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Calculated ro-vibrational spectrum of H_2D^+

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Ab initio data for the rotational levels of the (0, 0, 0), (0, 1, 0) and (0, 0, 1) states of H_2D^+ are fitted and assignments suggested for the spectrum of Shy, Farley and Wing (1981, *Phys. Rev.*, A, **24,** 1146).

In a recent paper, I, we published an *ab initio* study on the ro-vibrational levels of H_3^+ and H_2D^+ [1]. For H_3^+, fitted rotational parameters were computed in excellent agreement with those obtained experimentally by Oka [2]. The results on H_2D^+ are of particular interest because of the spectrum recorded by Shy, Farley and Wing (SFW) [3] in the region of the ν_2 and ν_3 fundamentals which arise when the ν_E fundamental of H_3^+ is split by deuteration. As yet neither vibrational nor rotational assignments have been made to this spectrum, but since I, Amano and Watson [4] have recorded data for the ν_1 band of H_2D^+ in good agreement with our predictions.

The interest in this problem led us to re-interpret our previous results for the lowest 3 vibrational states of H_2D^+. In doing so it became apparent that the strong mixing and overlap between rotational levels belonging to the ν_2 and ν_3 fundamentals makes vibrational assignments for these levels peculiarly problematic. In particular, some of the ν_2 rotational levels given in I were incorrectly assigned.

In this note we present fits for levels of the lowest 3 vibrational states of H_2D^+. Combined fits to the ν_2 and ν_3 levels were performed without any prior vibrational assignment. This allows us to assign correctly ro-vibrational data for our calculated states with $J \leqslant 4$. It also allows us to generate a list of transitions between higher rotational states and hence make tentative assignments to the transitions observed by SFW. We hope that the parameters will also aid in the assignment of other regions of the spectrum of this highly asymmetric ($\kappa \simeq -0{\cdot}07$) molecule.

Table 1 presents rotational parameters for the ground, ν_2 and ν_3 vibrational states. These were obtained by minimizing the energy mismatch between ladders of levels with a particular J and symmetry. This fit is very satisfactory as it reproduces the *ab initio* data to well within the accuracy of the calculation.

Table 1. Rotational constants in cm^{-1} for the lowest 3 vibrational states of H_2D^+

	Ground state		ν_2	ν_3
	[4]	This work	This work	This work
A	43·362	43·391	42·150	46·499
B	29·143	29·095	30·450	27·633
C	16·610	16·580	14·110	17·418
Δ_J	0·001	0·010	0·004	0·018
Δ_{JK}	−0·008	0·0	−0·010	0·007
Δ_K	0·032	0·030	0·048	0·030
δ_J	0·004	0·002	0·051	−0·001
δ_K	0·020	0·009	0·073	0·012
	Band origins		2184·0	2309·7
	scaled†		2207·9	2335·0
	Coupling constants‡		$G_{23} = -25{\cdot}615$	
			$F_{23} = -1{\cdot}685$	

† Adjusted by $\nu_E^{\mathrm{obs}}(H_3^+)/\nu_E^{\mathrm{calc}}(H_3^+)$, see text.
‡ See [5].

Table 2. Low-lying rotational states of H_2D^+.

J	τ	k	j†	ν_2 Frequency/cm^{-1}	j†	ν_3 Frequency/cm^{-1}
1	+1	1^f	o	72·5	e	74·0
	−1	0^e	e	40·6	o	48·6
	0	1^e	o	52·6	e	67·8
2	+1	2^f	e	209·2	o	233·9
	0	1^f	o	173·3	e	177·0
	−2	0^e	e	111·9	o	142·6
	−1	1^e	o	116·1	e	156·4
	+2	2^e	e	221·1	o	234·8
3	+3	3^f	o	450·1	e	487·0
	0	2^f	e	332·9	o	375·7
	−1	1^f	o	314·0	e	328·6
	−3	0^e	e	208·8	o	275·8
	−2	1^e	o	209·7	e	284·2
	+1	2^e	e	374·3	o	382·0
	+2	3^e	o	445·1	e	487·1
4	+3	4^f	e	758·9	o	826·0
	+2	3^f	o	647·3	e	675·4
	−1	2^f	e	491·8	o	560·1
	−2	1^f	o	484·0	e	524·6
	−4	0^e	e	333·4	o	442·6
	−3	1^e	o	333·2	e	442·0
	0	2^e	e	582·0	o	579·9
	+1	3^e	o	624·4	e	675·0
	+4	4^e	e	760·3	o	825·9

† Parity of j in the basis: e = even, o = odd.

Table 3. Observed and calculated transitions in the ν_2/ν_3 band of H_2D^+.

Observed [3]		Calculated		
Frequency/cm^{-1}	Intensity ratio†	$(J\ \tau\ k) \rightarrow (\nu\ J'\ \tau'\ k')$	Frequency/cm^{-1}	Intensity ratio†
1837·573 1837·687	2·4	$7\ -7\ 0^e\ \ \nu_2\ 6\ -6\ 0^e$	1834·908 1834·913	3
		$7\ -6\ 1^e\ \ \nu_2\ 6\ -5\ 1^e$		
1892·541 1892·557	2·5	$6\ -6\ 0^e\ \ \nu_2\ 5\ -5\ 0^e$	1895·325 1895·340	3
		$6\ -5\ 1^e\ \ \nu_2\ 5\ -4\ 1^e$		
1895·994 1896·344	2·2	$6\ -4\ 1^f\ \ \nu_2\ 5\ -3\ 1^f$	1898·650 1898·879	3
		$6\ -3\ 2^f\ \ \nu_2\ 5\ -2\ 2^f$		
1934·195 1934·562	1·0	$6\ +5\ 6^f\ \ \nu_3\ 5\ +5\ 5^f$	1933·617 1933·632	1
		$6\ +6\ 6^e\ \ \nu_3\ 5\ +4\ 5^e$		
1952·023		$5\ -2\ 2^f\ \ \nu_2\ 5\ -5\ 0^e$	1951·800	
		$5\ +1\ 3^f\ \ \nu_2\ 4\ +2\ 3^f$	1952·424	

† The ratios are given as more to less intense, independently of frequency ordering.

Table 2 shows the *ab initio* data used in the ν_2/ν_3 fit with assignments taken from the fit. This table thus updates table 8 of I.

Using the fit we have generated a full spectrum for the ν_2 and ν_3 bands involving $J \leqslant 8$. To do this we have scaled the band origins by the error between the calculated and observed value for the ν_E band in H_3^+, about 1 per cent. A list of transitions may be obtained from the authors† but in any case can be computed from the parameters of table 1.

Table 3 shows the parts of the spectrum which lie near the transitions recorded by SFW. For comparison we also give the observed intensity ratios of the doublets and ones calculated from a 3 : 1 ratio between the ortho and para H_2 in H_2D^+. Although errors in the calculated transition frequencies of about 3 cm^{-1} mean that our assignments can only be tentative, the agreement between the experimental and calculated intensity ratios must tend to confirm the assignments.

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† This replaces table 9 in I, which besides problems with assignments, contains several typographical errors.