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First Principles Calculation of the Molecular Constants of H_3^+, H_2D^+, D_2H^+, and D_3^+

STEVEN MILLER AND JONATHAN TENNYSON

Department of Physics and Astronomy, University College London, Gower Street,
London WC1E 6BT, United Kingdom

Ro-vibrational calculations on a recent ab initio potential energy surface for H_3^+ (W. Meyer *et al., J. Chem. Phys.* **84,** 891 (1986)) are presented for the isotopomers $H_{3-n}D_n^+$ ($n = 0, 1, 2, 3$). These calculations employ refinements recently developed for nuclear motion calculations and are thus of very high accuracy. The rotational levels with $J \leqslant 4$ are fitted to standard vibration–rotation Hamiltonians due to Watson. The results are in excellent agreement with the experimental results where available. The complete set of molecular constants form probably the most complete and accurate determination of such parameters yet available.

1. INTRODUCTION

Although H_3^+ has a comparatively long history (*1*), its spectrum was not observed until the work of Oka (*2*) and Shy *et al.* (*3*) in 1980. Since that date the intensity of spectroscopic activity has been great, with the last few years seeing the experimental characterization of all the infrared allowed fundamental bands of H_3^+ and its deuterated isotopomers (*4–9*). The activity among theoreticians has been no less intense. Since the pioneering work of Carney and Porter (*10*), many workers have been attracted by the challenge of a system with only two electrons, which thus lends itself to highly accurate electronic structure calculations (*11*). The combination of theory and experiment has been particularly important in unraveling the complexities of the highly asymmetric mixed isotopomers H_2D^+ (*7*) and D_2H^+ (*8*). This combination has led to the first tentative extraterrestrial sighting of H_2D^+ (*12*).

The advantage that calculations, such as those presented here, have over observation is that it is in principle possible to obtain full information about all the levels in the system, uninhibited by selection rules and intensity considerations. This led Amano and Watson (*4*) to comment that the accuracy of the pure rotational frequencies they calculated from analysis of the ν_1 band of H_2D^+ was "not greatly improved over the ab initio estimates."

In this paper we present new ab initio results for H_3^+ and its isotopomers which we expect to be of comparable accuracy to the experimental results for many situations and of greater accuracy in the cases where observation gives only partial information. We expect these results to be a significant improvement over previous ab initio estimates for two reasons. First, a new ab initio surface for H_3^+ has been calculated by Meyer, Botschwina, and Burton (MBB) (*13*). As shown by MBB, and confirmed by Table I, their best surface yields highly accurate theoretical estimates for band origins of H_3^+ and its isotopomers. As our analysis shows, this high accuracy is maintained for the

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rotational levels. Second, recent refinements have been proposed to the methods used to perform the nuclear motion calculations. In particular the use of more sophisticated methods of selecting basis functions (*14*) and of a two-step variational technique for rotationally excited states (*15*) has led to a significant enhancement in the accuracy and possible range of such calculations.

2. METHOD

This work follows closely the approach used over a number of years by Tennyson and Sutcliffe (TS) (*16–18*) which is based upon the use of scattering coordinates. In these coordinates the triatomic vibration–rotation Hamiltonian is represented as an atom interacting with a diatom:

$$H = K_V + K_{VR} + V(r_1, r_2, \theta) \tag{1}$$

with

$$K_V = -\frac{\hbar^2}{2}\left[\frac{1}{\mu_1 r_1^2}\left(\frac{\partial}{\partial r_1} r_1^2 \frac{\partial}{\partial r_1} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\mu_2 r_2^2}\left(\frac{\partial}{\partial r_2} r_2^2 \frac{\partial}{\partial r_2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\right)\right] \tag{2}$$

$$K_{VR} = \delta_{k'k}\hbar^2\Bigg[\frac{(J(J+1) - 2k^2)}{2\mu_1 r_1^2} + \frac{k^2}{2}\operatorname{cosec}^2\theta\left(\frac{1}{\mu_1 r_1^2} + \frac{1}{\mu_2 r_2^2}\right) + \delta_{k'k+1}\frac{\hbar^2}{2\mu_1 r_1^2} C_{Jk}^{+}\left(-\frac{\partial}{\partial\theta} + k\cot\theta\right) + \delta_{k'k-1}\frac{\hbar^2}{2\mu_1 r_1^2} C_{Jk}^{-}\left(\frac{\partial}{\partial\theta} + k\cot\theta\right), \tag{3}$$

where r_1 is the diatom bondlength, r_2 the atom–diatom distance, and θ the angle between r_1 and r_2. The reduced masses are given by

$$\mu_1^{-1} = m_2^{-1} + m_3^{-1}$$
$$\mu_2^{-1} = m_1^{-1} + (m_2 + m_3)^{-1}, \tag{4}$$

where the atom has mass m_1 and the two diatom masses are m_2 and m_3. The above is for the z-axis embedded along r_2. The Hamiltonian for z embedded along r_1 is simply obtained by interchanging r_1 and r_2 and μ_1 and μ_2 in Eq. (3). The coefficients $C_{Jk}^{\pm}$ are the usual step up and down coefficients

$$C_{Jk}^{\pm} = (J(J+1) - k(k \pm 1))^{1/2}. \tag{5}$$

In the above, k represents the projection of the total angular momentum, J, on the body-fixed z-axis. The only term in H which couples states which differ in k is K_{VR}. Recently TS (*15*) solved the H_2D^+ ro-vibrational problem in two steps by (a) treating k as a good quantum number and (b) using the lowest solutions of step (a) to solve the full problem. By this means they analyzed levels with $J \leqslant 20$. In this work the same technique is used to obtain highly converged results for levels with $J \leqslant 4$. This, and the use of basis set selection according to the value of the diagonal matrix elements (*14*) in the first variational step, enabled us to converge all the levels calculated here to better than 0.01 cm^{-1}. This level of accuracy is sufficient to eliminate any significant splitting of degenerate levels caused by our neglect of the full symmetry of the symmetric isotopomers. It should also remove the irregularities in TS's H_2D^+ results noted by Foster *et al.* (*7*).

3. CALCULATIONS

For all calculations presented here we used Morse oscillator-like functions to carry the radial coordinates and associated Legendre functions for the bending coordinate. The radial basis set parameters were as optimized previously by TS for the relevant system (*11, 17, 18*). The basis set for each calculation which treated k as a good quantum was chosen by selecting the lowest 600 functions for a $J = 0$ calculation. The rotationally excited states were determined by using the lowest 300 vibrational levels for each k. In both steps we probably could have obtained good results with fewer functions, but we were keen to ensure the accuracy of our calculations. All the calculations used program suite SELECT, TRIATOM, and ROTLEV (*19*). Although preliminary calculations were performed on several of the potentials due to MBB, all the results quoted here are for MBB's corrected 87 CGTO potential which is their most accurate.

Table I compares our calculated zero-point energies and vibrational fundamentals with those predicted by MMB for the same potential. The experimental results for the observed fundamentals are also given. Our calculations agree well with MBB's and both give agreement with experiment to better than 0.05%.

In Tables II–V we present the results of our rotational analysis for each of the isotopomers. For space reasons we have not given the energies of the individual levels (which can be obtained from the authors). Instead we present the results of fitting our calculated levels to the various model Hamiltonians developed by Watson and coworkers (*4, 5, 7–9*). This approach allows us to make a direct comparison between the molecular constants obtained ab initio and from experiment.

The most striking feature of the tables is the consistent good agreement between ab initio and experimental parameters for all the bands considered. Although previously, fairly accurate ab initio results had been obtained (*4, 17*) for the ground state molecular parameters, the agreement for the excited states was not so good. This failing was attributed to both inaccuracies in the potential and in the nuclear motion calculations (*18*). In this work, the improved representation of the ground state is also repeated for the vibrationally excited state parameters.

In Tables II–V values are given for the standard deviations, σ, of our fits. The band origins were not included in our fitting, but set to the value obtained from the $J = 0$ calculation as given in Table I. Hence our fits for ground state, ν_1, and (ν_2, ν_3) levels were conducted separately and each gave a separate standard deviation. The empirical fits necessarily involved fitting levels simultaneously from both the ground and the excited states, thus giving only a single standard deviation. It should be remembered that the standard deviation only measures the quality of the parameterization of the levels and gives no information about other errors in either the ab initio or the experimental results. For all the ions considered our fits are better for the ground than the vibrationally excited states. This is probably due to the increasing density of vibrational states and the resulting increase in Coriolis effects. Only Coriolis interactions within the (ν_2, ν_3) manifold were explicitly accounted for in the fits. In all tables, the

TABLE I

Comparison of ab Initio and Experimental Vibrational Frequencies in cm^{-1}

Isotopomer	Band	*Ab initio*		Experiment	
		MBB(13)	This work	Band origin	Ref.
H_3^+	ν_1(A-type)	3178.4	3178.348		
	ν_2(E-type)	2521.3	2521.282	2521.308(9)	5
	zpe	4363.5	4363.501		
D_3^+	ν_1(A-type)		2301.250		
	ν_2(E-type)		1835.060	1834.669(1)	9
	zpe		3113.733		
H_2D^+	ν_1(s.str.)	2993.0	2992.962	2992.49(2)	4
	ν_2(bend)	2206.3	2206.244	2205.869(8)	7
	ν_3(as.str.)	2335.0	2334.986	2335.449(9)	7
	zpe		3979.905		
D_2H^+	ν_1(s.str.)	2737.4	2737.302	2737.00(3)	6
	ν_2(bend)	1967.8	1967.825	1968.17(2)	8
	ν_3(as.str.)	2079.2	2079.212	2078.41(2)	8
	zpe		3563.086		

Note. Also given is the calculated zero-point energy (zpe) for each isotopomer. The estimated experimental error is shown in brackets in units of the last figure for each band origin.

estimated error in each of the experimental constants is given in brackets in units of the last figure of the relevant constant.

Table II compares the ab initio and empirical molecular constants for H_3^+. All the ab initio constants were derived using the parameterization utilized by Watson *et al.* (*5*) in their analysis of the ν_2 band of H_3^+, which was based on Watson's analysis of X_3 systems (*20*). The small standard deviations for our fits show that this gave a good representation of our data. Because of the selection rules for infrared transitions in H_3^+, it was necessary for Watson *et al.* to determine C_0 by scaling TS's ab initio value using the error in B_0. Our calculations show that their scale factor of 1.00115 is very close to 1.00122, the ratio of our C_0 to TS's. Table II also gives our values for the parameters q^j and q^k which give rise to the splitting of the $G = 0$ levels but which cannot be determined empirically as nuclear spin statistics forbid occupation of the levels with $s = (-1)^J$ (*5*).

Table III compares the ab initio and empirical molecular constants for D_3^+. For this ion Watson *et al.* (*9*) modified their previous parameterization procedure for the de-

TABLE II

Vibration–Rotation Parameters for H_3^+ in cm^{-1}

	Ground State		ν_1 State
Parameter	*Ab Initio*	Experiment	*Ab Initio*
		(5)	
B	43.550	43.565(2)	42.502
C	20.604	20.605(3)	20.009
$10^2 D^{JJ}$	4.19	4.18(2)	4.11
$10^2 D^{JK}$	-7.71	-7.61(4)	-8.00
$10^2 D^{KK}$	3.84	3.74(4)	4.13
$10^3 d^j$	1.9	1.7(2)	2.3
$10^3 d^k$	-5.2	-4.1(4)	-5.6
$10^5 h_3$	-0.7	-1.1(1)	-1.7
$10^2 \sigma$	0.2	1.4	0.5

	ν_2 State	
Parameter	*Ab Initio*	Experiment
		(5)
B	44.171	44.226(3)
C	19.399	19.340(6)
$C\zeta$	-18.602	-18.651(4)
$10^2 \eta^J$	-13.97	-14.03(9)
$10^2 \eta^K$	14.34	16.77(19)
$10^2 D^{JJ}$	4.84	5.28(3)
$10^2 D^{JK}$	-9.85	-10.88(9)
$10^2 D^{KK}$	5.43	6.1(6)
$10^3 \beta$	3.1	3.16(4)
q	-5.379	-5.372(3)
$10^2 q^j$	1.98	
$10^2 q^k$	0.38	
$10^3 d^j$	-0.5	2.0(1)
$10^3 d^k$	1.2	-1.9(4)
$10^3 e^j$	4.0	4.04(3)
$10^3 e^k$	-5.4	-7.2(1)
$10^5 h_3$	-0.7	-1.1(1)
$10^2 \sigma$	1.9	1.4

TABLE III

Vibration–Rotation Parameters for D_3^+ in cm^{-1}

	Ground State		ν_1 State
Parameter	*Ab Initio*	Experiment	*Ab Initio*
		(9)	
B	21.818	21.8240(3)	21.425
C	10.511	10.5104	10.301
$10^2 D^{JJ}$	0.99	0.995(2)	0.97
$10^2 D^{JK}$	-1.75	-1.734(5)	-1.74
$10^2 D^{KK}$	0.84	0.788	0.85
$10^3 d^j$	0.8		1.0
$10^3 d^k$	-2.3		-1.7
$10^5 h_3$	0.1		0.1
$10^2 \sigma$	0.0	0.24	0.0

	ν_2 State	
Parameter	*Ab Initio*	Experiment
		(9)
B	21.971	21.9748(3)
C	10.125	10.1506(4)
$C\zeta$	-9.747	-9.7417(3)
$10^2 \eta^J$	-3.22	-2.241(9)
$10^2 \eta^K$	3.04	1.51(3)
$10^2 D^{JJ}$	1.08	1.100(3)
$10^2 D^{JK}$	-2.01	-1.92(1)
$10^2 D^{KK}$	1.03	0.867(9)
$10^3 \beta$	-0.5	-0.515(2)
q	-1.842	-1.8385(3)
$10^3 q^j$	3.3	3.39(1)
$10^3 q^k$	-4.2	-1.35(15)
$10^3 d^j$	-0.9	
$10^3 d^k$	1.7	
$10^3 e^j$	1.8	
$10^3 e^k$	-2.3	
$10^5 h_3$	-0.1	-0.082(6)
$10^2 \sigma$	0.2	0.24

generate ν_2 band to make their Pade approximants "more physically meaningful." However, we found that this parameterization gave a significantly worse, standard deviation 0.04 cm^{-1} compared to 0.005 cm^{-1}, fit to our data. We therefore used the same method as in Table II to represent our data. Of course, as the fitting procedures for the ν_2 levels are no longer identical any close comparison between the ab initio and empirical parameters must be made with caution. Again for D_3^+, the $\Delta G = 0$ selection rule meant that Watson *et al.* had to scale ab initio values to obtain C_0 and D_0^{KK}. The good agreement between their and our values confirm the validity of this procedure.

Table IV compares the ab initio and empirical molecular constants for H_2D^+. For this ion spectra have been recorded and fitted for both the ν_1 and strongly coupled (ν_2, ν_3) bands. Pure rotational spectra have also been observed, but only for two key transitions (*21*). All the ab initio data on H_2D^+ were parameterized using the effective Hamiltonian (as opposed to supermatrix) of Foster *et al.* (*7*). This Hamiltonian is based upon Watson's I^r A-reduced asymmetric rotor Hamiltonian (*22*), but with the sextic terms represented by Pade-type expressions (*7*). We followed the approach of Foster *et al.* of using three of the possible seven sextic constants (the Φ's). Using all seven constants was found to reproduce our data to better than the accuracy of the calculations. However, we would suggest that the values presented for the three sextic constants retained in our fits are of no great physical significance. Note also the large errors for the corresponding empirical constants.

The largest disagreement between previous ab initio and experimental determinations of the molecular constants of H_2D^+ was for terms related to the Coriolis coupling. The discrepancy was largest for the set (C_2, C_3, ξ_{23}) (*7*), apparently because TS's calculations gave a relatively poor estimation of the gap between the ν_2- and ν_3-band origins. However, most of this difference remains in our more accurate redetermination and, due to correlation between these parameters, may simply be due to differences in the fitting procedures adopted.

Table V compares the ab initio and empirical constants for D_2H^+. Again experimental fits are available from analysis of both the ν_1 and (ν_2, ν_3) bands. In analyzing the (ν_2, ν_3) band, Foster *et al.* (*8*) slightly modified the effective Hamiltonian Coriolis constants used in their previous analysis of H_2D^+ (*7*). We found that this modification, while producing fits with similar or even slightly smaller standard deviations than the original parameterization, showed an extreme interdependence between the parameters which rapidly led to unphysical quantities. The ab initio data of Table V are therefore fitted using the effective Hamiltonian the same as that of Table IV.

For H_2D^+ and D_2H^+, analysis of the ν_1 band supplies an additional set of empirical constants for the ground state. In fitting these transitions, Amano and co-workers (*4*, *6*) used the I^r A-reduced Hamiltonian (*22*) to sixth order, without Pade approximants. It is interesting to observe that many of our ground state parameters, for example all three Δ's for both ions, lie in between the two sets of empirical values.

4. CONCLUSIONS

We have presented the results of a series of calculations on the low-lying rotational and vibrational states of H_3^+ and its deuterated isotopomers using the accurate potential

TABLE IV

Vibration-Rotation Parameters for H_2D^+ in cm^{-1}

	Ground State			ν_1 State	
Parameter	*Ab Initio*	Experiment		*Ab Initio*	Experiment
		(7)	(4)		(4)
A	43.440	43.466(8)	43.36(7)	41.604	41.52(7)
B	29.115	29.137(2)	29.14(1)	29.303	29.36(2)
C	16.603	16.602(2)	16.611(8)	16.389	16.39(1)
$10^2\Delta^{JJ}$	1.02	1.0(1)	1.18(9)	1.00	1.5(1)
$10^2\Delta^{JK}$	0.02	0.3(1)	-0.8(5)	0.25	-1.6(7)
$10^2\Delta^{KK}$	3.08	3.8(2)	0.32	2.61	3.2
$10^2\delta^j$	0.39	0.402(3)	0.38(2)	0.38	0.35(3)
$10^2\delta^k$	1.80	1.98(3)	2.0(4)	2.14	3.6(7)
$10^5\Phi^{JJJ}$	0.5	-1.7(2)	1.7(2)	0.8	19(2)
$10^5\Phi^{JJK}$	-1.8	0.3(8)	-13(6)	-2.8	120(70)
$10^5\Phi^{JKK}$	8.4	82(3)	-5(13)	13.4	-70(17)
$10^2\sigma$	0.4	0.24	1.8	0.8	1.8

	ν_2 State		ν_3 State	
Parameter	*Ab Initio*	Experiment	*Ab Initio*	Experiment
		(7)		(7)
A	42.251	42.30(3)	46.331	46.31(1)
B	30.382	30.41(3)	27.688	27.682(9)
C	14.269	14.91(14)	17.256	16.63(14)
$10^2\Delta^{JJ}$	1.27	1.9(2)	0.95	0.5(1)
$10^2\Delta^{JK}$	-2.32	-2.4(7)	1.68	0.5(8)
$10^2\Delta^{KK}$	5.71	6.3(6)	3.15	4.2(8)
$10^2\delta^j$	0.62	0.42(6)	0.23	0.43(5)
$10^2\delta^k$	1.66	2.1(3)	2.18	2.0(7)
$10^5\Phi^{JJJ}$	2.4	5(3)	0.4	-2.0(7)
$10^5\Phi^{JJK}$	-2.3	-4(24)	-17.2	-30(5)
$10^5\Phi^{JKK}$	17.6	81(54)	35.6	6(20)
ξ_{23}	-22.616	-24.4(4)		
α_{23}	1.592	1.59(7)		
$10^2\eta^j$	-5.61	-5.0(6)		
$10^2\eta^k$	4.20	-6(5)		
$10^2\sigma$	1.0	0.24		

TABLE V

Vibration–Rotation Parameters for D_2H^+ in cm^{-1}

	Ground State			ν_1 State	
Parameter	***Ab Initio***	**Experiment**		***Ab Initio***	**Experiment**
		(8)	(6)		(6)
A	36.194	36.24(2)	36.19(2)	35.419	35.41(2)
B	21.859	21.869(6)	21.904(7)	21.616	21.58(1)
C	13.067	13.057(3)	13.086(5)	12.935	12.98(1)
$10^2\Delta^{JJ}$	0.59	0.47(2)	1.18(4)	0.62	0.78(3)
$10^2\Delta^{JK}$	0.17	0.8(2)	-0.8(2)	-0.32	-1.4(3)
$10^2\Delta^{KK}$	1.98	2.7(5)	1.74	2.57	3.6(4)
$10^2\delta^{j}$	0.21	0.219(8)	0.225(6)	0.22	0.03(2)
$10^2\delta^{k}$	1.22	1.39(9)	1.6(3)	1.29	1.3(1)
$10^5\Phi^{JJJ}$	1.0	-3.1(5)	2.74(8)	1.3	15.9(7)
$10^5\Phi^{JJK}$	-4.7	15(11)		-5.9	-9.2(9)
$10^5\Phi^{JKK}$	7.3	64(56)		8.7	105(1)
$10^2\sigma$	0.4	2.5	3.0	0.4	3.0

Table V cont.

	ν_2 State		ν_3 State	
Parameter	***Ab Initio***	**Experiment**	***Ab Initio***	**Experiment**
		(8)		(8)
A	38.103	38.11(2)	34.813	34.86(1)
B	20.877	20.83(1)	23.059	23.08(1)
C	13.234	13.06(4)	11.707	11.92(3)
$10^2\Delta^{JJ}$	1.12	0.24(7)	0.12	1.32(9)
$10^2\Delta^{JK}$	-0.68	0.42(30)	0.73	-3.7(5)
$10^2\Delta^{KK}$	3.46	3.17(39)	1.74	7.3(8)
$10^2\delta^{j}$	-0.11	0.39(2)	0.61	0.13(3)
$10^2\delta^{k}$	2.39	0.25(28)	1.11	2.6(2)
$10^5\Phi^{JJJ}$	-3.3	1.9(30)	3.7	6(3)
$10^5\Phi^{JJK}$	25.0	-16(18)	-43.3	-130(260)
$10^5\Phi^{JKK}$	-5.3	25(23)	50.5	300(600)
ξ_{23}	-22.456	-21.93(9)		
α_{23}	-0.700	-0.82(2)		
$10^2\eta^{j}$	-4.47			
$10^2\eta^{k}$	1.47			
$10^2\sigma$	0.8	2.5		

surface of Meyer *et al.* (*13*). Comparison with the available experimental results suggests that these calculations are highly reliable, yielding a complete set of parameters of accuracy similar to those derived empirically. Undoubtedly they represent the most accurate first principles determination of the molecular constants of any polyatomic.

It is our intention to perform further calculations on these ionic systems for highly rotationally excited states. The aim of this work will be to study spectral regions where the separation between rotational and vibrational levels becomes comparable and hence Coriolis interactions are of enhanced importance.

Finally we note that these calculations were performed on a potential energy surface whose minimum is at an H_3^+ bondlength of 0.8743 Å. Watson *et al.* (*9*) extrapolated their results to a value of 0.8746 Å. The good agreement between theory and experiment displayed by the results of this paper and the closeness of these values suggest that they must be near the true geometry parameter for this system.

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