000	4727.047(8)	0.000		
7	5	4	4	604.103(12)	-0.011	4728.944(12)	-0.004		
7	4	4	3	604.767(8)	-0.005	4729.542(8)	-0.006		

^aIn all cases, $j_{\rm H}=3\leftarrow1$ and $n=0\leftarrow0$. For $S_0(1)$, $v=0\leftarrow0$; for $S_1(1)$, $v=1\leftarrow0$; and for $S_2(1)$, $v=2\leftarrow0$. ^bEstimated line position uncertainties in units of the last quoted digit are given in parentheses.

^cCalculation based on the XC(fit) potential surface of Bissonette et al. (Ref. 27).



FIG. 7. The $Q_1(0)$ and $Q_1(1)$ bands of the D₂-Ar complex, measured using *ortho*-D₂ (upper trace) and normal D₂ (lower trace). There are residual $Q_1(1)$ lines in the upper trace because the *ortho* conversion of the D₂ sample used was not complete. Experimental conditions are given in Table I.

those of H₂-Ar and D₂-Ar, showing sharp lines and an intermediate number of bound levels (l values up to about 9), as expected. However, as noted previously,^{6,7} the lines of the $S_1(0)$ band are much broader than those of H₂-Ar and

 D_2 -Ar would be at a similar pressure. The excess linewidth for $S_1(0)$ is due to relatively rapid predissociation of the upper state $(v=1, j_{\rm H}=2)$ levels. Predissociation effects are more prominent here because of the lower symmetry of HD, which results in a much greater effective anisotropy of the intermolecular potential for HD–Ar. The v=1, $j_{\rm H}=2$ upper state of the HD-Ar $S_1(0)$ band is able to predissociate to v = 1, $j_{\rm H} = 1$, unlike in H₂-Ar and D₂-Ar where the allowed predissociation channels are strictly limited by the selection rule $\Delta j_{\rm H}=2$. The HD-Ar $Q_1(0)$ band remains relatively sharp because it can only predissociate by $\Delta v = 1$ processes, which are much slower than the $\Delta v = 0$ processes open for $S_1(0)$. The measured line positions for HD-Ar $Q_1(0)$ are listed in Table IX, which includes some weak $\Delta n = 1$ transitions not shown in Fig. 11. New measurements are not given here for $S_1(0)$ since the width of the lines in this band means that the previously reported⁷ positions cannot be significantly improved upon.

A number of detailed calculations^{19,22,24,26} of HD–Ar $S_1(0)$ predissociation linewidths were made for comparison with the earlier observation⁷ of this band. In view of this interest, an effort was made here to obtain more accurate experimental widths from the present spectrum. A nonlinear least-squares fit was made in the regions of the unblended *N*-

TABLE VI. Observed transitions in the $Q_1(0)$ band of D_2 -Ar.^a

<i>l'</i>	J'	<i>←</i>	<i>l</i> ″	J″	n'	\leftarrow	n″	Observed ^b (cm ⁻¹)	Obs-calc XC ^c (cm ⁻¹)	Obs-calc TT3 ^d (cm ⁻¹)
3	3		2	2	0		1	2971.347(30)	-0.021	0.485
4	4		3	3	0		1	2972.723(15)	0.010	0.530
5	5		4	4	0		1	2974.351(15)	0.003	0.547
6	6		5	5	0		1	2976.220(15)	0.158	0.434
9	9		10	10	0		0	2987.050(7)	-0.001	0.025
8	8		9	9	0		0	2987.483(4)	0.009	0.036
7	7		8	8	0		0	2987.975(4)	0.004	0.031
6	6		7	7	0		0	2988.513(4)	0.001	0.028
5	5		6	6	0		0	2989.078(7)	-0.006	
4	4		5	5	0		0	2989.674(4)	-0.004	0.021
3	3		4	4	0		0	2990.286(4)	0.000	0.024
2	2		3	3	0		0	2990.906(4)	0.002	0.024
1	1		2	2	0		0	2991.527(7)	-0.002	0.019
2	2		1	1	0		0	2994.025(7)	-0.001	0.017
3	3		2	2	0		0	2994.636(4)	0.000	0.017
4	4		3	3	0		0	2995.239(4)	0.004	0.020
5	5		4	4	0		0	2995.818(4)	-0.002	0.014
6	6		5	5	0		0	2996.389(4)	0.003	0.018
7	7		6	6	0		0	2996.934(4)	0.004	0.018
8	8		7	7	0		0	2997.451(4)	0.005	0.018
9	9		8	8	0		0	2997.927(4)	0.004	0.014
10	10		9	9	0		0	2998.353(7)	0.008	0.014
5	5		6	6	1		0	3009.696(20)	-0.016	-0.126
4	4		5	5	1		0	3011.683(10)	-0.011	-0.074
3	3		4	4	1		0	3013.326(10)	0.012	-0.033
2	2		3	3	1		0	3014.670(10)	0.015	-0.020
1	1		2	2	1		0	3015.755(10)	0.009	-0.022
5	5		4	4	1		0	3016.473(20)	0.025	-0.089

^aIn all cases, $v = 1 \leftarrow 0$ and $j_{\rm H} = 0 \leftarrow 0$.

^bEstimated line position uncertainties in units of the last quoted digit are given in parentheses.

^cCalculation based on the XC(fit) potential surface of Bissonette et al. (Ref. 27).

^dCalculation (Ref. 33) based on the TT₃ potential surface of Le Roy and Hutson (Ref. 14).

TABLE VII. Observed transitions in the $Q_1(1)$ band of D_2 -Ar.^a

l'	J'	\leftarrow	ļ″	J''	Observed ^b (cm ⁻¹)	Obs-calc XC ^c (cm ⁻¹)
8	9	1	1	10	2973.596(4)	0.005
7	8	1	0	9	2974.784(4)	-0.003
6	7		9	8	2976.221(4)	-0.001
5	6		8	7	2977.795(4)	0.004
4	5		7	6	2979.443(4)	-0.003
3	4		6	5	2981.159(4)	0.002
2	3		5	4	2982.903(7)	0.007
6	5		3	4	3000.062(4)	-0.004
7	6		4	5	3001.746(4)	-0.005
8	7		5	6	3003.380(4)	0.000
9	8		6	7	3004.926(4)	0.000
10	9		7	8	3006.356(4)	0.007
11	10		8	9	3007.573(4)	0.008

^aIn all cases, $v = 1 \leftarrow 0$, $j_{\rm H} = 1 \leftarrow 1$, and $n = 0 \leftarrow 0$.

^bEstimated line position uncertainties in units of the last quoted digit are given in parentheses.

^cCalculation based on the XC(fit) potential surface of Bissonette *et al.* (Ref. 27).

and *T*-branch lines, using a sum of Lorentzian lines having adjustable widths, positions, and strengths. The measured widths resulting from the fit are compared with theory in Table X. The agreement is generally satisfactory, especially considering that these calculations were based on the now-obsolete BC₃(6,8) potential.¹³ In particular, the observed decrease in width with increasing *l* for the T(2)-T(6) transi-



FIG. 8. The S(0) bands of the D₂–Ar complex accompanying the pure rotational band (top trace) and the fundamental band (lower trace) of D₂. Arrows mark the positions of the rotation–vibration transitions of free D₂, and, for $S_1(0)$, the D₂ quadrupole line is visible at this position. Experimental conditions are given in Table I.



FIG. 9. Expanded views of the central portions of the $S_0(0)$ and $S_1(0)$ bands of the D₂-Ar complex. Experimental conditions are given in Table I.

tions, which is quite evident in the spectrum (Fig. 11), is well reproduced by all three calculations.

Figure 11 illustrates another distinctive feature of HD: the presence of a HD electric dipole transition, $R_1(2)$, in



FIG. 10. Spectra showing weak transitions of the D₂-Ar complex involving the excited van der Waals stretching mode: $\Delta n = -1$ lines of $Q_1(0)$ (upper trace), $\Delta n = +1$ lines of $Q_1(0)$ (middle trace), and $\Delta n = +1$ lines of $S_1(0)$ (lower trace). Some of the features in the $Q_1(0)$ region are due to CH₄ impurity in the gas sample, as indicated.

TABLE VIII. Observed transitions in the $S_0(0)$ and $S_1(0)$ bands of D_2 -Ar.^a

				J''	S_0	(0)	$S_1(0)$		
l' J'	<i>←</i>	<i>l</i> "	Observed ^b (cm ⁻¹)		Obs-calc XC ^c (cm ⁻¹)	Observed ^b (cm ⁻¹)	Obs-Calc XC ^c (cm ⁻¹)		
8	10		11	11	161.719(20)	0.003	3148.060(6)	-0.003	
7	9		10	10	162.895(15)	0.004	3149.252(3)	-0.001	
6	8		9	9	164.326(15)	0.002	3150.702(3)	0.000	
5	7		8	8	165.900(15)	-0.003	3152.297(3)	0.001	
4	6		7	7	167.589(15)	0.009	3153.990(3)	0.002	
3	5		6	6	169.323(15)	-0.008	3155.752(3)	0.000	
2	4		5	5	171.140(15)	-0.001	3157.575(3)	0.005	
1	3		4	4	172.995(25)	-0.005	3159.442(8)	0.007	
0	2		3	3			3161.320(10)	-0.031	
4	2		1	1			3170.274(10)	-0.006	
5	3		2	2			3172.150(8)	0.003	
6	4		3	3	187.560(15)	-0.012	3173.950(3)	0.001	
7	5		4	4	189.331(15)	0.003	3175.690(3)	0.001	
8	6		5	5	191.004(15)	-0.007	3177.361(3)	0.003	
9	7		6	6	192.598(15)	-0.003	3178.939(3)	0.002	
10	8		7	7	194.055(15)	-0.002	3180.395(3)	0.001	
11	9		8	8	195.257(20)	-0.025	3181.655(3)	0.004	
1	3		4	4			3183.997(20) ^d	-0.001	
0	2		3	3			3186.149(20) ^d	0.025	
3	1		0	0			3191.988(20) ^d	0.020	
4	2		1	1			3192.820(20) ^d	-0.039	
5	3		2	2			3193.287(20) ^d	-0.056	

^aIn all cases, $j_{\rm H}=2\leftarrow 0$. For $S_0(0)$, $v=0\leftarrow 0$; and for $S_1(0)$, $v=1\leftarrow 0$. Unless otherwise indicated, $n=0\leftarrow 0$.

^bEstimated line position uncertainties in units of the last quoted digit are given in parentheses.

Calculation based on the XC(fit) potential surface of Bissonette et al. (Ref. 27).

^dFor these weak transitions, $n = 1 \leftarrow 0$.

addition to the $Q_1(1)$ and $S_1(0)$ quadrupole lines. Some weaker sharp lines in the region of the $S_1(0)$ spectrum are due to CH₄ impurity. The somewhat wavy background underlying the $Q_1(0)$ band in the top trace of Fig. 11 is partly



FIG. 11. The $Q_1(0)$ and $S_1(0)$ bands of the HD–Ar complex. Note the presence of the $R_1(2)$ electric dipole transition of the HD monomer, in addition to the $Q_1(1)$ and $S_1(0)$ quadrupole transitions also present in H₂ and D₂. The stick spectrum above the $S_1(0)$ trace indicates some weak lines due to CH₄ impurity in the gas sample. Experimental conditions are given in Table I.

due to the unresolved P(l) and R(l) branches of the HD–Ar $Q_1(1)$ band, though this is not obvious from the portion shown here (about 35% of the HD molecules are in the $j_H=1$ state at 77 K).

IV. CONCLUSIONS

All of the bands observed here may be subject to predissociation, not just $S_1(0)$ of HD–Ar, since the upper states have much greater energy than is required to break the complex apart.⁷ However, calculations^{13,17,18,20,23,32} indicate that the relevant predissociation line broadening is generally expected to be of the order of 0.05 cm⁻¹ or less (much less in some cases). Thus predissociation broadening is masked in the current results by the combined effects of pressure broadening and instrumental resolution.

The calculations²⁷ represented here, based on the new exchange-Coulomb (XC(fit)] potential surface, do an excellent job of reproducing the present experimental results in Tables II–VIII. In many regions, the smoothness of the agreement between experiment and theory suggests that the actual experimental uncertainties might be somewhat smaller than is given in Tables II–VIII. This is partly a reflection of the fact that the relative wave number accuracy (precision) of the Fourier transform IR measurements is better than its absolute accuracy. There are also a few data for which the difference between observed and calculated values is larger

TABLE IX. Observed transitions in the $Q_1(0)$ band of HD-Ar.^a

<i>l'</i>	J'	\leftarrow	<i>l</i> "	J''	n'	\leftarrow	n″	Observed ^b (cm ⁻¹)
3	3		2	2	0		1	3611.414(20)
4	4		3	3	0		1	3613.466(20)
8	8		9	9	0		0	3624.997(8)
7	7		8	8	0		0	3625.375(5)
6	6		7	7	0		0	3625.958(5)
5	5		6	6	0		0	3626.622(5)
4	4		5	5	0		0	3627.338(5)
3	3		4	4	0		0	3628.090(5)
2	2		3	3	0		0	3628.867(5)
1	1		2	2	0		0	3629.651(6)
0	0		1	1	0		0	3630.458(8)
1	1		0	0	0		0	3632.041(8)
2	2		1	1	0		0	3632.817(6)
3	3		2	2	0		0	3633.589(5)
4	4		3	3	0		0	3634.334(5)
5	5		4	4	0		0	3635.050(5)
6	6		5	5	0		0	3635.740(5)
7	7		6	6	0		0	3636.375(5)
8	8		7	7	0		0	3636.947(5)
9	9		8	8	0		0	3637.380(8)
3	3		4	4	1		0	3649.712(15)
2	2		3	3	1		0	3651.694(15)
1	1		2	2	1		0	3653.222(15)
3	3		2	2	1		0	3655.222(20)

^aIn all cases, $v = 1 \leftarrow 0$ and $j_{\rm H} = 0 \leftarrow 0$.

^bEstimated line position uncertainties in units of the last quoted digit are given in parentheses.

than the quoted uncertainty. These are mostly broad, weak, or overlapped lines whose measurement was more difficult.

The present data may also be compared with calculations³³ based on the TT₃ potential of Le Roy and Hutson.¹⁴ As an example, we show this comparison here for the H₂–Ar and D₂–Ar $Q_1(0)$ bands in Tables II and VI. In some regions, the TT₃ surface gives a good fit to the experimental values, but in other regions there are fairly large systematic deviations. Overall, the dimensionless rms deviation between the present IR data and theory is 5.6 for TT₃, as compared to 0.7 for XC(fit). It is interesting that some of the largest discrepancies with the TT₃-based calculations occur for the transitions involving the excited van der Waals

TABLE X. Widths of transitions in the $S_1(0)$ band of HD-Ar (in cm⁻¹).

		Observed width ^a	Calculated width			
Transition	l',J'	(this work)	Ref. 19	Ref. 22	Ref. 24	
N(9)	6,8	0.59(7)	0.663	0.74		
N(8)	5,7	0.73(7)	0.723	0.73		
N(7)	4,6	0.74(7)	0.769	0.70	0.76	
N(6)	3,5	0.78(8)	0.795	0.66	0.78	
N(5)	2,4	0.87(10)	0.801	0.61	0.70	
<i>T</i> (2)	5,3	0.84(10)	0.758	0.79	0.71	
<i>T</i> (3)	6,4	0.68(6)	0.643	0.69	0.60	
T(4)	7,5	0.56(4)	0.535	0.50	0.54	
<i>T</i> (5)	8,6	0.47(3)	0.425	0.42	0.40	
<i>T</i> (6)	9,7	0.38(3)	0.329	0.34	0.33	
T(7)	10,8	1.33(19)	0.726		0.76	

^aThe quantity in parentheses is an estimate of the uncertainty.

stretching states, n=1, of H₂-Ar and D₂-Ar. Clearly, the n=1 level positions contain important information on the shape of the potential, especially for larger intermolecular separations (see Fig. 1). This point is discussed further in the following paper.²⁷

The results of the present and following²⁷ research reestablish hydrogen-argon as having the best known intermolecular potential surface among weakly bound triatomic systems. In particular, extensive information on the hydrogen stretching dependence of the potential comes from newly observed bands involving H₂ in its v=0 and 2 vibrational states, as well as D₂ in v=0. And new information on the shape of the potential comes from the observation of weak transitions involving the excited van der Waals stretching state, n=1.

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