Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Electronic Supplementary Information to MARVEL analysis of the rotational-vibrational states of the molecular ions H_2D^+ and D_2H^+

Tibor Furtenbacher, Tamás Szidarovszky, Csaba Fábri,
and Attila G. Császár*

Laboratory of Molecular Structure and Dynamics
Institute of Chemistry, Eötvös University
H-1518 Budapest 112, P.O. Box 32, Hungary

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Comments to Table 1

1c 85SaKaHi Very accurate measurement for the pure rotational transition (0 0 0) $2_{20} \leftarrow$ (0 0 0) 2_{21} of *para*-H_2D^+.

1d 05AmHi This experimental study considerably improved the accuracy of previous transition measurements. The $1_{01} \leftarrow 0_{00}$ transition of *para*-H_2D^+ reported but not measured by Amano and Hirao (05AmHi) is incorrect, see the related discussion by Asvany *et al* (08AsRiMuWi).

1e 09YoMaMoTa Measurement of eight very accurate pure rotational transitions.

1f 84BoDeDeDe Very accurate measurement of the pure rotational transition (0 0 0) $1_{10} \leftarrow$ (0 0 0) 1_{11} of *ortho*-H_2D^+.

1g 84WaCoPeWo Very accurate measurement of the 372.4 GHz pure rotational transition (0 0 0) $1_{10} \leftarrow$ (0 0 0) 1_{11} in a 10 cm diameter glow discharge tube system. Nonlinear least-squares averaging was done on 13 independent sets of spectral data.

1h 06Amano This source reports 7 observed transitions in its Table 1 but the first comes from 85SaKaHi, while the second and third ones from 05AmHi. A fourth transition was measured by Jennings *et al.* (90JeDeBaEv) but was not published before though cited in 90PoMc. The energy level schemes reported in Fig. 3 of this paper list energy differences significantly different from the improved MARVEL results of the present study, especially for *para*-H_2D^+.

1i 08AsRiMuWi The first detection of a pure rotational line, the $1_{01} \leftarrow 0_{00}$ transition of *para*-H_2D^+, using action spectroscopy.

1j 86FoMcPeWa Diode laser studies of the ν_2 and ν_3 bands of H_2D^+. The seven transitions 86FoMcPeWa.01 – 86FoMcPeWa.07 come from the PhD thesis of Shy. The transition 86FoMcPeWa.44 was relabeled by Miller *et al* (89MiTeSu). This source contains 7 transitions which are part of FCs and thus could not be validated.

1k 84AmWa This source contains 7 "CD" transitions but they have not been used in this study. 84AmWa.26, at 3168.702(5) cm^{-1}, was relabeled by Kozin *et al.* (88KoPoZo) but this relabeling was questioned by Polyansky and McKellar (90PoMc). We kept the original label, (1 0 0) $5_{05} \leftarrow$ (0 0 0)4_{04}. The 84AmWa.01 transition at 2839.096 cm^{-1} could not be validated, since the MARVEL wavenumber difference is 2839.387 cm^{-1}, based on the energy levels, in cm^{-1}, (1 0 0) 3_{13} = 3243.059(2) and (0 0 0) 4_{14} = 403.672(1). This source contains one transition which is part of an FC and thus could not be validated.

1l 85Amano Remeasurement of the transitions reported in 84AmWa and it contains an additional 10 transitions. There are 12 "CD" transitions reported in this paper but none was used during the present MARVEL analysis.

1m 07AsHuMuKu Transitions were obtained by using laser induced reaction techniques. This paper also contains relative intensities.

1n 02FaDaKoPo This paper also contains relative intensities.

1o 06HlKoPlKo Measured second overtone transition wavenumbers using cavity ringdown absorption spectroscopy.

Comments to Table 2

2c 03HiAm Very accurate measurement for the pure rotational transition (0 0 0) $1_{10} \leftarrow (0\ 0\ 0)1_{01}$.

2d 05AmHi Includes two highly accurate far-infrared measurements originally due to Jennings *et al.* (90JeDeBaEv), as reported in 90PoMc.

2e 08AsRiMuWi Very accurate measurement for the pure rotational transition (0 0 0) $1_{11} \leftarrow (0\ 0\ 0)0_{00}$ of *ortho*-D_2H^+.

2f 86FoMcWa 72 new lines were reported for the ν_2 and ν_3 bands between 1800–2300 cm^{-1}. These authors were able to analyze and label 16 of the lines measured by Shy as part of his PhD thesis. They also suggested slight changes in the original analysis of 84LuAm of the ν_1 band: they omitted one line and interchanged the labels of two others. The transition at 2248.0330 cm^{-1} was relabeled during the present study. This source contains 13 transitions which are part of FCs and thus could not be validated.

2g 90PoMc All five entries of Table I of this paper concerning observed lines (four reassignments and one added transition involving the ν_2 band) are confirmed by the present MARVEL analysis.

2h 84LuAm Observed 35 lines in the 2600–3000 cm^{-1} region and assigned them to the ν_1 fundamental band. This source contains 5 transitions which are part of FCs and thus could not be validated.

2i 02FaDaKoPo Observed 16 lines in the 3800–4200 cm^{-1} region and assigned them to the $2\nu_2$, $2\nu_3$, and $\nu_2 + \nu_3$ bands.

2j 07AsHuMuKu The following three transitions had to be relabeled during the present MARVEL analysis: 6466.9360, 6518.5230, and 6535.9530 cm^{-1}.

2k 06HlPlBaKo Measured second overtone transition wavenumbers using cavity ringdown absorption spectroscopy.

Table 1: Energy levels of *ortho*-H_2D^+ [a]

$v_1v_2v_3$	J K_a K_c	MARVEL	Variational	$v_1v_2v_3$	J K_a K_c	MARVEL	Variational
0 0 0	1 1 1	60.023000(0)[b]	60.03	0 2 0	1 1 1	4343.4630(110)	4343.43
	1 1 0	72.445638(1)	72.46		1 1 0	4361.6545(170)	4361.63
	2 1 2	138.852284(5)	138.84		2 1 2	4412.3819(70)	4412.34
	2 1 1	175.928199(5)	175.94		2 1 1	4466.7744(110)	4466.75
	3 1 3	254.053741(5)	254.02	0 1 1	1 0 1	4495.1644(40)	4495.04
	3 1 2	326.1545(6)	326.16		2 0 2	4555.9039(110)	4555.74
	3 3 1	458.3355(13)	458.36	0 0 2	1 1 1	4677.2577(240)	4677.09
	3 3 0	459.8252(13)	459.85	0 3 0	1 1 1	6342.8376(50)	6342.80
	4 1 4	403.6723(7)	403.61		1 1 0	6363.8070(50)	6363.77
	4 1 3	516.1487(25)	516.14	0 2 1	0 0 0	6400.7110(50)	6400.71
	5 1 4	738.7663(10)	738.73		1 0 1	6441.9056(50)	6441.75
	6 1 6	801.7726(10)	801.61		2 0 2	6519.0565(19)	6518.90
0 1 0	1 1 1	2258.7900(25)	2258.78		2 2 1	6646.2826(50)	6646.15
	1 1 0	2278.4161(25)	2278.42		2 2 0	6649.4350(50)	6649.30
	2 1 2	2322.7337(50)	2322.70		3 0 3	6622.4283(50)	6622.25
	2 1 1	2379.3649(25)	2379.37	1 2 0	1 1 1	7046.6976(50)	7046.70
	3 1 3	2416.6823(50)	2416.61		1 1 0	7064.8260(50)	7064.83
	3 3 1	2651.4503(50)	2651.46		2 1 2	7126.8620(50)	7126.85
	4 1 4	*2540.1865(50)*	2540.33		2 1 1	7177.9636(50)	7177.97
	4 1 3	2690.7903(25)	2690.74				
	5 1 5	2694.3303(8)	2694.15				
0 0 1	0 0 0	2335.4260(50)	2335.30				
	1 0 1	2383.9595(25)	2383.83				
	2 0 2	2477.7583(17)	2477.64				
	2 2 1	2568.4601(16)	2568.34				
	2 2 0	2569.5615(24)	2569.45				
	3 0 3	2610.7184(25)	2610.59				
	3 2 2	2710.2562(50)	2710.15				
	3 2 1	2717.3172(25)	2717.21				
	4 0 4	2777.3247(25)	2777.18				
	4 2 3	2894.4554(25)	2894.34				
	5 0 5	2975.2573(50)	2975.46				
1 0 0	1 1 1	3050.4890(13)	3050.48				
	1 1 0	3063.2993(10)	3063.30				
	2 1 2	3128.8678(7)	3128.85				
	2 1 1	3167.1162(7)	3167.11				
	3 1 3	3243.0593(17)	3243.02				
	3 1 2	3317.0594(17)	3317.05				
	3 3 1	3434.8892(25)	3434.90				
	3 3 0	3436.8275(25)	3436.85				
	4 1 4	3391.0607(25)	3390.99				
	4 1 3	3505.1275(25)	3505.10				
	5 1 5	*3572.3743(50)*	3571.63				
	5 1 4	3724.3357(50)	3724.29				

[a] The uncertainties of the MARVEL energy levels are given in parentheses and in units of 10^{-4} cm^{-1}.
[b] The value reported for the root is taken from 88KoPoZo and its uncertainty is fixed to zero.

Table 2: Energy levels of *para*-H_2D^+ [a]

$v_1v_2v_3$	J K_a K_c	MARVEL	Variational
0 0 0	0 0 0	0.000000(0)	0.00
	1 0 1	45.701106(1)	45.70
	2 0 2	131.652642(5)	131.64
	2 2 1	218.655105(1)	218.66
	2 2 0	223.858275(1)	223.87
	3 0 3	251.3833(8)	251.38
	3 2 2	354.781506(3)	354.78
	3 2 1	376.344097(3)	376.36
	4 2 2	*581.3895(50)*	581.50
0 1 0	0 0 0	2205.8771(50)	2205.87
	1 0 1	2246.6978(25)	2246.68
	2 0 2	2318.3413(50)	2318.33
	2 2 1	2415.4641(25)	2415.45
	2 2 0	2427.0701(25)	2427.08
	3 2 1	2580.2811(25)	2580.29
	4 2 2	2788.5833(50)	2788.54
0 0 1	1 1 1	2402.7913(25)	2402.66
	1 1 0	2409.3191(50)	2409.18
	2 1 2	2491.0477(23)	2490.92
	2 1 1	2512.4801(17)	2512.36
	3 1 3	2618.5866(25)	2618.45
	3 1 2	2664.2611(400)	2664.14
	3 3 1	2820.8204(25)	2820.71
	3 3 0	2820.8011(50)	2820.69
	4 1 4	*2775.3363(50)*	2775.29
	4 1 3	2860.4745(25)	2860.36
1 0 0	0 0 0	2992.5041(17)	2992.49
	1 0 1	3038.1774(10)	3038.16
	2 0 2	3123.3129(10)	3123.29
	2 2 1	3203.8444(17)	3203.84
	2 2 0	3209.8178(17)	3209.81
	3 0 3	3241.2975(25)	3241.25
	3 2 2	3339.8571(25)	3339.84
	3 2 1	3363.9034(25)	3363.90
	4 0 4	3390.5803(25)	3390.53
	4 2 3	3515.7525(50)	3515.72
	4 2 2	3570.3071(50)	3570.31
0 1 1	1 1 1	4512.5665(110)	4512.43
0 3 0	0 0 0	6287.6671(50)	6287.62
	1 0 1	6330.9730(50)	6330.92
0 2 1	1 1 1	6466.5201(31)	6466.38
	1 1 0	6479.4431(50)	6479.29
	2 1 2	6537.0453(41)	6536.90
1 2 0	0 0 0	6991.5781(50)	6991.58
	1 0 1	7039.3620(50)	7039.36
	2 0 2	7123.2301(50)	7123.21

[a] The uncertainties of the MARVEL energy levels are given in parentheses and in units of 10^{-4} cm^{-1}.
[b] The value of the vibrational ground state was fixed to zero with zero uncertainty.

Table 3: Energy levels of *para*-D_2H^+ [a]

$v_1v_2v_3$	J K_a K_c	MARVEL	Variational	$v_1v_2v_3$	J K_a K_c	MARVEL	Variational
0 0 0	1 0 1	34.915000(0)[b]	34.92	0 2 0	1 1 0	3881.7014(430)	3881.63
	1 1 0	57.986306(3)	57.99		2 1 2	3921.9670(210)	3921.89
	2 1 2	110.2575(4)	110.26	0 0 2	1 0 1	4058.4803(80)	4058.42
	2 2 1	179.1613(8)	179.17		1 1 0	4101.0726(90)	4101.01
	3 0 3	196.0975(5)	196.09		2 1 2	4097.8982(50)	4097.84
	3 1 2	251.3000(16)	251.31	0 1 1	0 0 0	4060.7884(140)	4060.74
	4 1 4	317.2512(25)	317.23		1 1 1	4130.7917(270)	4130.75
	4 2 3	419.4610(1000)	419.47		2 1 1	4179.7620(90)	4179.72
	5 1 4	574.7927(5)	574.80	1 0 2	1 0 1	6524.9223(50)	6524.85
0 1 0	1 0 1	1998.5372(91)	1998.49		1 1 0	6558.9250(50)	6558.85
	1 1 0	2027.0450(50)	2027.01		2 1 2	6570.8665(50)	6570.79
	2 1 2	2062.9390(91)	2062.89	1 1 1	0 0 0	6616.0270(50)	6615.97
	2 2 1	2145.6161(33)	2145.58				
	3 0 3	2133.5003(48)	2133.45				
	3 1 2	2205.7910(91)	2205.76				
	3 2 1	2253.0440(100)	2253.01				
	4 1 4	2234.4080(100)	2234.35				
	4 2 3	2357.0802(8)	2357.04				
	4 3 2	2471.9675(50)	2471.94				
	5 0 5	2356.1872(100)	2356.11				
0 0 1	0 0 0	2078.4300(50)	2078.40				
	1 1 1	2128.6944(25)	2128.66				
	2 0 2	2194.0598(25)	2194.03				
	2 1 1	2225.1523(17)	2225.12				
	2 2 0	2257.5805(50)	2257.56				
	3 1 3	2306.7325(50)	2306.70				
	3 2 2	2389.4923(50)	2389.47				
	4 1 3	2508.5938(8)	2508.57				
	5 1 5	2565.2823(50)	2565.24				
1 0 0	1 0 1	2771.5155(50)	2771.49				
	1 1 0	2793.9510(50)	2793.92				
	2 1 2	2845.7150(50)	2845.68				
	2 2 1	2912.6934(25)	2912.67				
	3 0 3	2930.8212(100)	2930.78				
	3 1 2	2985.0880(100)	2985.06				
	3 2 1	3028.4956(50)	3028.48				
	3 3 0	3107.2270(100)	3107.22				
	4 1 4	3050.5190(100)	3050.47				
	4 2 3	3150.5422(50)	3150.52				
	5 0 5	3192.1973(50)	3192.14				

[a] The uncertainties of the MARVEL energy levels are given in parentheses and in units of 10^{-4} cm^{-1}.
[b] The value reported for the root is taken from 88KoPoZo and its uncertainty is fixed to zero.

Table 4: Energy levels of *ortho*-D_2H^+ [a]

$v_1v_2v_3$	J K_a K_c	MARVEL	Variational	$v_1v_2v_3$	J K_a K_c	MARVEL	Variational
0 0 0	0 0 0	0.000000(0)	0.00	0 2 0	1 1 1	3871.3773(130)	3871.30
	1 1 1	49.254255(3)	49.26		2 0 2	3909.9139(300)	3909.84
	2 0 2	101.7191(4)	101.72	0 1 1	1 0 1	4122.9541(90)	4122.90
	2 1 1	136.365255(10)	136.37		1 1 0	4119.1125(67)	4119.07
	2 2 0	182.065249(10)	182.07	0 0 2	0 0 0	4042.7722(90)	4042.71
	3 1 3	200.0296(6)	200.02		1 1 1	4062.8893(20)	4062.83
	3 2 2	283.3168(5)	283.32		2 0 2	4097.0946(40)	4096.99
	4 1 3	399.0510(3)	399.06	1 2 0	1 1 1	6482.0330(50)	6481.95
	4 3 1	523.3879(10)	523.41		1 1 1	6536.3190(25)	6536.24
010	0 0 0	1968.1623(50)	1968.12		2 0 2	6567.7773(50)	6567.69
	1 1 1	2014.1062(5)	2014.06		3 1 3	6636.0961(50)	6636.01
	2 0 2	2055.0977(17)	2055.05				
	2 1 1	2099.9224(8)	2099.88				
	2 2 0	2149.5617(17)	2149.52				
	3 1 3	2136.4989(8)	2136.44				
	3 2 2	2236.3627(7)	2236.32				
	3 3 1	2339.7327(17)	2339.70				
	4 0 4	2233.4226(50)	2233.36				
	4 2 2	2394.5590(50)	2394.52				
	5 2 4	2505.5320(50)	2505.50				
0 0 1	1 0 1	2118.5880(50)	2118.55				
	1 1 0	2136.2443(25)	2136.21				
	2 1 2	2202.7797(17)	2202.74				
	2 2 1	2254.6720(25)	2254.64				
	3 0 3	2297.5800(25)	2297.54				
	3 1 2	2350.9708(8)	2350.94				
	3 2 1	2397.5023(50)	2397.48				
	4 1 4	2439.8386(8)	2439.80				
	4 2 3	2541.2848(50)	2541.26				
	5 1 4	2689.9240(50)	2689.89				
1 0 0	1 1 1	2785.3320(25)	2785.30				
	2 0 2	2837.5540(17)	2837.52				
	2 1 1	2871.4721(50)	2871.44				
	2 2 0	2915.6038(25)	2915.58				
	3 1 3	2934.5471(50)	2934.51				
	3 2 2	3015.8074(25)	3015.78				
	3 3 1	3106.5893(50)	3106.57				
	4 0 4	3049.0956(50)	3049.05				
	4 2 2	3181.5940(50)	3181.57				
	4 3 1	3251.6508(50)	3251.64				
	5 2 4	3314.9500(50)	3314.92				

[a] The uncertainties of the MARVEL energy levels are given in parentheses and in units of 10^{-4} cm^{-1}.
[b] The value of the vibrational ground state was fixed to zero with zero uncertainty.