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Collision-induced absorption by H_2-He pairs in the H_2 fundamental band at 78 and 298 K

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Measurements of collision-induced absorption spectra in the H_2 fundamental band are reported for gaseous mixtures of hydrogen and helium at temperatures of 78 and 298 K and frequencies from about 3900 to 5200 cm^{-1}. Spectral line shapes are calculated from the fundamental theory with the isotropic interaction approximation, which has been successful in all previous comparisons of the kind for pure hydrogen and hydrogen–rare-gas mixtures. In the present case, however, the comparison of measured and calculated absorption profiles suggests that small differences between theory and measurement may exist for H_2-He in the H_2 fundamental band, which are marginally greater than the combined uncertainties of theory and measurement. Presumably, these are due to the neglect of the anisotropy of the interaction; the H_2-He system in the H_2 fundamental band is more sensitive to the anisotropy of the interaction than the systems and bands studied previously.

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I. INTRODUCTION

The atmospheres of the outer planets consist of hydrogen and helium, with but traces of other substances. It is clear that neither the hydrogen molecule (H_2) nor the helium atom (He) absorb significantly in the infrared region of the electromagnetic spectrum and yet various H_2 $S(j)$ and $Q(j)$ lines appear prominently as highly diffuse, dark fringes in the emission spectra of these atmospheres [1, 2]; atmospheres are essentially opaque in such rotovibrational bands of H_2. "Collision-induced" absorption (emission) is due to dipole moments induced by intermolecular interactions [3], for example, by polarization of the collisional partner in the electric multipole field of H_2 and by momentary rearrangement of electronic charge in the presence of exchange interactions (Pauli principle) [4–6]. The induced dipoles are modulated by vibrational, rotational, and translational motion of the molecules involved. The exact knowledge of the resulting rovibrotranslational spectra, which depend on frequency, gas densities of He and H_2, and temperature, is important in astrophysics for the modeling of stellar and planetary atmospheres, especially for the measurement of vertical temperature profiles and for the determination of certain parameters, such as the abundance ratio of helium and hydrogen. Perhaps even more importantly, collision-induced spectra reveal many interesting details of the interaction of binary, ternary, etc., molecular complexes and are thus invaluable for fundamental studies of supramolecular systems of various sizes and composition [7].

Since the first observations of the collision-induced fundamental bands of various molecular gases by Crawford *et al.* [8, 9], close to 1000 experimental and theoretical studies have been reported [10, 11]. Although the collision-induced absorption spectra of the H_2 fundamental band have been extensively studied over a wide temperature range, we were not able to find a listing of the absorption coefficient at a given temperature as a function of frequency. As a matter of fact, the spectral profiles are often reproduced merely in figures which are so small that the information cannot be extracted with the desirable accuracy.

In that previous paper [12] we measured the collision-induced spectra of H_2-H_2 and H_2-He at wavelengths near 2 μm at room temperature by using a 3-m-long high-pressure cell attached to a Czerny-Turner grating spectrometer. In this work we present the results of similar measurements at ambient temperature and 78 K. The binary absorption coefficients for H_2-He were measured in the frequency range from roughly 3900 to 5100 cm^{-1}.

II. EXPERIMENT

A. Procedures

The spectra are recorded with the help of a Fourier-transform spectrometer with a resolution of 0.5 cm^{-1} full width at half maximum (FWHM). We use an optical filter for work in the frequency range from 2000 to 6000 cm^{-1}. The spectrometer is calibrated with lines of CO in the fundamental band. Thirty-two scans are superimposed for each interferogram; a four-term Blackmann-Harris apodization function is used. The high-pressure absorption cell can be used at pressures up to 500 bar; its optical path length is 215.4 ±0.1 cm. This cell is made from an AISI 316 L stainless-steel high-pressure pipe, with a central bore of 16 mm diameter; its ends are closed with two high-pressure flanges made from a heavy, cylindrical body screwed and soldered with the pipe. The optical windows are synthetic sapphire, or other materials where necessary, 25 mm in diameter and up to 20 mm thick. The windows are in contact with a stainless-steel disk sealed to the cell with an indium wire. The surface of the window and the mating steel surface are carefully polished for optical quality of the window. A coiled copper tube and a chamber concentric with the pipe allow the circulation of a coolant. This chamber, surrounded with several layers of aluminized Mylar, is enclosed in a vacuum tank, connected at one end to the spectrometer and with the other to a dry-ice–acetone cooled PbS detector; atmospheric absorption was thus avoided. The cell is connected to a high pressure manifold, including an electric power diaphragm-type compressor. The pressures are measured with a 0–160 bar strain-gauge-type pressure transducer (accuracy 0.1% full scale). The temperature is measured by five T-type thermocouples so that any gradient of temperature may be discovered. A resistive wire wound around the pipe is used as heater for the temperature regulation. A temperature controller connected with a 100-Ω platinum resistance thermometer monitors the coolant circulation and the heater. The ambient temperature is kept constant and the gas temperature is estimated to be known to ≈2 K; at low temperature the uncertainty is ≈1 K. High-purity hydrogen and helium gases (better than 99.9999%) are used without further purification. No catalyst is employed so that this work deals only with normal hydrogen, i.e., with an ortho- to para-H_2 abundance ratio of 3:1. The densities ρ are expressed in amagat units; densities of H_2 are obtained from the initial pressure and temperature of the gas, using the SESAME library EOS Tables [13]. The partial pressures of He in the gas mixtures are determined by an experimental technique [14] and the densities of He are deduced from McCarty's equation of state [15]. The density of H_2 is known with an accuracy of 1% and that of He with about 2%. The density ranges used in the measurements are 14–18 amagat of hydrogen and 72–102 amagat of helium at 298 K; at 78 K the corresponding density ranges are 1–35 and 7–328, respectively.

The absorption coefficient $\alpha(\nu)$ at the frequency ν is obtained from a measurement of incident and transmitted intensity I_0 and I_t, respectively, according to

$$\alpha(\nu) = l^{-1} \ln [I_0(\nu)/I_t(\nu)] ,$$

where l is the optical path length. The homogeneity of the gas mixture inside the cell is determined by recording spectra every 15 min or so until no further variation of absorption with time is noticed.

B. Binary absorption coefficients

With the help of spline interpolation, the absorption coefficient $\alpha(\nu)$ is determined at frequency spacings of 10 cm^{-1}. At each frequency point, we study the variation of the absorption coefficient with the product of hydrogen and helium densities. Within the small experimental errors a linear dependence is found, except in the region of the intercollisional dips, where such a dependence must not be expected. In other words, the absorption is produced by H_2-He pairs, with no discernible interference by ternary absorption processes (except in the intercollisional dips). The binary absorption coefficients are determined by applying a linear least-squares procedure to the spline-interpolated experimental $\alpha(\nu)$ values. The spectra are shown in Figs. 1 and 2 (solid trace with discernible noise). A listing of the measured spectrum at the temperatures of 78 and 298 K is provided in Table I.

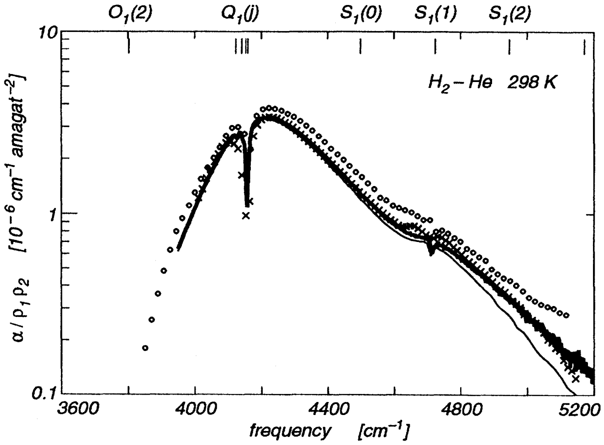

FIG. 1. Measured absorption spectra of H_2-He pairs at 298 K: heavy solid line, present work; thin solid line, [12]; ×, [16]; ○, [17].

In Table I, to the right of each value of the absorption coefficient α_{12}, our estimate of the experimental uncertainty $\Delta\alpha$ is given. These numbers represent twice the standard deviation of the least-squares fits, plus 3% (at 298 K) or 4% (at 78 K). The main source of uncertainties in the measurements arises from the pure hydrogen base line determinations, especially at the lower temperature, in the low- and high-frequency wings (< 4000 and > 5000 cm^{-1}, respectively), where the absorption is weak and the measurement involves subtraction of two signals of comparable magnitude.

C. Comparison with other measurements

Also shown in Figs. 1 and 2 are previous measurements (dots, circles, etc., [12, 16, 17]). We note that the agreement among the various measurements may not be as good as one would expect, but we must remember that

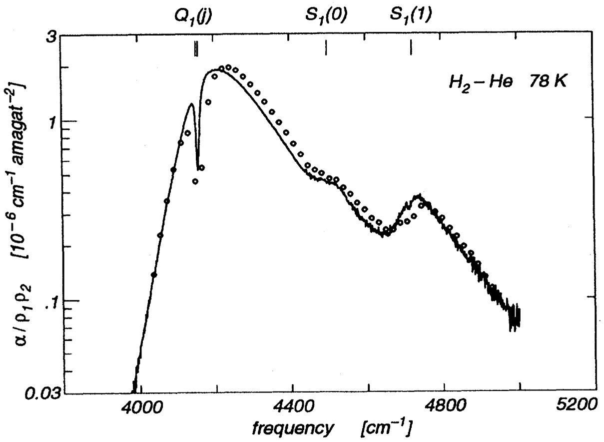

FIG. 2. Measured absorption spectra of H_2-He pairs at 78 K: solid line, present work; ○, [17].

most of the data shown had to be read from small figures. At least some of the spread of the data seen in Figs. 1 and 2 may be due to the limited accuracy with which the data could be extracted from the figures. We believe that our measurement is the most accurate one presently available for H_2-He pairs in the H_2 fundamental band.

D. Many-body effects

The relatively sharp absorption dips, which appear near the $Q_1(j)$ and $S_1(1)$ transition frequencies of H_2, are due to interference of the overlap dipole components induced in subsequent collisions [18]. These are many-body effects and have been experimentally analyzed at room temperature elsewhere [12].

III. THEORY

Quantum-chemical methods exist which permit the computation of the dipole surface of systems such as H_2-He from first principles [19]. Induced dipole surfaces of H_2-He have been reported [20–23]. The collisional complex is treated like one molecule in the self-consistent field and the size-consistent, coupled electron pair approximations which separates correctly at distant range [23]. Recent work has made an all-out effort to obtain data of an estimated absolute accuracy in the 3% range [24] and accounts for the dependence of the dipole strengths on the vibrational coordinate and centrifugal distortion of the H_2 molecule; we will use this most highly refined dipole surface in our calculation of the absorption profile below.

For meaningful line shape calculations, an accurate interaction potential is needed besides the dipole surface. We choose the isotropic part of one of the most advanced *ab initio* potentials for H_2-He [25], which has been slightly modified so that it is consistent with selected experimental data [26]. In the line shape calculations, we account for the dependence of the interaction potential on the vibrational coordinate, which was found to be important for the vibrational bands [7].

Line shapes are computed with the help of a quantum-mechanical computer code describing the dynamics of the

TABLE I. Listing of the measured absorption coefficient of H_2-He pairs and the estimated experimental uncertainties at 78 and 298 K. (Units of density are the amagal, abbreviated here "am"; 1 am ≈ 2.69×10^{19} molecules/cm^3.)

ν	$T = 298$ K		$T = 78$ K		ν	$T = 298$ K		$T = 78$ K		ν	$T = 298$ K		$T = 78$ K	
	α_{12}	$\Delta\alpha$	α_{12}	$\Delta\alpha$		α_{12}	$\Delta\alpha$	α_{12}	$\Delta\alpha$		α_{12}	$\Delta\alpha$	α_{12}	$\Delta\alpha$
(cm^{-1})		(10^{-9} cm^{-1} am^{-2})			(cm^{-1})		(10^{-9} cm^{-1} am^{-2})			(cm^{-1})		(10^{-9} cm^{-1} am^{-2})		
3800	97.5	30			4260	3197	147	1654	77	4730	654	47	390	28
3810	128	29			4270	3127	138	1573	73	4740	654	55	404	27
3820	140	32			4280	3053	133	1481	70	4750	636	52	378	26
3830	158	28			4290	2976	124	1402	64	4760	625	55	342	27
3840	191	38			4300	2894	134	1328	63	4770	613	36	336	22
3850	236	38			4310	2803	116	1249	62	4780	607	46	307	25
3860	247	33			4320	2693	110	1171	52	4790	572	36	296	32
3870	230	39			4330	2604	113	1093	53	4800	565	48	263	20
3880	278	43			4340	2526	104	1025	50	4810	547	50	261	24
3890	317	33			4350	2424	98	951	48	4820	518	37	248	30
3900	354	37	23.5	8.2	4360	2333	94	885	44	4830	495	53	226	23
3910	392	37	22.9	4.1	4370	2228	105	832	40	4840	494	32	214	25
3920	434	34	25.4	4.1	4380	2145	102	763	46	4850	459	48	211	28
3930	488	39	28.7	4.5	4390	2059	97	719	38	4860	448	43	187	23
3940	551	42	31.7	6.1	4400	1978	92	666	33	4870	437	40	182	21
3950	615	41	32.3	4.1	4410	1885	90	633	42	4880	413	42	175	28
3960	691	41	35.5	6.1	4420	1820	81	579	36	4890	406	40	169	19
3970	775	44	42.0	5.2	4430	1720	87	552	30	4900	394	36	150	20
3980	860	42	50.1	6.4	4440	1649	83	527	36	4910	361	36	145	23
3990	946	49	59.9	6.6	4450	1587	75	499	28	4920	341	39	132	24
4000	1051	54	67.7	6.0	4460	1515	69	476	29	4930	340	36	118	22
4010	1164	63	87.5	8.7	4470	1457	73	481	21	4940	339	29	119	30
4020	1280	67	109	11	4480	1403	70	473	38	4950	316	35	121	22
4030	1408	69	135	11	4490	1336	73	474	21	4960	303	32	104	25
4040	1549	71	166	11	4500	1256	63	457	33	4970	302	32	110	15
4050	1682	76	202	12	4510	1226	74	461	36	4980	283	45	96.0	18.8
4060	1836	83	263	15	4520	1179	68	438	31	4990	271	33	85.9	16.9
4070	1986	90	319	18	4530	1123	61	421	25	5000	270	33	85.2	11.3
4080	2135	96	403	18	4540	1083	59	392	27	5010	255	32	80.6	21.2
4090	2307	98	501	25	4550	1036	54	370	33	5020	242	30	79.4	14.2
4100	2453	108	622	32	4560	984	60	349	26	5030	228	33	75.4	13.6
4110	2603	122	761	36	4570	955	49	328	18	5040	220	31	70.5	12.5
4120	2680	128	914	42	4580	911	55	309	18	5050	216	35	72.4	13.6
4125	2581	119	1002	46	4590	890	50	297	26	5060	198	42	70.2	7.9
4130	2659	132	1087	56	4600	865	55	275	22	5070	180	29	67.0	7.5
4140	2688	157	1235	62	4610	844	48	266	23	5080	175	44	73.6	17.2
4150	2200	195	1056	116	4620	806	51	257	19	5090	172	34	56.3	14.1
4156	1076	94	548	54	4630	787	58	249	22	5100	167	30	43.4	18.2
4160	1551	180	792	122	4640	770	44	242	20	5110	146	33		
4170	2808	189	1510	126	4650	763	48	246	20	5120	148	38		
4180	3137	156	1743	112	4660	742	47	244	29	5130	155	32		
4190	3268	157	1839	84	4670	740	49	264	18	5140	133	36		
4200	3345	150	1887	85	4680	738	45	283	26	5150	132	39		
4210	3366	148	1906	92	4690	731	54	301	24	5160	146	34		
4220	3355	139	1890	80	4700	720	56	330	22	5170	123	41		
4230	3329	148	1852	83	4710	659	52	334	33	5180	110	42		
4240	3306	146	1793	85	4714	596	51	328	34	5190	102	40		
4250	3264	137	1734	74	4720	637	47	362	29	5200	110	39		

interacting pair [22, 24, 27]. A total of about 100 000 radial matrix elements is computed for the four principal dipole components. The numerical uncertainties of the line shape calculations are kept so small ($\approx 1\%$) that the overall uncertainty of the parameter-free line shape calculations is given essentially by twice the uncertainties of the dipole surface, or about 6%. The line shape calculation focuses strictly on the binary system of H_2 and He; no attempts were made here to describe theoretically the relatively sharp absorption dips discernible in the measurement near the $Q_1(j)$ and $S_1(1)$ transition frequencies of H_2, which have been explained by van Kranendonk [18] as arising from intercollisional interference of the overlap dipole components induced in successive collisions.

Results of the line shape calculations are shown in the Figs. 3 and 4 as heavy dotted lines. We emphasize that the line shape calculations are completely *ab initio*, without any adjustable parameters (except for the refinements of the interaction potential, which was based on other measurements and done elsewhere [26]).

IV. CONCLUSION

The agreement of theory (dotted curves, Figs. 3 and 4) and measurement is generally satisfactory, except in two narrow regions near the H_2 $Q_1(j)$ and $S_1(1)$ transition frequencies (marked at the top of the figures), where the intercollisional dips are seen in the measurement. As we mentioned above, our binary theory does not attempt to model these many-body features.

At the higher temperature, Fig. 3, theory suggests absorption which is consistently above the measurement by several percent; maximal deviations of up to 12% occur near the $S_1(1)$ line. At the lower temperature, Fig. 4, theory seems to suggest slightly less absorption than the measurement. For the most part, though, the differences between theory and measurement are less than the combined uncertainties of theory ($\sim 6\%$) and measurement ($\sim 5\%$). Only near the H_2 $S_1(1)$ transition frequency (Fig. 3) and in the "blue" wing of the $S_1(1)$ line (Fig. 4) the differences approach and slightly exceed this estimate of the combined uncertainties and may thus be significant.

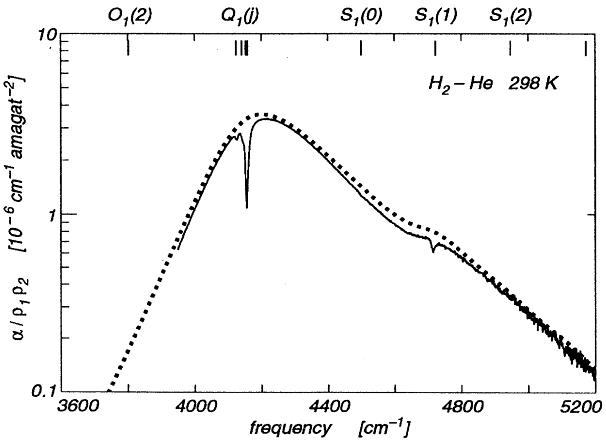

FIG. 3. Absorption spectra of H_2-He pairs at 298 K: solid line, measurement; dotted curve, *ab initio* calculation, based on the isotropic interaction approximation.

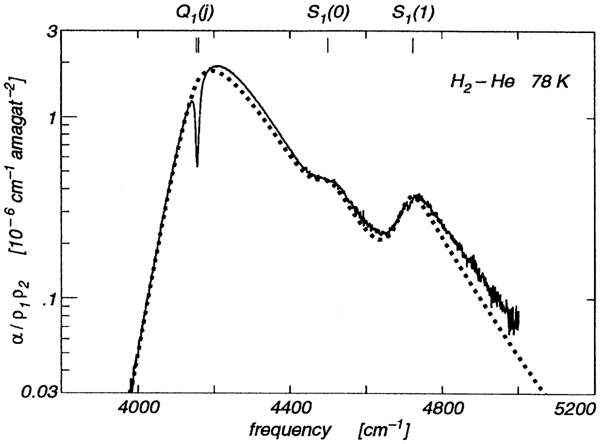

FIG. 4. Absorption spectra of H_2-He pairs at 78 K: solid line, measurement; dotted curve, *ab initio* calculation, based on the isotropic interaction approximation.

In all the exacting comparisons of measured and calculated spectral profiles mentioned above, line shapes were calculated with the assumption of *isotropic* interaction. An exact treatment would have made use of an anisotropic interaction potential, e.g., for an atom-diatom pair,

$$V(R, \cos\vartheta) = V_0(R) + \sum_{\ell>0} V_\ell(R)\, P_\ell(\cos\vartheta)\,.$$

However, never before was this felt to be necessary; surprisingly close agreement (roughly ±5%) of measured and computed line profiles was observed in the studies mentioned above even if the anisotropy of the interaction was neglected.

Specifically, such comparisons of theory and measurement have been made in the rototranslational (far-infrared) absorption band of hydrogen [28] and hydrogen-helium mixtures [23, 29]. In these cases, the consistency of theory and measurement was impressive, better than our conservative estimates would have suggested. Furthermore, in the fundamental band of pure hydrogen, close agreement of theory and measurement was likewise observed [30, 31]. In view of the agreement observed previously in every one of these comparable studies, we find the less than perfect agreement of theory and measurement seen above a little surprising.

Theoretical efforts are being undertaken to study the effects of the anisotropy of the interaction on the collision-induced absorption spectra [32–34] which was neglected in the present work. One consequence of accounting for the anisotropy is a mixing of dipole components. Specifically, the quadrupole-induced dipole component (elsewhere labeled $\lambda L = 23$ [7]) mixes with the isotropic overlap component ($\lambda L = 01$), which for H_2-He is very strong. While in the isotropic interaction approximation we have used here a relatively sharp $S_1(1)$ line is obtained (Fig. 4), there is little doubt that the admixture of $\lambda L = 01$ must broaden the S line, which should improve the agreement with the experimental data [32, 33]. Furthermore, it is well known that accounting for the anisotropy tends to lower absorption by several percent, especially at the higher temperatures [33] — which again seems to be what is needed for improving the agreement with the data. The anisotropy of the vibrationally excited H_2 molecule (the final state of the observed transitions) is more anisotropic than the vibrational ground state (which is also the final state in the case of the rototranslational band). Consequently, it is perhaps not surprising that similar marginal discrepancies were *not* observed for H_2-H_2 and H_2-He in the far infrared. In the fundamental band for H_2-H_2 pairs, the isotropic dipole component ($\lambda L = 01$) is much weaker than for H_2-He, so that the observed close agreement of theory and measurement there seems to be natural. More work is required to shed light on these admittedly marginal inconsistencies of H_2-He pairs in the fundamental band.

ACKNOWLEDGMENTS

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