

Improved analysis of the infrared spectrum of D₂H⁺

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Improved analysis of the infrared spectrum of D_2H^+

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The rotational analysis of the Coriolis-coupled ν_2/ν_3 bands in the infrared spectrum of the D_2H^+ molecular ion has been reexamined. By making four reassignments and adding one new transition, it has been possible to achieve a much better fit of the bands using fewer molecular parameters. The reassigned ν_2/ν_3 data were combined in a simultaneous least-squares analysis with existing ν_1 band infrared data and with two newly measured pure rotational transitions. The resulting molecular parameters and calculated energy levels are the best currently available for this fundamental molecular ion.

I. INTRODUCTION

Infrared spectra of H_3^+ and its deuterated isotopes have been extensively studied¹⁻¹³ since their first observation in 1980 by Oka¹ and by Shy, Farley, Lamb, and Wing.² Because of their lightness, these molecular ions show much larger centrifugal distortion effects than most molecules, and their spectra are correspondingly more difficult to assign and fit. On the other hand, because only two electrons are involved, very reliable potential surfaces can be calculated,¹⁴ and it has thus been possible to predict the infrared spectra with increasing accuracy from first principles.¹⁵

In the case of the isotope D_2H^+ , 31 infrared transitions were first detected by Shy⁴ in the 1780–1970 cm^{-1} region, but no assignments were made at that time. Later, Lubic, and Amano⁹ observed 35 lines of D_2H^+ in the 2600–3000 cm^{-1} region and assigned them to the ν_1 fundamental band. In 1986, Foster *et al.*¹¹ reported 72 new lines of the ν_2 and ν_3 bands in the 1800–2300 cm^{-1} region and were able to analyze these together with 16 of the lines measured by Shy.⁴ The analysis of the ν_2 and ν_3 bands was complicated not only by centrifugal distortion effects, but also by the strong Coriolis coupling that exists between the $(\nu_1\nu_2\nu_3) = (010)$ and (001) states. Although the experimental measurement accuracy was about 0.002 cm^{-1} or better, Foster *et al.*¹¹ were only able to obtain a standard deviation of 0.025 cm^{-1} in their fit of 88 lines, using a 39-parameter Hamiltonian containing terms up to J^6 .

Foster *et al.*¹¹ also suggested slight changes in the original⁹ analysis of the ν_1 band: the omission of one line and an interchange in the assignment of two others. These changes were confirmed in a later reanalysis of the ground and (100) excited states of D_2H^+ made by Kozin *et al.*,¹⁶ who also made one further reassignment in ν_1 . Energy levels and molecular parameters for D_2H^+ were calculated from first principles by Tennyson and Sutcliffe¹⁷ in 1985. Very recently, Miller *et al.*¹⁸ have improved these results, added intensity calculations, and presented comprehensive tables of the rotational and fundamental vibrational spectra of D_2H^+ and H_2D^+ . These calculations tended to confirm the aforementioned reassignments in the ν_1 band of D_2H^+ , with one

exception, and they also suggested a new assignment for one line in the ν_2 band.

In the present paper, we have critically examined the analysis of the ν_2 and ν_3 bands of D_2H^+ . By making four reassignments (one of which is that of Miller *et al.*¹⁸), it has been possible to achieve a greatly improved fit of these bands. The new standard deviation of about 0.0046 cm^{-1} , obtained using 30 parameters with terms up to J^4 , represents a reduction by a factor of 5 as compared with the earlier¹¹ 39-parameter fit. The new assignments for ν_2 and ν_3 have been incorporated into a simultaneous least-squares fit of all the assigned lines in the ν_1 , ν_2 , and ν_3 infrared bands, which also includes two highly accurate recent far infrared measurements of pure rotational transitions by Jennings *et al.*¹⁹ By combining all the available data in this way we obtain a reliable and consistent set of experimental molecular parameters and energy levels for D_2H^+ . The results should be of help in searches for further pure rotational transitions of D_2H^+ , as well as for future comparisons of the observed and *ab initio* calculated energy levels.

II. REASSIGNMENT OF ν_2 BAND TRANSITIONS

The difficulties that have been encountered in assigning the spectrum of D_2H^+ , which have resulted in the continuing reassignments of transitions, are connected with the molecule's large centrifugal distortion effects and with the Coriolis interaction between the (010) and (001) excited states. The problem has been compounded by the fact that the spectra were recorded using laser techniques so that the wave number coverage was not complete and the experimental relative intensities of the lines were not reliable.

The centrifugal distortion and Coriolis effects require the use of a Hamiltonian with many adjustable parameters. Thus for the ν_1 band, 35 transitions were fitted with 20 parameters, and for ν_2 and ν_3 , 88 transitions were fitted with 39 parameters. Under these circumstances, incorrect assignments can be difficult to identify; the least-squares fitting program tries hard to mask any such errors by adjusting the many parameters available to it. In order to combat such difficulties, we began the reanalysis of the ν_2/ν_3 region in

TABLE I. Reassigned transitions in the ν_2 and ν_3 bands of D_2H^+ .

Obs. line (cm^{-1})	Assignment	Comment
2038.634	ν_2 $3_{30} \leftarrow 3_{21}$	Assignment interchanged
2038.936	ν_2 $5_{05} \leftarrow 4_{14}$	
2040.760	ν_2 $5_{15} \leftarrow 4_{04}$	As suggested by Miller <i>et al.</i> (Ref. 18) Previously (Ref. 11) assigned to ν_2 $6_{06} \leftarrow 5_{15}$
2106.497	ν_2 $5_{24} \leftarrow 4_{13}$	Previously (Ref. 11) assigned at 2106.301 cm^{-1}
2275.870	ν_2 $4_{32} \leftarrow 3_{03}$	Newly added transition

D_2H^+ by limiting the number of adjustable parameters and by including all the known^{9,11,16} ground state combination differences explicitly in the fit. One pure rotational transition, $2_{20} \leftarrow 2_{11}$, that was available¹⁹ at the time was also included. The effect of adjusting fewer parameters and constraining the ground state was to restrict the freedom of the least-squares fit and thus to make any misassigned transitions more noticeable. The less well-fitting transitions among the original¹¹ assignments were then examined in detail to see how the fit was affected by their omission and whether an alternate assignment was possible.

This procedure resulted in four reassignments and one added transition, as summarized in Table I. All involved the ν_2 band. First, the correct assignments of the $3_{30} \leftarrow 3_{21}$ and $5_{05} \leftarrow 4_{14}$ transitions near 2040 cm^{-1} were found to be interchanged from those given previously¹¹. Second, the line observed at 2040.760 cm^{-1} was found to be much better fitted when assigned to $5_{15} \leftarrow 4_{04}$, rather than to $6_{06} \leftarrow 5_{15}$, in agreement with the suggestion made by Miller *et al.*¹⁸ Third, the

TABLE II. Unassigned lines in the ν_2/ν_3 band regions of H_2D^+ and D_2H^+ (in cm^{-1}).^a

H_2D^+	D_2H^+
1995.953	1909.451
2134.930	2034.113
2215.966	2106.301
2242.960	2167.812
2274.932	
2302.478	
2413.832	
2418.019	

^a These lines were observed by Foster *et al.* (Refs. 10 and 11) but not reported in the original papers. The assignments to one or the other isotope are not certain.

$5_{24} \leftarrow 4_{13}$ transition, previously assigned to an observed line at 2106.301 cm^{-1} , was found to be much better fitted when assigned instead to a nearby observed line at 2106.497 cm^{-1} . And fourth, with help from the calculations of Miller *et al.*,¹⁸ a line observed at 2275.870 cm^{-1} was assigned to the transition $4_{32} \leftarrow 3_{03}$.

The lines at 2106.497 and 2275.870 cm^{-1} were among a handful of transitions that were observed by Foster *et al.*^{10,11} but not reported in the original papers since they could not be assigned. Indeed, the 2275.870 cm^{-1} line was originally believed to be due to H_2D^+ , but this assignment was uncertain because of the difficulty in distinguishing experimentally between the two isotopes, especially for weaker lines. We are confident of the new assignment to D_2H^+ given here because of the good fit achieved, and the lack¹⁸ of any suitable alternative assignment to H_2D^+ . For the sake of completeness, we list here in Table II the remaining unassigned

TABLE III. Observed infrared transitions of D_2H^+ (in cm^{-1}).

ν_2 band ^a			ν_3 band ^a			ν_1 band ^b		
J_{KaKc}	Obs.	R^c	J_{KaKc}	Obs.	R^c	J_{KaKc}	Obs.	R^c
$4_{23} \leftarrow 5_{14}$	1782.287 ^d	-6	$4_{14} \leftarrow 4_{31}$	1916.451 ^d	0	$2_{02} \leftarrow 3_{13}$	2637.524	1
$3_{12} \leftarrow 4_{23}$	1786.330 ^d	0	$4_{13} \leftarrow 5_{14}$	1933.801 ^d	5	$1_{01} \leftarrow 2_{12}$	2661.258	-3
$6_{15} \leftarrow 6_{24}$	1807.347 ^d	1	$3_{12} \leftarrow 4_{13}$	1951.920 ^d	5	$1_{11} \leftarrow 2_{02}$	2683.613	-6
$3_{03} \leftarrow 4_{14}$	1816.249	-1	$2_{21} \leftarrow 3_{22}$	1971.355	4	$2_{02} \leftarrow 2_{11}$	2701.189	0
$1_{11} \leftarrow 2_{20}$	1832.041 ^d	0	$2_{11} \leftarrow 3_{12}$	1973.852	-2	$1_{10} \leftarrow 1_{01}$	2759.036	-1
$3_{22} \leftarrow 4_{13}$	1837.312 ^d	-7	$2_{02} \leftarrow 3_{03}$	1997.962	-1	$2_{11} \leftarrow 2_{02}$	2769.753	-2
$1_{10} \leftarrow 2_{21}$	1847.885	2	$1_{10} \leftarrow 2_{11}$	1999.879	-2	$3_{21} \leftarrow 3_{12}$	2777.196	0
$3_{13} \leftarrow 3_{22}$	1853.182 ^d	8	$2_{12} \leftarrow 3_{13}$	2002.750	0	$2_{20} \leftarrow 2_{11}$	2779.238	1
$5_{14} \leftarrow 5_{23}$	1854.231 ^d	-3	$3_{03} \leftarrow 3_{22}$	2014.263	-3	$4_{22} \leftarrow 4_{13}$	2782.543	2
$2_{02} \leftarrow 3_{13}$	1855.068	1	$1_{11} \leftarrow 2_{12}$	2018.437	0	$1_{11} \leftarrow 0_{00}$	2785.332	-1
$2_{12} \leftarrow 3_{03}$	1866.841 ^d	1	$0_{00} \leftarrow 1_{01}$	2043.515	1	$2_{02} \leftarrow 1_{11}$	2788.300	3
$3_{03} \leftarrow 3_{12}$	1882.201 ^d	1	$2_{12} \leftarrow 2_{11}$	2066.415	0	$3_{12} \leftarrow 3_{03}$	2788.990	-2
$2_{12} \leftarrow 2_{21}$	1883.777	0	$3_{31} \leftarrow 3_{30}$	2068.461	1	$2_{21} \leftarrow 2_{12}$	2802.436	2
$1_{01} \leftarrow 2_{12}$	1888.280 ^d	-4	$3_{30} \leftarrow 3_{31}$	2069.869	0	$2_{12} \leftarrow 1_{01}$	2810.800	4
$2_{21} \leftarrow 3_{12}$	1894.316	0	$1_{11} \leftarrow 1_{10}$	2070.708	0	$4_{13} \leftarrow 4_{04}$	2815.314	-3
$5_{23} \leftarrow 5_{32}$	1895.431 ^d	-3	$2_{21} \leftarrow 2_{20}$	2072.607	0	$3_{22} \leftarrow 3_{13}$	2815.778	2
$1_{11} \leftarrow 2_{02}$	1912.387 ^d	-2	$2_{20} \leftarrow 2_{21}$	2078.419	-6	$3_{03} \leftarrow 2_{12}$	2820.564	3
$2_{11} \leftarrow 2_{20}$	1917.857 ^d	2	$1_{10} \leftarrow 1_{11}$	2086.990	1	$3_{13} \leftarrow 2_{02}$	2832.828	3
$2_{02} \leftarrow 2_{11}$	1918.732	-1	$2_{11} \leftarrow 2_{12}$	2114.895	1	$4_{04} \leftarrow 3_{13}$	2849.066	-4
$0_{00} \leftarrow 1_{11}$	1918.908	-7	$1_{01} \leftarrow 0_{00}$	2118.588	2	$4_{14} \leftarrow 3_{03}$	2854.421	2
$1_{01} \leftarrow 1_{10}$	1940.551	-3	$2_{12} \leftarrow 1_{11}$	2153.525	1	$2_{21} \leftarrow 1_{10}$	2854.707	3
$2_{20} \leftarrow 3_{13}$	1949.533	6	$2_{02} \leftarrow 1_{01}$	2159.145	0	$2_{20} \leftarrow 1_{11}$	2866.350	4
$1_{10} \leftarrow 1_{01}$	1992.130	1	$2_{11} \leftarrow 1_{10}$	2167.166	1	$5_{05} \leftarrow 4_{14}$	2874.948	-6
$4_{22} \leftarrow 4_{13}$	1995.508	-7	$3_{03} \leftarrow 2_{02}$	2195.861	-9	$5_{15} \leftarrow 4_{04}$	2876.954	2
$2_{11} \leftarrow 2_{02}$	1998.203	0	$3_{13} \leftarrow 2_{12}$	2196.475	-2	$3_{22} \leftarrow 2_{11}$	2879.442	1

TABLE III. (continued).

ν_2 band ^a			ν_3 band ^a			ν_1 band ^b		
J_{KaKc}	Obs.	R^c	J_{KaKc}	Obs.	R^c	J_{KaKc}	Obs.	R^c
$3_{21} \leftarrow 3_{12}$	2001.744	1	$3_{22} \leftarrow 2_{21}$	2210.331	4	$4_{23} \leftarrow 3_{12}$	2899.242	-1
$2_{02} \leftarrow 1_{11}$	2005.844	2	$3_{12} \leftarrow 2_{11}$	2214.605	3	$6_{06} \leftarrow 5_{15}$	2899.362	2
$3_{12} \leftarrow 3_{03}$	2009.696	-1	$3_{21} \leftarrow 2_{20}$	2215.437	-5	$5_{24} \leftarrow 4_{13}$	2915.899	3
$2_{20} \leftarrow 2_{11}$	2013.196	4	$4_{14} \leftarrow 3_{13}$	2239.809	7	$3_{21} \leftarrow 2_{12}$	2918.238	2
$1_{11} \leftarrow 0_{00}$	2014.106	2	$5_{15} \leftarrow 4_{14}$	2248.033	-1	$3_{31} \leftarrow 2_{20}$	2924.524	-3
$4_{31} \leftarrow 4_{22}$	2014.433	11	$4_{13} \leftarrow 3_{12}$	2257.293	2	$3_{30} \leftarrow 2_{21}$	2928.067	-3
$3_{03} \leftarrow 2_{12}$	2023.243	1	$4_{23} \leftarrow 3_{22}$	2257.968	-2	$4_{32} \leftarrow 3_{21}$	2951.532	-5
$4_{13} \leftarrow 4_{04}$	2024.230	8	$5_{05} \leftarrow 4_{04}$	2263.828	4	$4_{31} \leftarrow 3_{22}$	2968.334	1
$3_{12} \leftarrow 2_{21}$	2026.631	-2	$4_{22} \leftarrow 3_{21}$	2267.719	-2	$4_{40} \leftarrow 3_{31}$	2990.154	2
$2_{12} \leftarrow 1_{01}$	2028.024	2	$5_{14} \leftarrow 4_{13}$	2290.873	-6			
$4_{04} \leftarrow 3_{13}$	2033.393	2						
$3_{13} \leftarrow 2_{02}$	2034.780	1						
$2_{21} \leftarrow 2_{12}$	2035.359	2						
$3_{22} \leftarrow 3_{13}$	2036.333	-7						
$4_{14} \leftarrow 3_{03}$	2038.310	0						
$3_{30} \leftarrow 3_{21}$	2038.634	3						
$5_{05} \leftarrow 4_{14}$	2038.936	-5						
$4_{23} \leftarrow 4_{14}$	2039.834	-4						
$5_{15} \leftarrow 4_{04}$	2040.760	1						
$3_{31} \leftarrow 3_{22}$	2056.416	-1						
$2_{21} \leftarrow 1_{10}$	2087.630	3						
$3_{22} \leftarrow 2_{11}$	2099.998	-7						
$2_{20} \leftarrow 1_{11}$	2100.307	6						
$5_{24} \leftarrow 4_{13}$	2106.497	6						
$3_{31} \leftarrow 2_{20}$	2157.667	-6						
$3_{31} \leftarrow 2_{02}$	2238.014	-8						
$4_{32} \leftarrow 3_{03}$	2275.870	3						
$4_{40} \leftarrow 3_{31}$	2279.090	-1						
$4_{41} \leftarrow 3_{30}$	2279.521	2						

^a From Foster *et al.* (Ref. 11) except as noted.^b From Lubic and Amano (Ref. 9).^c Indicates the residual (Obs.-Calc.) in units of 0.001 cm⁻¹ from the present least-squares fit.^d From Shy (Ref. 4).

lines from the diode laser studies^{10,11} of the ν_2 and ν_3 bands of H₂D⁺ and D₂H⁺. One of them is, of course, the 2106.301 cm⁻¹ line mentioned above, which had previously been assigned as ν_2 , $5_{24} \leftarrow 4_{13}$. It should be noted that these are mostly weak and/or poorly measured lines, and that the experimental assignment to one or the other isotope is subject to uncertainty.

III. LEAST-SQUARES ANALYSIS

Our final analysis of D₂H⁺ incorporated the ν_2 band reassignments already mentioned, and simultaneously included the ν_1 band along with the coupled ν_2/ν_3 bands. Thus

TABLE IV. Observed pure rotational transitions of D₂H⁺.

Assignment J_{KaKc}	Observed frequency ^a (MHz)	Obs.-Calc. (MHz)
$2_{20} \leftarrow 2_{11}$	1 370 051.6	+ 0.02
$1_{11} \leftarrow 0_{00}$	1 476 605.5	- 0.05

^a From Jennings, Demuyneck, Banek, and Evenson (Ref. 19). The experimental uncertainty is about 0.3 MHz.

all the infrared data were automatically fitted with the same ground vibrational state parameters. The collected infrared transitions are listed in Table III; they were all given equal weight in the fit. The ν_1 band data were taken from Lubic and Amano,⁹ and incorporated the same reassignments as already suggested in the literature,^{11,16,18} except that 2990.154 cm⁻¹ was assigned to $4_{40} \leftarrow 3_{31}$, contrary to Kozin *et al.*¹⁶ but in agreement with the other analyses.^{9,11,18} The fit also included two far infrared pure rotational transitions, $2_{20} \leftarrow 2_{11}$ as already mentioned, and $1_{11} \leftarrow 0_{00}$ which became available while our analysis was in progress.¹⁹ These rotational transitions are listed in Table IV; they were given an increased weight of 10⁴ in the fit to reflect their higher accuracy relative to the infrared data. The final fit did not explicitly include the ground state combination differences from the infrared spectra, but, of course, this information is implicitly contained in the infrared data.

The Hamiltonian and computer program used were those described by Foster *et al.*,^{10,11} except that only terms up to J^4 were included. We tested both Padé and conventional forms of the Hamiltonian and found that they gave very similar results. The final fit reported here is that which was obtained using a conventional Hamiltonian. The Hamiltonian was the same as that described in Eqs. (1)–(4) of Ref. 10, except for the replacement of Eq. (2) by

TABLE V. Molecular parameters (in cm^{-1}) for D_2H^+ from the present analysis.^a

Parameter	(010) state	(001) state	(100) state	(000) state
G_v	1968.168 8 (21)	2078.430 0 (24)	2736.981 4 (24)	0.0
A	38.128 61(154)	34.876 98(178)	35.423 88(87)	36.199 12(38)
B	20.813 99(152)	23.053 67(147)	21.626 98(108)	21.868 98(41)
C	12.294 11(4258)	12.671 45(4247)	12.936 04(50)	13.069 88(33)
$10^2 \Delta^{KK}$	3.353 0 (385)	0.860 0 (469)	2.448 9 (87)	1.977 8 (133)
$10^2 \Delta^{JK}$	-0.205 9 (357)	0.790 4 (383)	-0.238 1 (102)	0.231 1 (89)
$10^2 \Delta^{JJ}$	0.387 88(370)	0.847 55(551)	0.588 36(274)	0.559 42(157)
$10^2 \delta^K$	0.508 7 (192)	2.520 5 (172)	1.309 8 (96)	1.179 1 (94)
$10^2 \delta^J$	0.275 08(243)	0.208 32(268)	0.221 80(149)	0.211 37(69)
ξ_{23}		-19.870 (120)		
α_{23}^{ab}		1.2597(213)		
$10^2 \eta_{23}^K$		-1.4672(160)		
$10^2 \beta_{23}^{aaab}$		-0.7554(200)		

^a The quantities in parentheses are standard deviations (1σ) from the least-squares fit in units of the last quoted digit. The parameters are defined in Eq. (1) and in Ref. 11.

$$(H_{\text{diag}})_v = H_{2v} + H_{4v},$$

$$(H_{\text{off-diag}})_v = [J_b^2 - J_c^2 \{h_{2v} + h_{4v}\}]_+ \quad (1)$$

The off-diagonal block connecting the (010) and (001) vibrational states was exactly the same as described in Ref. 11. It involves the Coriolis coupling parameter ξ_{23} , an off-diagonal-type H_{22} coupling described by the parameter α_{23}^{ab} , and k_a -dependent centrifugal distortion corrections to these terms given, respectively, by η_{23}^K and β_{23}^{aaab} .^{10,11} No interactions terms were included between the (100) state and either (010) or (001), since the latter two states are well separated from (100).

The molecular parameters resulting from the least-

squares fit are given in Table V, and the residuals (observed minus calculated line positions) are given in Tables III and IV. The overall standard deviation for the infrared data was 0.0043 cm^{-1} , with that for ν_1 being about 0.0035 cm^{-1} and that for ν_2/ν_3 being about 0.0046 cm^{-1} . These values are greatly improved from the previous standard deviations for ν_1 of about 0.030 cm^{-1} (Ref. 9) or 0.007 cm^{-1} (Ref. 16), and for ν_2/ν_3 of about 0.025 cm^{-1} (Ref. 11). The new pure rotational data were also fitted very well in the present analysis (see Table IV).

Most of the parameters in Table V are better determined than in previous analyses, as would be expected from the lower standard deviation and the simultaneous nature of the

TABLE VI. Energy levels (in cm^{-1}) for the ground and first three excited vibrational states of D_2H^+ , as calculated from the present molecular parameters (Table V).

J_{KaKc}	Vibrational state ($\nu_1\nu_2\nu_3$)				J_{KaKc}	Vibrational state ($\nu_1\nu_2\nu_3$)			
	(010)	(001)	(100)	(000)		(010)	(001)	(100)	(000)
0 ₀₀	1968.1688	2078.4300	2736.9814	0.0000	4 ₄₀	2656.1636	2703.3018	3367.2247	643.2357
1 ₀₁	1998.5435	2118.5852	2771.5209	34.9165	5 ₀₅	2356.1926	2579.5685	3192.2057	460.4333
1 ₁₁	2014.1038	2128.6967	2785.3331	49.2543	5 ₁₅	2356.5041	2565.2847	3192.6961	460.9535
1 ₁₀	2027.0453	2136.2436	2793.9539	57.9893	5 ₁₄	2497.5528	2689.9286	3304.6532	574.7953
2 ₀₂	2055.0962	2194.0616	2837.5517	101.7142	5 ₂₄	2505.5395	2722.2398	3314.9456	585.6174
2 ₁₂	2062.9386	2202.7786	2845.7128	110.2594	5 ₂₃	2605.0660	2766.3333	3371.9443	643.3191
2 ₁₁	2099.9178	2225.1539	2871.4688	136.3631	5 ₃₃	2637.3927	2739.4005	3422.5792	696.0154
2 ₂₁	2145.6165	2254.6699	2912.6935	179.1620	5 ₃₂	2637.5153	2753.6435	3436.1909	709.6317
2 ₂₀	2149.5549	2257.5873	2915.6004	182.0631	5 ₄₂	2849.4997	2869.9642	3542.9327	820.3066
3 ₀₃	2133.5005	2297.5849	2930.8207	196.0983	5 ₄₁	2843.5275	2871.5001	3543.8598	821.2198
3 ₁₃	2136.4933	2306.7370	2934.5393	200.0285	5 ₅₁	2998.1387	3023.9599	3692.4963	975.5682
3 ₁₂	2205.7956	2350.9646	2985.0900	251.3001	5 ₅₀	2998.0279	3023.9917	3692.5132	975.5846
3 ₂₂	2236.3681	2389.4894	3015.8042	283.3190	6 ₀₆	2502.6715	2759.4826	3360.3138	630.3473
3 ₂₁	2253.0429	2397.5050	3028.4958	296.0483	6 ₁₆	2502.7696	2754.6465	3360.4748	630.5165
3 ₃₁	2339.7365	2446.1648	3106.5904	377.0731	6 ₁₅	2676.6515	2892.2781	3502.4892	774.9820
3 ₃₀	2334.6795	2446.9421	3107.2321	377.7044	6 ₂₅	2679.9410	2932.1905	3507.1356	779.8520
4 ₀₄	2233.4192	2425.6232	3049.0988	315.7443	6 ₂₄	2806.9233	2998.9379	3595.1917	869.3053
4 ₁₄	2234.4082	2439.8305	3050.5173	317.2512	6 ₃₄	2832.2278	2941.8815	3629.7418	905.2470
4 ₁₃	2339.9658	2508.5911	3131.0614	399.0492	6 ₃₃	2848.3340	3081.6854	3661.1428	936.9484
4 ₂₃	2357.0884	2541.2882	3150.5431	419.4655	6 ₄₃	2967.0717	3071.8745	3753.5160	1032.6404
4 ₂₂	2394.5642	2563.7691	3181.5901	450.7627	6 ₄₂	3063.2725	3079.5862	3757.5700	1036.6855
4 ₃₂	2471.9656	2574.1787	3247.5854	519.3494	6 ₅₂	3216.3794	3224.7604	3901.4402	1185.7729
4 ₃₁	2465.1850	2578.7024	3251.6524	523.3798	6 ₅₁	3215.4165	3225.1312	3901.6089	1185.9396
4 ₄₁	2657.2234	2703.1327	3367.1123	643.1263					

present fit. An exception to this occurs for the C rotational constants in the (010) and (001) states, and for the Coriolis coupling parameter ξ_{23} . Their relatively large uncertainties are a reflection of the strong correlations that exist among these three parameters, which for some reason are larger in the present fit than they were previously.^{11,20} A set of energy levels for the ground and fundamental vibrational states of D_2H^+ , as determined from the present molecular parameters, is given in Table VI.

IV. CONCLUSIONS

The present results serve as a reminder of the extreme care that must be exercised in the least-squares fitting of complex molecular spectra when there are limited data and many adjustable parameters. In the present analysis, we benefited from the availability of the pure rotational transitions of Jennings *et al.*¹⁹ and the new calculations of Miller *et al.*¹⁸ It is hoped that our results will, in turn, be of assistance in searches for further rotational transitions of D_2H^+ and in future comparisons between experiment and *ab initio* theory for this basic molecular ion.

In conclusion, the analysis of the Coriolis-coupled ν_2/ν_3 infrared bands of D_2H^+ , as originally studied by Foster *et al.*,¹¹ has been reexamined. Four reassignments have been made and one new transition added, and the net effect is that the bands can be fitted using fewer parameters and with a five times smaller standard deviation. These data have been combined with measurements⁹ of the ν_1 band and with new pure rotational transitions¹⁹ in a simultaneous least-squares fit to obtain an optimized set of molecular parameters. A table of energy levels has been calculated from these parameters which should be helpful in future studies of the D_2H^+ molecular ion.

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¹T. Oka, Phys. Rev. Lett. **45**, 531 (1980).

²J. T. Shy, J. W. Farley, W. E. Lamb, Jr., and W. H. Wing, Phys. Rev. Lett. **45**, 535 (1980).

³J. T. Shy, J. W. Farley, and W. H. Wing, Phys. Rev. A **24**, 1146 (1981).

⁴J. T. Shy, Ph.D. dissertation, University of Arizona, 1982 (University Microfilms International, Ann Arbor, Michigan, U.S.A., No. 8305995).

⁵T. Oka, in *Molecular Ions: Spectroscopy, Structure and Chemistry*, edited by T. A. Miller and V. Bondybey (North-Holland, Amsterdam, 1983), pp. 73–90.

⁶J. K. G. Watson, S. C. Foster, A. R. W. McKellar, P. Bernath, T. Amano, F. S. Pan, M. W. Crofton, R. S. Altman, and T. Oka, Can. J. Phys. **62**, 1875 (1984).

⁷T. Amano and J. K. G. Watson, J. Chem. Phys. **81**, 2869 (1984).

⁸T. Amano, J. Opt. Soc. Am. B **2**, 790 (1985).

⁹K. G. Lubich and T. Amano, Can. J. Phys. **62**, 1886 (1984).

¹⁰S. C. Foster, A. R. W. McKellar, I. R. Peterkin, J. K. G. Watson, F. S. Pan, M. W. Crofton, R. S. Altman, and T. Oka, J. Chem. Phys. **84**, 91 (1986).

¹¹S. C. Foster, A. R. W. McKellar, and J. K. G. Watson, J. Chem. Phys. **85**, 664 (1986).

¹²W. A. Majewski, M. D. Marshall, A. R. W. McKellar, J. W. C. Johns, and J. K. G. Watson, J. Mol. Spectrosc. **122**, 341 (1987).

¹³J. K. G. Watson, S. C. Foster, and A. R. W. McKellar, Can. J. Phys. **65**, 38 (1987).

¹⁴For example, W. Meyer, P. Botschwina, and P. G. Burton, J. Chem. Phys. **84**, 891 (1986).

¹⁵For example, S. Miller, J. Tennyson, and B. T. Sutcliffe, Mol. Phys. **66**, 429 (1989), and references therein.

¹⁶I. N. Kozin, O. L. Polyansky, and N. F. Zobov, J. Mol. Spectrosc. **128**, 126 (1988).

¹⁷J. Tennyson and B. T. Sutcliffe, Mol. Phys. **56**, 1175 (1985).

¹⁸S. Miller, J. Tennyson, and B. T. Sutcliffe, Mol. Phys. **66**, 429 (1989).

¹⁹D. A. Jennings, C. Demuynck, M. Banek, and K. M. Evenson (private communication).

²⁰The correlations (κ , as defined by Watson, Refs. 10–13) for the parameters C_2 , C_3 , and ξ_{23} in the present fit were 227×10^3 , 126×10^3 , and 168×10^3 , respectively. These are about 50 times larger than obtained previously (Ref. 11) for D_2H^+ , and are similar in magnitude to those obtained for H_2D^+ (Ref. 10).