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A calculation of the rovibrational spectra of the H_3^+, H_2D^+ and D_2H^+ molecules

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Variationally exact rovibrational calculations are performed for the H_3^+, H_2D^+ and D_2H^+ molecules using two recent fits to the *ab initio* potential energy data of Burton *et al.* (1985, *Molec. Phys.*, **55**, 527). For the best surface, vibrational fundamentals are $\nu_{A_1} = 3175\,\mathrm{cm}^{-1}$ and $\nu_E = 2518$ $(2521)\,\mathrm{cm}^{-1}$ for H_3^+; $\nu_1 = 2989$ $(2992)\,\mathrm{cm}^{-1}$, $\nu_2 = 2203\,\mathrm{cm}^{-1}$, and $\nu_3 = 2332\,\mathrm{cm}^{-1}$ for H_2D^+, and $\nu_1 = 2733$ (2737), $\nu_2 = 1965$, $\nu_3 = 2027$ for D_2H^+ (where experimental results are given in parenthesis). Rotational constants, which agree well with the experimental constants, where available, are calculated for H_3^+ and D_2H^+. Results are presented for the (0, 1, 0) and (0, 0, 1) states of D_2H^+ which are yet to be characterized experimentally.

1. INTRODUCTION

The study of H_3^+, the electronically simplest stable polyatomic molecule, has a long history which has been well reviewed by Oka [1]. Its vibration–rotation spectrum, however, was only observed comparatively recently [2, 3] and has several regions, particularly for the astrophysically important [4], isotopically mixed species, H_2D^+ and D_2H^+, which remain poorly characterized [5].

H_3^+ has excited much theoretical interest as the comparative simplicity of a two-electron system has inspired hope that high accuracy results may be obtained *ab initio*. Several good quality potential energy calculations were performed in the 1970s [6–9], and Carney and Porter made a pioneering study of the rovibrational levels of H_3^+ and the related deuterated ions [7, 10–12].

In a recent paper [13], henceforth referred to as I, we performed rovibational calculations on H_3^+ and H_2D^+ using the *ab initio* potential energy surface of Schinke *et al.* [9]. The rotational constants obtained in I agreed well with the experimental results where available ($\sim$0·1 per cent [14]), and subsequent re-analysis of our data [15] allowed us to tentatively assign the H_2D^+ spectrum of Shy *et al.* [5]. The spectra of the isotopically mixed H_3^+ species are particularly difficult to analyse because of their asymmetry ($\kappa \approx 0$) and the strong Coriolis

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interactions between the ν_2 and ν_3 fundamentals, which are degenerate in the symmetric ions. More disappointing in I was the 1 per cent ($25\,cm^{-1}$) error obtained for this degenerate bending fundamental for H_3^+.

Since that work was completed there have been significant developments, both experimentally [14, 16–21] and theoretically [22–24] in the spectroscopy of H_3^+. Amano and Watson have observed absorptions in the H_2D^+ ν_1 stretching fundamental [16], obtaining a band origin and rotational constants in good agreement with ours [15]. Watson *et al.* [14] have remeasured the ν_E bending fundamental of H_3^+, using our *ab initio* values to fill the gaps in their spectrum. Lubic and Amano [17] have observed the ν_1 stretching fundamental of D_2H^+. Also Carrington and Kennedy have presented a more detailed consideration [18] of their extensive near-dissociation spectrum of H_3^+ [25], although this data still awaits a full theoretical explanation.

Burton and co-workers have considered theoretically both the electronic [22] and nuclear motion [23] problems for H_3^+. In the former work they pay considerable attention to the problem of obtaining a satisfactory analytic representation of their high accuracy *ab initio* data. Their calculations give an energy at the H_3^+ minimum which is variationally better by $550\,cm^{-1}$ than the best value of Carney and Porter [7], and by $420\,cm^{-1}$ than the surface of Schinke *et al.* [9] used by us in I. However, Burton *et al.*'s surface has only been used for pure vibrational calculations on the symmetric H_3^+ and D_3^+ ions [22, 23].

In this work we perform rovibrational calculations on two different analytic representations of the PNO–CI data of Burton *et al.* [22]. Doing so allows us to assess the accuracy of these potentials by comparison with previous calculations and experimental results, where available, and to assess the method of performing vibrational calculations proposed by Burton *et al.* [23]. We also present data for the rovibrational levels of D_2H^+ molecule, for which transitions have been observed [14], but for which an assigned spectrum is still awaited.

2. ROVIBRATIONAL LEVELS OF H_3^+

Calculations were performed using the method previously developed by us for the rovibrational levels of floppy molecules [26, 27] and implemented in the program ATOMDIAT [28] as generalized for an arbitrary potential function [29]. The hamiltonian is expressed in body-fixed atom–diatom scattering coordinates r, R and θ where $\mathbf{r}$ represents the diatomic bond; $\mathbf{R}$ connects the diatomic centre of mass to the atom and θ is the angle between $\mathbf{r}$ and $\mathbf{R}$. For a given potential variational solutions are found by diagonalizing the secular matrix obtained when basis functions are used to carry the nuclear motions. In this work the two radial coordinates are carried by Morse oscillator-like functions [26] and the θ coordinate by associated Legendre functions. The reader is referred to I for further details of the method.

In this work we compare two fits to the PNO–CI data of Burton *et al.* [22]. First, the SPF^+ surface which Burton *et al.* considered their most satisfactory representation [22], which we denote surface A, and second a subsequent refit by Martire and Burton [30] denoted surface B, which they regarded as superior to the SPF^+ surface.

Unlike Schinke *et al.* [9] who considered 650 geometries giving a surface covering nearly all configuration space, Burton *et al.* performed calculations at only 78 geometries, confining their consideration to the region about equilibrium which is of greatest importance for the spectroscopic properties of the molecule. As our method makes no assumptions about equilibrium structure and hence samples large regions of configuration space, it was necessary to adapt the surfaces for geometries far from equilibrium to remove effects due to spurious minima. This was done by setting the potentials to the $H^+ + H + H$ dissociation limit for geometries where any atom–atom separation was less than 0·7 a.u. or greater than 4·0 a.u. This had the desired effect of confining the low-lying vibrational states to the region of configuration space explicitly considered by Burton *et al.*

Table 1 presents results for the low-lying vibrational levels ($J = 0$) of H_3^+. These calculations were performed with a basis specifically optimized for H_3^+ in I, details of which are given in the table. For comparison, the available experimentals results, our previous calculations and those of Burton *et al.* on surface *A* are also given.

As one would expect, there is a broad agreement between the theoretical results. However, calculations using Burton *et al.*'s potentials show improved agreement with experiment for the bending fundamental compared to the results obrained in I using Schinke *et al.*'s potential. For potential *B* a discrepancy of

Table 1. The zero point energy and lowest vibrational band origins of H_3^+ in cm^{-1}.

Quantum numbers				I	Burton *et al.*	This work†		Experiment
v_A	v_E	l	Symmetry	[13]	[22]	Surface *A*	Surface *B*	[31]
0	1	1	*E*	2494·3 2494·4	2508·51 2508·85	2507·85 2507·97	2518·27 2518·39	2521·308 ±0·009 [16]
1	0	0	A_1	3191·1	3188·50	3187·64	3174·97	3196
0	2	0	A_1	4725·0	4768·51	4757·90	4771·89	4797
0	2	2	*E*	4958·0 4958·3	4986·86 4990·69	4978·36 4978·55	4998·95 4999·14	4986
1	1	1	*E*	5544·9 5545·3	5556·10 5559·51	5550·95 5551·44	5548·54 5549·00	5579
2	0	0	A_1	6276·3	6276·56	6272·75	6260·35	
0	3	1	*E*	6943·3 6944·4		6986·8 6988·0	7002·8 7003·9	
0	3	3	A_1	7235·0		7279·4	7290·8	
0	3	3	A_2	7451·3		7466·2	7506·7	
1	2	0	A_1	7740·3		7748·0	7768·4	
$E_0/(cm^{-1})$				4330·54‡	4352·24	4351·17	4349·23	

† Basis set parameters $n \leqslant 7$, $m \leqslant 10$, $j \leqslant 19$ and Morse-like functions with $r_e = 2{\cdot}1\,a_0$, $D_e = 45\,000\,cm^{-1}$, $\omega_e = 2590\,cm^{-1}$ for r and $R_e = 1{\cdot}71\,a_0$, $D_e = 50\,500\,cm^{-1}$ and $\omega_e = 1866\,cm^{-1}$ for R [28].

‡ Zero point energies quoted in I are all 2·8 cm^{-1} too small. We are grateful to P. Bartlett for bringing this error to our attention.

Table 2. Rotational levels of H_3^+ ground vibrational state relative to $J = 0$ level in cm^{-1}. Basis set parameters: $n \leqslant 4$, $m \leqslant 4$ and $j \leqslant 15$ with Morse-like functions given by $r_e = 1{\cdot}71\,a_0$, $D_e = 22\,000\,\mathrm{cm}^{-1}$, $\omega_e = 2590\,\mathrm{cm}^{-1}$ for r and $R_e = 1{\cdot}68\,a_0$, $D_e = 57\,000\,\mathrm{cm}^{-1}$ and $\omega_e = 2410\,\mathrm{cm}^{-1}$ for R [28].

J	K	k	j†	Frequency/cm^{-1}
1	0	1^f	o	86·769
	1	0^e	e	63·982
	1	1^e	o	63·983
2	1	2^f	e	236·831
	1	1^f	o	236·828
	2	0^e	e	168·926
	2	1^e	o	168·924
	0	2^e	e	259·319
3	0	3^f	o	515·730
	2	2^f	e	427·068
	2	2^f	o	427·068
	3	0^e	e	314·664
	3	1^e	o	314·648
	1	3^e	e	493·664
	1	3^e	o	493·667
4	1	4^f	e	831·717
	1	3^f	o	831·722
	3	2^f	e	657·247
	3	1^f	o	657·181
	4	0^e	e	500·935
	4	1^e	o	500·918
	2	2^e	e	766·763
	2	3^e	o	766·756
	0	4^e	e	853·251

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

only 3 cm^{-1} (~0·1 per cent) remains. Our results for surface A are consistently lower than those obtained by Burton *et al.* for the same surface, giving differences up to 11 cm^{-1} for some band origins. As our method is exact, for a given potential, within the usual limits of the variational procedure, this can only be due to lack of basis set convergence in Burton *et al.*'s calculation or their approximate treatment of the Watson term in the hamiltonian [23].

Table 2 shows rotational levels of the H_3^+ ground vibrational state calculated using surface B and a basis optimized for this purpose in I. These levels were fitted to the same perturbation hamiltonian used to represent the most recent experimental results on H_3^+ [14]. We have also fitted the results in I to the same hamiltonian. The constants, given in table 3, reproduce the *ab initio* levels with a standard deviation of about 0·002 cm^{-1}.

The agreement between *ab initio* calculation and experiment, as shown by table 3, is very good, especially for the higher order rotational constants. The small, 0·115 per cent, error in the B and C constants of I [14] is doubled for the potential of Burton *et al.* (for both surface A and surface B). These constants are highly sensitive to the equilibrium geometry of the molecule and these errors probably reflect slight errors in the minima of the *ab initio* potentials. This sensitivity can be gauged by comparing the minimum energy H–H distance of

Table 3. Rotational constants for the ground state of H_3^+.

Parameter	Experiment [14]	I [13]	This work Surface *B*
B/cm^{-1}	43·5646 ± 0·0016	43·519	43·468
C/cm^{-1}	20·6051 ± 0·0030	20·577	20·564
$10^2 D_{JJ}/\mathrm{cm}^{-1}$	4·18 ± 0·02	4·2	4·2
$10^2 D_{JK}/\mathrm{cm}^{-1}$	−7·61 ± 0·04	−7·9	−7·7
$10^2 D_{KK}/\mathrm{cm}^{-1}$	3·74 ± 0·04	3·9	3·8
$10^5 h_3/\mathrm{cm}^{-1}$	−1·1 ± 0·1	−0·7	−0·7
$10^3 d_J/\mathrm{cm}^{-1}$	1·7 ± 0·2	2·0	2·0
$10^3 d_K/\mathrm{cm}^{-1}$	−4·1 ± 0·1	−5·8	−5·3

Schinke *et al.*, 1·6531 a_0, with that of surface *B*, 1·6536 a_0. The earlier calculations of Carney and Porter [12] show larger errors compared to experiment [14] and used an equilibrium H–H separation of 1·6585 a_0.

3. VIBRATIONAL LEVELS OF H_2D^+

The vibrational ($J = 0$) levels of H_2D^+ were computed using a basis set optimized for this purpose in I. Results, and details of the basis, are given in table 4. For comparison the results obtained in I and the experimental ν_1 stretching fundamental of Amano and Watson [16] are also given. The *ab initio* calculations give agreement with each other; again surface *B* reproduces the experimental value to 0·1 per cent.

H_2D^+ is thought to be of great significance in the H/D fractionation process which is known to lead to an extra abundance of deuterated molecules in interstellar clouds [4]. H_2D^+ has just been observed in the interstellar medium [32], and the $1_{10} \leftarrow 1_{11}$ and $2_{20} \leftarrow 2_{21}$ pure rotational transitions, which were thought

Table 4. The zero point energy and lowest vibrational band origins of H_2D^+ in cm^{-1}.

Quantum numbers			I	This work†	
ν_1	ν_2	ν_3	[13]	Surface *A*	Surface *B*
0	1	0	2184·0	2196·1	2202·7
0	0	1	2309·7	2321·3	2331·8
1	0	0	2999·9	2999·7	2989·1‡
0	2	0	4245·3	4270·3	4281·5
0	1	1	4424·9	4446·3	4458·9
0	0	2	4564·1	4578·8	4601·7
1	1	0	5025·1	5041·8	5034·8
1	0	1	5232·9	5234·1	5239·1
$E_0/(\mathrm{cm}^{-1})$			3948·72§	3968·58	3966·72

† Basis set parameters $n \leqslant 7$, $m \leqslant 10$, $j \leqslant 19$ and Morse-like functions with $r_e = 1{\cdot}71\,a_0$, $D_e = 22\,000\,\mathrm{cm}^{-1}$ and $\omega_e = 2590\,\mathrm{cm}^{-1}$ for r and $R_e = 1{\cdot}65\,a_0$, $D_e = 47\,200\,\mathrm{cm}^{-1}$ and $\omega_e = 1964\,\mathrm{cm}^{-1}$ for R [28].

‡ Experimental value 2992·488 ± 0·016 cm^{-1} [16].

§ See second footnote, table 1.

the most promising for astrophysical observation, were recently recorded in the Laboratory [19–21]. The observed frequencies are in good agreement with out *ab initio* predictions. For example, the $1_{10} \leftarrow 1_{11}$ transition was observed at 372 342 MHz [19] compared to 372 053 MHz for the surface of Schinke *et al.*, 371 408 MHz for surface *A* and 371 238 MHz for surface *B*.

4. RO-VIBRATIONAL LEVELS OF D_2H^+

We optimized radial basis functions for D_2H^+ by minimizing the energies of the lowest 5 solutions of a $n \leqslant 4$, $m \leqslant 4$, $j \leqslant 14$ calculation with $J = 0$ and j even on surface *A*. The optimized parameters are given in table 5 which also gives the band origins obtained for both surface *A* and *B*. For comparison, the results of the only previous calculation on the vibrational levels of D_2H^+, by Carney and Porter [11], are also given. Good agreement is obtained, although Carney and Porter's potential is slightly stiffer in ν_1 and weaker in the ν_2 and ν_3 coordinates than surface *B*, which again gives best agreement with experiment. It reproduces the observed ν_1 stretching fundamental frequency with an error of only 0·1 per cent.

Table 6 gives energies for the rotational levels of the lowest 3 vibrational states of D_2H^+. The parameters are for Watson's I^r *A*-reduced hamiltonian [33] with basis set optimized for the $J = 0$ calculations discussed above.

Following our experience with H_2D^+ [15], rotational levels were only assigned to vibrational states after a fit (see below) had been performed. In table 6, the levels are also assigned a value of the approximate quantum number k, the projection of J along $\mathbf{R}$. As, for symmetry considerations, the D_2 bond was chosen as $\mathbf{r}$, the diatomic axis in the calculations, $\mathbf{R}$ is not the coordinate with the smallest moment of inertia. A more usual z axis is along $\mathbf{r}$ (the D_2 bond direction) giving a projection Ω of J [27]. However, full calculations, such as ours, which do not neglect Coriolis terms are invariant to such changes in embedding.

Table 5. The zero point energy and lowest vibrational band origins of D_2H^+.

Quantum numbers			Carney and Porter [10]	This work†	
ν_1	ν_2	ν_3		Surface *A*	Surface *B*
0	1	0	1961	1958·3	1964·7
0	0	1	2072	2067·3	2075·1
1	0	0	2742	2742·7	2733·2‡
0	2	0	3819	3806·0	3814·5
0	0	2	4041	4025·7	4038·2
0	1	1	4046	4040·4	4059·1
1	1	0	4644	4640·1	4644·1
1	0	1	4688	4675·5	4668·4
2	0	0	5391	5383·4	5380·4
0	3	0	5609	5565·4	5571·4
$E_0/(\mathrm{cm}^{-1})$			3948·72 [11]	3552·94	3551·14

† Basis set parameters $n \leqslant 7$, $m \leqslant 10$, $j \leqslant 19$ and Morse-like functions with $r_e = 1{\cdot}83\,a_0$, $D_e = 19\,800\,\mathrm{cm}^{-1}$ and $\omega_e = 1780\,\mathrm{cm}^{-1}$ for r and $R_e = 1{\cdot}62\,a_0$, $D_e = 37\,000\,\mathrm{cm}^{-1}$ and $\omega_e = 2304\,\mathrm{cm}^{-1}$ for R [28].

‡ Experimental value $2736{\cdot}997 \pm 0{\cdot}026\,\mathrm{cm}^{-1}$ [17].

Table 6. Low-lying ro-vibrational states of D_2H^+. Rotational energies are relative to the relevant $J = 0$ vibrational state (reported as frequency $\tilde{\gamma}$). Basis set parameters: $n \leqslant 4$, $m \leqslant 4$, $j \leqslant 15$ and as table 5.

J	τ	k	j†	(0, 0, 0) $\tilde{\gamma}/\mathrm{cm}^{-1}$	j†	(0, 1, 0) $\tilde{\gamma}/\mathrm{cm}^{-1}$	j†	(0, 0, 1) $\tilde{\gamma}/\mathrm{cm}^{-1}$
1	+1	1^f	o	57·849	o	58·8	e	57·9
	0	0^e	e	49·151	e	45·9	o	50·2
	−1	1^e	o	34·820	o	30·3	e	40·2
2	0	2^f	e	136·022	e	131·6	o	146·5
	+1	1^f	o	178·767	o	177·1	e	176·2
	−2	0^e	e	101·479	e	87·0	o	115·5
	−1	1^e	o	109·992	o	94·6	e	124·5
	+2	2^e	e	181·660	e	181·1	o	178·9
3	+3	3^f	o	376·906	o	365·8	e	368·2
	0	2^f	e	282·677	e	268·0	o	310·6
	−1	1^f	o	250·643	o	237·4	e	272·6
	−2	0^e	e	199·626	e	168·8	o	228·1
	−3	1^e	o	195·609	o	165·3	e	219·7
	+2	2^e	e	376·291	e	371·0	o	367·2
	+1	3^e	o	295·310	o	284·4	e	318·8
4	+2	4^f	e	522·181	e	496·8	o	499·4
	+3	3^f	o	641·916	o	688·0	e	624·1
	−2	2^f	e	398·111	e	371·9	o	429·8
	−1	1^f	o	418·449	o	388·5	e	462·9
	−4	0^e	e	315·204	e	266·8	o	347·0
	−3	1^e	o	316·503	o	266·4	e	362·4
	0	2^e	e	449·645	e	426·4	o	484·8
	+1	3^e	o	518·144	o	503·0	e	495·4
	+4	4^e	e	642·037	e	687·0	o	624·1

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

Table 7. Rotational constants in cm^{-1} for the lowest 3 vibrational states of D_2H^+.

	Ground state			
Parameter	Experiment [17]	This work	$\nu_2 = 1$ This work	$\nu_3 = 1$ This work
A	36·194 ± 0·018	36·122	37·955	34·720
B	21·9039 ± 0·0064	21·803	20·809	23·154
C	13·0856 ± 0·0047	13·042	12·906	12·140
$10^2\Delta_J$	1·18 ± 0·04	0·5	0·0	1·5
$10^2\Delta_{JK}$	−0·8 ± 0·2	0·5	−0·1	−1·3
$10^2\Delta_K$	[1·74]†	1·7	3·7	2·2
$10^3\delta_J$	2·25 ± 0·06	1·0	1·7	1·9
$10^3\delta_K$	1·6 ± 0·3	5·6	6·8	2·7
$10^4\Phi_J$	2·74 ± 0·08			
	Band origins		1964·7	2075·1
	Coupling constants‡ [32]		$G_{23} = 21·537$ $F_{23} = -0·768$	

† Fixed, see [17].

‡ The coupling constant G_{23} in table 1 of [15] was reported incorrectly and should have the value $-22·460\,\mathrm{cm}^{-1}$. We thank Dr. J. K. G. Watson and Dr. A. R. W. McKellar for drawing this error to our attention. The constant $\delta_K(\nu_2)$ in the same table should be $0·007\ \mathrm{cm}^{-1}$

Table 7 shows our fitted rotational constants for the lowest vibrational levels of D_2H^+. The parameters are for Watson's I^r A-reduced hamiltonian [33] with Coriolis interaction parameters due to Barbe *et al.* [34]. For the combined fit to the rotational levels of the (0, 1, 0) and (0, 0, 1) vibrations, the constants were obtained by minimizing the energy mismatch between levels with a particular J and symmetry. The fit for these states has a standard deviation of 0·2 cm^{-1} which is similar to the accuracy of the *ab intio* data.

For the ground vibrational state, comparison is made with the empirical constants of Lubic and Amano [17]. The agreement is fair, but not as good for the higher distortion constants as that obtained for the (0, 0, 0) state of H_3^+ (see above) or H_2D^+ [15]. This can perhaps be attributed to the relatively large standard deviations for fits to both the *ab initio* and empirical data, in each case 0·03 cm^{-1}.

Table 7 gives fitted rotational constants for the lowest two excited states of D_2H^+. To aid assignment, we also give our best estimates of the vibrational band origins of these states.

5. CONCLUSIONS

We have performed calculations on H_3^+, H_2D^+ and D_2H^+ using two fits to the *ab initio* data of Burton *et al.* [22]. Surface B [30] yields fundamental frequencies for ν_1 stretch of H_2D^+ and D_2H^+ in good agreement with experiment and a value of the ν_E bending fundamental of H_3^+ in significantly better agreement with experiment than that obtained by us previously using the surface of Schinke *et al.* [9]. This surface reproduces all observed frequencies with an error of 0·1 per cent.

We have obtained rotational constants for H_3^+ by fitting to the low-lying rotational levels. Comparison with experiment shows good agreement, but suggests that if high accuracy data is to be obtained *ab initio*, the equilibrium separation must be reproduced to 5 figures. This is a difficult taks, even for the electronically simple H_3^+ molecule.

Finally, we present band origins and rotational constants for the lowest two excited vibrational states of D_2H^+. We hope this data might aid the characterisation of this particularly complicated region of the D_2H^+ spectrum.

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