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

C. Brodbeck, Nguyen-Van-Thanh, A. Jean-Louis, and J.-P. Bouanich
Laboratoire de Physique Moléculaire et Applications,
Université Paris–Sud, Bâtiment 350, 91405 Orsay Cedex, France

Lothar Frommhold
Department of Physics, University of Texas, Austin, Texas 78712

Measurements of the binary collision-induced absorption in hydrogen gas in the fundamental band of H_2 (near 2.3 μm) are obtained at temperatures of 298 and 78 K. Agreement is observed with existing measurements and with an *ab initio* quantum calculation of the spectral profile which is based on the isotropic interaction approximation. The comparison suggests that such calculations may be used to generate the most reliable predictions of the binary spectra of hydrogen over the range of temperatures considered here.

I. INTRODUCTION

Compressed gases composed of nonpolar molecules like H_2 absorb infrared radiation [1,2]. Absorption continua are observed in various rotovibrational bands which are forbidden in the noninteracting molecules. Collision-induced absorption arises from dipole moments induced by molecular interactions. For interacting H_2 molecules, dipole moments are induced mainly by polarization of a molecule in the quadrupole field of another molecule, and by exchange forces. Since molecular hydrogen is the most abundant constituent in the atmospheres of the major planets, the collision-induced absorption spectra of H_2 pairs are an important source of thermal emission and absorption [3,4]. The detailed knowledge of the spectral absorption profiles of the rototranslational and fundamental bands of H_2 is of considerable interest in astrophysics. For example, the spectrum of Jupiter shows a strong absorption between 2 and 2.3 μm which is due mainly to collisional H_2-H_2 complexes [5], and the properties of the atmospheres of various cool stars are to a large extent controlled by collision-induced absorption by H_2 pairs [6]; a small fraction of the H_2 pairs exist as bound van der Waals molecules [7].

Since the first observations of the collision-induced fundamental band of hydrogen by Welsh *et al.* [8] many experimental and theoretical studies have been undertaken; roughly nine hundred original papers have appeared in the field since 1949 [9,10]. Although the interaction-induced spectra of hydrogen in the fundamental band have been extensively investigated at room temperature [11–14] and near 78 K [11–17], we have not found in the literature listings of the absorption coefficient as function of frequency. Actually, the spectral profiles are often reproduced in small figures which do not lend themselves to an accurate reading of the collision-induced absorption coefficients. Listings of data of the kind are, however, necessary for the comparison of measurement and theory and also for all modeling attempts of planetary and stellar atmospheres.

II. EXPERIMENTAL RESULTS

In previous papers [18,19], we measured and analyzed the collision-induced spectra of H_2-H_2 and H_2-He complexes at room temperature and wavelengths of 2 and 5 μm by using a high pressure cell attached to a Czerny-Turner grating spectrometer. In this work, we present the results of similar measurements performed with a Fourier transform (FT) spectrometer in the fundamental band of pure hydrogen at ambient and liquid nitrogen temperature.

A. Experimental arrangement

The spectra were recorded with the help of a Bruker IFS 66V FT spectrometer with a resolution of 0.5 cm^{-1} full width at half maximum (FWHM). We used an optical filter to work in the frequency range from 2000 – 6000 cm^{-1}. The spectrometer was accurately calibrated with lines of CO in the fundamental band. Thirty-two scans were superimposed to yield each interferogram and we used a four-term Blackmann-Harris apodization function.

The high-pressure absorption cell has an optical pathlength of $l = 215.4 \pm 0.1$ cm. The pressures were measured with a 0–160 bar strain-gauge-type pressure transducer (accuracy 0.1% full scale) as previously described [20]. The ambient temperature is kept constant and the gas temperature was estimated to be known to ± 2 K; at the low temperature the uncertainty is ± 1 K.

High-purity ($> 99.9999\%$) hydrogen gas was purchased and used without further purification. No catalyst was used in this work which is concerned with "normal" hydrogen, i.e., hydrogen with an ortho- to para-H_2 abundance ration of 3:1. The densities ρ (in amagat units) of H_2 were obtained from the initial pressure and temperature of the gas by using the equation of state Tables [21]. The density of the hydrogen is known with an accuracy of 1%.

B. Experimental procedure

The absorption coefficient $\alpha(\nu)$ at the wave number ν is obtained from

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

where l is the optical path length and I_0 and I_t are the transmitted intensities of the empty and the pressurized

TABLE I. Listing of the absorption coefficient recorded at 298 K, in 10^{-9} cm^{-1} amagat^{-2} units.

ν (cm^{-1})	$\alpha^{(2)}$ (10^{-9} cm^{-1} am^{-2})	$\Delta\alpha^{(2)}$	ν (cm^{-1})	$\alpha^{(2)}$ (10^{-9} cm^{-1} am^{-2})	$\Delta\alpha^{(2)}$	ν (cm^{-1})	$\alpha^{(2)}$ (10^{-9} cm^{-1} am^{-2})	$\Delta\alpha^{(2)}$
3700	238	21	4220	3664	96	4760	2660	60
3710	247	17	4230	3583	80	4770	2563	67
3720	255	16	4240	3521	79	4780	2435	61
3730	273	21	4250	3428	80	4790	2358	70
3740	302	26	4260	3349	78	4800	2264	63
3750	298	31	4270	3253	77	4810	2160	56
3760	310	14	4280	3170	68	4820	2029	67
3770	321	25	4290	3084	75	4830	1957	57
3780	338	18	4300	2998	77	4840	1874	48
3790	358	17	4310	2897	68	4850	1777	48
3800	389	29	4320	2834	67	4860	1706	46
3810	407	25	4330	2746	64	4870	1636	46
3820	429	28	4340	2670	59	4880	1570	38
3830	447	21	4350	2622	93	4890	1502	47
3840	468	24	4360	2539	60	4900	1451	38
3850	500	29	4370	2480	59	4910	1377	35
3860	511	23	4380	2416	54	4920	1330	34
3870	517	33	4390	2377	55	4930	1296	44
3880	544	32	4400	2323	63	4940	1247	39
3890	584	24	4410	2288	82	4950	1207	47
3900	625	25	4420	2274	73	4960	1152	37
3910	646	26	4430	2234	62	4970	1112	42
3920	693	24	4440	2216	53	4980	1066	33
3930	745	27	4450	2219	52	4990	1033	37
3940	793	28	4460	2197	53	5000	988	39
3950	851	24	4470	2217	56	5010	940	38
3960	920	35	4480	2198	48	5020	914	39
3970	997	28	4490	2199	50	5030	876	39
3980	1080	28	4500	2162	53	5040	855	37
3990	1170	31	4510	2171	54	5050	817	30
4000	1273	33	4520	2130	50	5060	798	26
4010	1383	37	4530	2122	54	5070	768	30
4020	1504	36	4540	2102	54	5080	749	36
4030	1637	43	4550	2061	52	5090	718	31
4040	1782	39	4560	2032	52	5100	697	52
4050	1927	50	4570	2020	53	5110	681	35
4060	2088	48	4580	2005	47	5120	654	38
4070	2259	51	4590	2010	48	5130	639	28
4080	2445	63	4600	2011	48	5140	618	24
4090	2630	57	4610	2017	50	5150	603	32
4100	2831	61	4620	2054	47	5160	582	30
4110	3002	80	4630	2100	50	5170	568	33
4120	3165	84	4640	2150	58	5180	546	25
4126	3160	80	4650	2234	58	5190	534	28
4130	3316	91	4660	2295	50	5200	518	28
4140	3437	90	4670	2400	63	5210	494	21
4143	3344	92	4680	2482	57	5220	484	23
4150	3414	119	4690	2559	57	5230	455	27
4155	2596	87	4700	2643	67	5240	434	29
4160	3320	148	4710	2669	66	5250	423	24
4170	3734	94	4712	2606	71	5260	399	27
4180	3782	98	4720	2742	61	5270	387	29
4190	3791	81	4730	2763	62	5280	363	26
4200	3756	87	4740	2780	62	5290	343	28
4210	3709	89	4750	2731	75	5300	339	46

C. BRODBECK *et al.*

cell, respectively, at frequency ν. More precisely, we obtained for each absorption measurement of the cell filled with hydrogen of the pressure P a "background" spectrum of the cell filled with the same pressure P of helium, but no significant difference was observed between the spectra recorded with an empty cell and one filled with helium. In order to eliminate data affected by any slow drift of the source intensity, we accepted only such measurements for which the background spectra recorded before and after the sample spectrum were the same.

C. Intercollisional dips

The Q branch and, to a lesser extent, the $S(1)$ line show relatively narrow absorption minima ("dips") at the $Q_1(j)$ and $S_1(j)$ rotovibrational transition frequencies of the unperturbed H_2 molecule ($j = 0, 1, \ldots$). Van Kranendonk [22] showed that these dips arise from intercollisional interference effects. The dipole moments induced by electronic overlap in successive collisions are strongly anticorrelated which leads to decreased absorption at fre-

TABLE II. Listing of the absorption coefficient recorded at 78 K, in 10^{-9} cm^{-1} amagat^{-2} units.

ν (cm^{-1})	$\alpha^{(2)}$ (10^{-9} cm^{-1} am^{-2})	$\Delta\alpha^{(2)}$	ν (cm^{-1})	$\alpha^{(2)}$ (10^{-9} cm^{-1} am^{-2})	$\Delta\alpha^{(2)}$	ν (cm^{-1})	$\alpha^{(2)}$ (10^{-9} cm^{-1} am^{-2})	$\Delta\alpha^{(2)}$
3900	45.6	13	4330	1317	48	4780	2446	86
3910	47.6	14	4340	1244	49	4790	2139	89
3920	48.8	15	4350	1170	47	4800	1882	90
3930	51.3	14	4360	1098	39	4810	1655	70
3940	56.6	17	4370	1053	39	4820	1449	62
3950	57.3	16	4380	1004	40	4830	1294	72
3960	62.1	13	4390	963	40	4840	1157	55
3970	74.2	17	4400	946	40	4850	1022	43
3980	83.3	17	4410	928	39	4860	922	48
3990	92.5	17	4420	942	43	4870	826	44
4000	107	17	4430	964	45	4880	757	40
4010	127	20	4440	1034	49	4890	674	38
4020	150	19	4450	1132	55	4900	599	36
4030	187	23	4460	1277	49	4910	540	42
4040	234	19	4470	1482	65	4920	518	34
4050	289	22	4480	1732	66	4930	468	30
4060	365	25	4490	1998	68	4940	433	28
4070	465	25	4500	2182	89	4950	412	29
4080	596	30	4510	2339	89	4960	384	27
4090	772	44	4520	2265	97	4970	351	24
4100	999	47	4530	2134	80	4980	324	24
4110	1282	61	4540	1964	80	4990	301	25
4120	1650	65	4550	1769	73	5000	288	24
4130	2094	85	4560	1578	73	5010	269	17
4140	2587	107	4570	1418	64	5020	259	24
4150	3015	125	4580	1291	69	5030	250	19
4155	2831	115	4590	1169	61	5040	241	20
4160	3223	129	4600	1082	47	5050	230	20
4161	3205	113	4610	1014	47	5060	232	26
4170	3432	134	4620	981	44	5070	228	13
4180	3391	120	4630	964	44	5080	222	18
4190	3222	131	4640	996	50	5090	217	17
4200	3023	109	4650	1047	53	5100	208	25
4210	2825	107	4660	1183	53	5110	189	15
4220	2648	90	4670	1377	56	5120	171	25
4230	2469	82	4680	1638	67	5130	168	19
4240	2308	75	4690	1997	81	5140	157	20
4250	2154	76	4700	2374	79	5150	150	19
4260	2017	70	4710	2768	114	5160	136	15
4270	1893	63	4720	3078	101	5170	123	19
4280	1760	65	4730	3228	118	5180	118	18
4290	1671	57	4740	3282	95	5190	116	18
4300	1569	57	4750	3219	122	5200	104	27
4310	1477	54	4760	3042	90			
4320	1384	54	4770	2720	105			

quency shifts comparable to the reciprocal mean free time between collisions. These dips arise from many-body interactions and are not considered in detail here as we are interested in the spectra arising from binary collisions only. The dips have been previously analyzed experimentally [19,23] at room temperature and will be revisited at higher resolution in a forthcoming paper.

D. Binary absorption coefficient

With the help of spline interpolation of the measured absorption, $\alpha(\nu)$, the absorption coefficient was determined at frequencies spaced 10 cm^{-1} apart. For each of these frequencies, we studied [20] the variation of the absorption coefficient α with the *square* of the hydrogen density, ρ^2. Within the experimental errors a linear dependence was found, except in the region of the intercollisional dips. This proportionality entitles us to write the absorption coefficient as a function of the binary absorption coefficient $\alpha^{(2)}$, according to

$$\alpha(\nu) = \alpha^{(2)}(\nu)\, \rho^2 . \tag{2}$$

The binary absorption coefficients were determined by a linear least-squares procedure on the spline interpolated, $\alpha(\nu)$ values. The absolute uncertainties of $\alpha^{(2)}$ were estimated to be the largest value of either three times the standard deviation σ derived from the least-squares fit, or $2\sigma + 0.02\,\alpha^{(2)}$. We estimate that there is an irreducible experimental error of 2%. The binary absorption coefficients $\alpha^{(2)}(\nu)$ are listed in Table I for the temperature of 298 K and Table II for 78 K, along with their estimated uncertainties.

E. Comparison with other measurements

Our results of our measurements at room temperature are compared in Fig. 1 with the measurements of other authors [11–14]. Similarly, Fig. 2 compares the available data near 78 K [11–17]. A generally satisfactory agreement is observed, considering the fact that such data have often been communicated in small figures only which cannot be accurately read.

III. THEORY

For the computation of the induced dipole moment, the collisional complex consisting of two H₂ molecules was treated like one molecule in state of the art quantum chemical calculations. The basis set accounted for 95% of the correlation energy [24]. The radial, vibrational matrix elements appropriate for the fundamental band $(v = 0 \to v = 1)$ and their dependence on the rotational transitions $(j \to j')$ were determined with a numerical precision believed to be better than 2%. From these data, with the help of an advanced, isotropic H₂-H₂ interaction potential described elsewhere [24], *ab initio* quantum line shapes were computed at the temperatures of
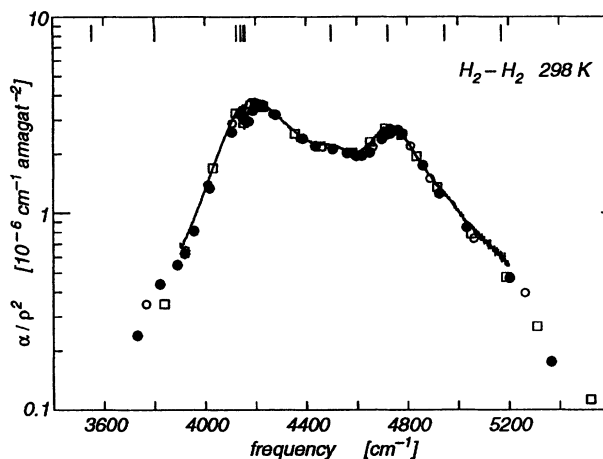

FIG. 1. Comparison of our measurement at 298 K in normal hydrogen with existing measurements by Hunt [11] (●, 300 K), Watanabe [13] (○, 300 K), Hunt and Welsh [12] (■, 300 K), and Reddy et al. [14] (□, 298 K).

the present experiments for comparison with these measurements. We note that spectral intensities are given by the square of the dipole moment so that the numerical precision of the absorption profiles may be expected to be in the four percent range if the isotropic potential approximation—the only significant approximation employed here—does not introduce additional uncertainty.

The results are shown in Figs. 3 and 4. For the comparison, we choose a logarithmic intensity scale so that the wings of the absorption profile may be compared with the same relative precision as the peaks. The agreement of theory and the present measurement is generally in the five percent range or better except, of course, in the narrow region of the intercollisional dips which are many-body features that cannot be reproduced from a binary theory.
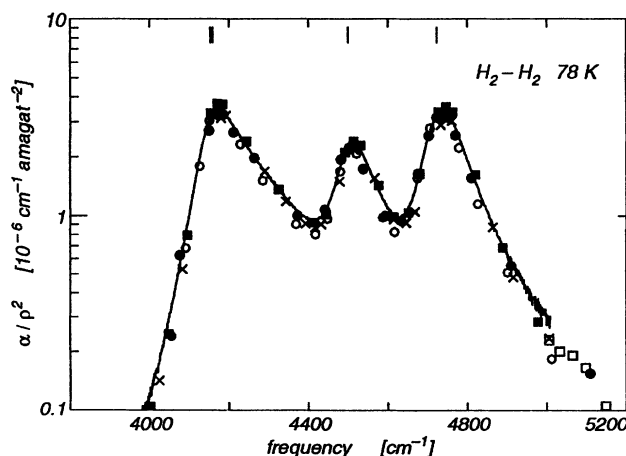

FIG. 2. Comparison of our measurement at 78 K in normal hydrogen with existing measurements by Watanabe and Welsh [15] (○, 77.3 K), Watanabe [13] (●, 77.3 K), Hunt [11] (×, 78 K), Sen et al. [16] (□, 77 K), Watanabe [13] (■, 77.3 K), and Reddy et al. [17] (+, 77 K).

FIG. 3. Comparison of our measurement at 298 K with an *ab initio* calculation (dots) based on an accurate isotropic potential.
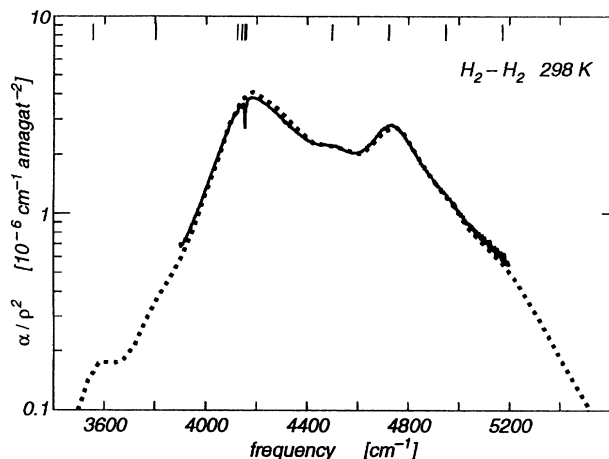

FIG. 4. Comparison of our measurement at 78 K with an *ab initio* calculation (dots) based on an accurate isotropic potential.

IV. CONCLUSION

Accurate measurements are provided of the binary collision-induced absorption spectra of compressed hydrogen at temperatures of 298 and 78 K which are shown to be in agreement with the previous measurements. Spectra computed from the fundamental theory with the assumption of an isotropic interaction potential are also in close agreement with the measurement, suggesting that at these temperatures this approximation is justified for hydrogen, a result significant for astrophysics where these spectra must be known reliably for an analysis of
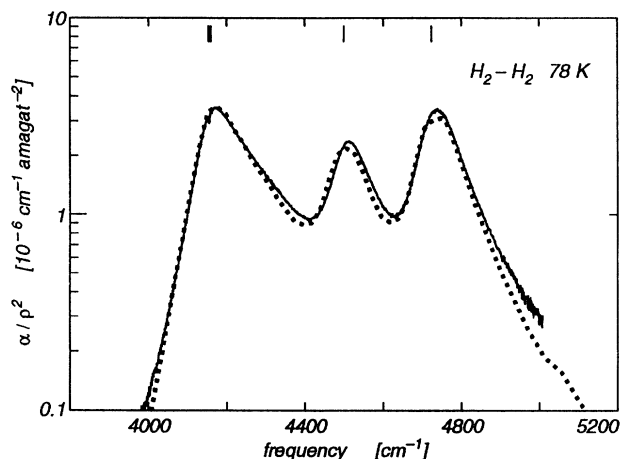
planetary and stellar atmospheres. Work is in preparation in our laboratories which seems to suggest that the isotropic potential approximation may *not* be adequate for similar systems like H_2-He; that work will be reported shortly.

[1] H. L. Welsh, *International Reviews of Science: Physical Chemistry* (Butterworths, London, 1972), Vol. 3, p. 33.

[2] L. Frommhold, *Collision-Induced Absorption in Gases* (Cambridge University Press, Cambridge, England, 1993).

[3] L. M. Trafton, Astrophys. J. **140**, 1340 (1964); **146**, 558 (1966); **179**, 971 (1973).

[4] L. M. Trafton, in *Spectral Line Shapes*, edited by J. Szudy (Ossolineum, Wroclaw, Poland, 1989), Vol. 5, p. 755.

[5] S. J. Kim, P. Drossart, J. Caldwell, and J.-P. Maillard, Icarus **84**, 54 (1990).

[6] A. Borysow, in *Induced Spectroscopy: Advances and Applications*, edited by G. Tabisz (Kluwer Academic, Dordrecht, in press). See also A. Borysow, *Molecules in the Stellar Environment*, edited by U. G. Jorgensen (Springer, New York, 1994).

[7] A. R. W. McKellar, J. Chem. Phys. **92**, 3261 (1990).

[8] H. L. Welsh, M. F. Crawford, and J. L. Locke, Phys. Rev. **76**, 580 (1949).

[9] N. H. Rich and A. R. W. McKellar, Can. J. Phys. **54**, 486 (1976).

[10] J. L. Hunt and J. D. Poll, Mol. Phys. **59**, 163 (1986).

[11] J. L. Hunt, Ph.D. thesis, University of Toronto, 1959.

[12] J. L. Hunt and H. L. Welsh, Can. J. Phys. **42**, 873 (1964).

[13] A. Watanabe, Ph. D. thesis, University of Toronto, 1964.

[14] S. P. Reddy, G. Varghese, and R. D. G. Prasad, Phys. Rev. A **15**, 975 (1977).

[15] A. Watanabe and H. L. Welsh, Can. J. Phys. **43**, 818 (1965).

[16] A. Sen, R. D. G. Prasad, and S. P. Reddy, J. Chem. Phys. **72**, 1716 (1980).

[17] S. P. Reddy, A. Sen, and R. D. G. Prasad, J. Chem. Phys. **72**, 6102 (1980).

[18] J.-P. Bouanich, C. Brodbeck, P. Drossart, and E. Lellouch, J. Quant. Spectros. Radiat. Transfer **42**, 141 (1989).

[19] J.-P. Bouanich, C. Brodbeck, Nguyen-Van-Thanh, and P. Drossart, J. Quant. Spectros. Radiat. Transfer **44**, 393 (1990).

[20] C. Brodbeck, Nguyen-Van-Thanh, A. Jean-Louis, and J.-P. Bouanich, in *Induced Spectroscopy: Advances and Applications* (Ref. [6]).

[21] J. Johnson, *NBS Technical Note 1025* (National Bureau of Standards, Washington, D.C., 1982).

[22] J. Van Kranendonk, Can. J. Phys. **46**, 1173 (1968).

[23] J. D. Kelly and S. L. Bragg, Phys. Rev. A **29**, 1168 (1984).

[24] W. Meyer, A. Borysow, and L. Frommhold, Phys. Rev. A **40**, 6931 (1989).