

A Spectroscopically Determined Potential Energy Surface for H_3^+ BIANCA M. DINELLI,¹ STEVEN MILLER, AND JONATHAN TENNYSON²*Department of Physics and Astronomy, University College London, Gower St., London WC1E 6BT, United Kingdom*

A potential energy surface for H_3^+ is determined by adjusting 11 parameters from the ab initio surface of Lie and Frye (*J. Chem. Phys.* **96**, 6784–6790, 1992) to a data set of 243 H_3^+ energy levels covering vibrational levels up to $3\nu_2$ and rotational levels up to $J = 9$. The surface is determined by successive refinements using variational calculations to reproduce the experimental data. A method which used cheaper but unconverged calculations for all but the final iteration of the fit is outlined. The resulting potential reproduces the observed data with a standard deviation of 0.053 cm^{-1} . Revised estimates of H_3^+ band origins up to $5\nu_2$ are presented. Predictions for the fundamental frequencies using this potential are good for D_3^+ but poor for the mixed isotopomers H_2D^+ and D_2H^+ . It is suggested that these errors, which are about 0.5 cm^{-1} , are due the breakdown of the Born–Oppenheimer approximation. Comparisons are made with known non-Born–Oppenheimer terms for H_2^+ and H_2 . © 1994 Academic Press, Inc.

1. INTRODUCTION

The molecular ion H_3^+ is of great importance astrophysically (1, 2) and is the subject of a series of still poorly understood spectra recorded by Carrington and co-workers (3). Its spectrum was first observed by Oka (4) via the allowed ν_2 fundamental. Several bands of H_3^+ have since been studied experimentally: $\nu_2(l = 1) \leftarrow 0$ (5–8), $\nu_1 \leftarrow 0$ (7), $2\nu_2(l = 2) \leftarrow 0$ (9, 10), $2\nu_2(l = 2) \leftarrow \nu_2(l = 1)$ (8), $2\nu_2(l = 0) \leftarrow \nu_2(l = 1)$ (8), $\nu_1 + \nu_2(l = 1) \leftarrow \nu_2(l = 1)$ (7), $\nu_1 + \nu_2(l = 1) \leftarrow \nu_1$ (8), and $3\nu_2(l = 1) \leftarrow 0$ (11). This data has been compiled for astronomical studies (12). Parallel studies on the fundamental bands of deuterated H_3^+ started with the observation of the ν_2 band of D_3^+ by Shy *et al.* (13) and have continued with work on the mixed isotopomers H_2D^+ (14, 15) and D_2H^+ (16, 17).

All these spectroscopic studies relied heavily on ab initio calculations of the transition frequencies. The first assignments used a potential energy surface (18) and rovibrational calculations by Carney and Porter (19). More recently a surface due to Meyer, Botschwina, and Burton (MBB) (20) has become widely used and has proved very successful. However, this surface is not entirely satisfactory. First, there are systematic differences between observed and calculated transition frequencies which rise to about 3 cm^{-1} for the second bending overtone (11). This is important as attempts, currently in progress, to observe the third and fourth bending overtone will rely on accurate theoretical predictions for assignments. Second, the most successful of MBB's surfaces (the corrected seventh-order fit to their 87GTO calculation, referred to as MBB* below) is not completely ab initio in the sense that MBB adjusted one constant to better reproduce the observed frequency of the bending fundamental. Although this surface

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has proved very successful, this adjustment procedure is flawed as it was based on a slightly incorrect mass of H_3^+ and used one datum to determine one constant.

Recently Lie and Frye (LF) (21) have published a new ab initio surface which they fit to the same form as MBB. Although LF's electronic structure calculations are variationally superior to MBB's, their surface does not actually perform as well as the *corrected* surface of MBB. We therefore decided to use the wealth of experimental data on H_3^+ to determine a potential energy surface for this system of true spectroscopic accuracy. We hope that predictions made with this surface will help with the assignment of further transitions in the H_3^+ system, particularly those involving states which begin to sample the dynamically interesting region where the ion goes quasilinear.

The whole concept of a potential energy surface is based on the Born–Oppenheimer (22) approximation (BO) which allows the motions of electrons and nuclei to be treated separately. This approximation, which underpins much of chemical physics, is rarely doubted except when electronic states happen to be (nearly) degenerate. However BO is based on the large mass ratio between nuclei and electrons. This ratio is smallest for hydrogen-containing species and one would thus expect H_3^+ to be the polyatomic molecule for which the BO approximation is least reliable. As we demonstrate below, our H_3^+ surface clearly shows non-BO effects when applied to H_2D^+ and D_2H^+ . As such it must be considered an effective H_3^+ potential energy surface which implicitly includes BO corrections terms.

2. METHOD

Both the LF and MBB potential energy surfaces use the same functional form to give an analytic representation of the potential

$$V = \sum_{n,m,k} V_{n,2m,3k} S_a^n S_e^{2m+3k} \cos(3k\phi), \quad n + 2m + 3k \leq N, \quad (1)$$

where the $V_{n,2m,3k}$ are the coefficients determined by fitting and the value of N determines the order of the fit. Here we concern ourselves only with $N = 7$ which gives a 31-term fit, one of which ($V_{0,0,0}$) merely sets the energy zero.

In (1), the coordinates (S_a , S_e , ϕ) are related to the atom–atom distances (R_{12} , R_{23} , R_{31}) by two transformations. The first transformation changes the atom–atom distances to Morse coordinates

$$\tilde{R} = \left[1 - \exp\left(-\beta \frac{R - R_e}{R_e}\right) \right] / \beta. \quad (2)$$

The second transformation is to symmetry-adapted deformation coordinates

$$S_a = (\tilde{R}_{12} + \tilde{R}_{23} + \tilde{R}_{31}) / \sqrt{3} \quad (3)$$

$$S_x = (2\tilde{R}_{12} - \tilde{R}_{23} - \tilde{R}_{31}) / \sqrt{6} = S_e \cos(\phi) \quad (4)$$

$$S_y = (\tilde{R}_{23} - \tilde{R}_{31}) / \sqrt{2} = S_e \sin(\phi). \quad (5)$$

In this work an improved H_3^+ potential is generated by refitting selected constants in expansion (1) to spectroscopic data. As this cannot be done directly, a fitting procedure must be developed which involves using a given potential to generate the experimental data, estimating the errors in the computed data, adjusting (some of) the parameters in the potential, and repeating the procedure until a satisfactory fit is

achieved. Similar procedures have been used for other chemically bound triatomics, such as water (23, 24) and HCN (25).

As the starting potentials for H₃⁺ are already among the most accurate known for a molecule larger than a diatomic, care must be taken in the fitting. In particular it is important that the step of calculating the observed data from the potential does not introduce any errors, as these will inevitably be reflected in the final potential fit (see Fernley *et al.* (26) for a full discussion of this point).

Miller, Tennyson, and co-workers (27, 28) have performed a series of rovibrational calculations on H₃⁺ using an exact (within the Born–Oppenheimer approximation), body-fixed internal coordinate Hamiltonian and large basis sets. The emphasis of these calculations has been on accuracy rather than on computational cheapness. As the fitting procedure outlined necessarily means many recalculations, calculations of the size of our most recent work (28) for the fitting are computationally too expensive for us. Conversely, significantly reduced calculations run the risk of seriously degrading the quality of the resulting potential.

We therefore developed the following procedure for performing the fitting. First, our fit was performed using “observed” energy levels (see, e.g., (10)) rather than transition frequencies. This allowed us to make a number of exploratory preliminary fits with only a few rotational levels included, although our final fits included all $J \leq 9$. Second, most preliminary fits and the initial iterations of the final fit were performed with smaller *unconverged* calculations. Allowance was made for the errors inherent in this procedure by correcting each calculated energy level by the convergence error for that obtained from the starting potential. As we show below this procedure proved highly successful and meant that we only performed one full, final iteration with a large, converged basis function for the H₃⁺ data. This fit, to 11 constants and involving calculations with $0 \leq J \leq 9$ took about 40 hr on a single processor of a Cray-YMP. An iteration of an unconverged fit typically took less than 6 hr depending on the number of constants being determined.

All variational calculations were performed in scattering coordinates using the two-step variational procedure (29) implemented in the TRIATOM program suite (30) and basis functions tested in our previous work on H₃⁺ (27, 28). The least-squares fitting was performed using a program used previously for fitting more conventional perturbation series representations to conventional spectra (31).

3. CALCULATIONS

Our previous calculation covered H₃⁺ bands up to and including $4\nu_2$. This calculation used 1700 basis functions for the first (“vibrational”) step of the calculation and $600 \times (J + 1)$ functions for the final step. In both cases the basis functions were energy selected (30). In this work, as we only consider vibrational levels up to $3\nu_2$, only 1200 functions were retained in the first step. This basis is sufficient to converge nearly all the levels considered here to 0.001 cm^{-1} (0.003 cm^{-1} in the worst case) and is the one we designate “converged.”

For the majority of calculations we used an energy-selected basis with 600 functions for the first step and $350 \times (J + 1)$ functions for the second. This “unconverged” basis gives errors for individual levels typically up to 0.5 cm^{-1} , although for reasons we are unclear about, the unconverged $J = 4$ calculations were in error by considerably more than this for some levels.

The mass of each atom in the H₃⁺ was taken as $(3M_{\text{H}} - m_e)/3$, where the mass of atomic hydrogen, M_{H} , is $1.007825035 \text{ a.m.u.}$ (32) and m_e is the mass of an electron.

The conversion of a.m.u. to electron masses (or a.u.) was taken to be 1822.88851 (32); other fundamental constants were taken as before (33).

The data set contained 243 energy levels (5-12, 34): 36 associated with the vibrational ground state, 81 with ν_2 , 14 with ν_1 , 64 with $2\nu_2(2)$, 14 with $2\nu_2(0)$, 23 with $\nu_1 + \nu_2$, and 11 with $3\nu_2(1)$. As a result of our preliminary fits the $2\nu_2(2)$ level ($J = 6, G = 2^-$) was reassigned (34).

Observable levels of H_3^+ are either *ortho* (spin, $\frac{3}{2}$) or *para* (spin, $\frac{1}{2}$) nuclear spin species. As these levels form two stacks with no interconnecting transitions (5), it was in addition necessary to assume some value for the separation between the ground state ($J = 1, K = 1$) and ($J = 1, K = 0$) levels. A value of 22.838 cm^{-1} was taken as being close to all accurate ab initio determinations. This constraint was relaxed in fits, discussed below, which included data from mixed isotopomers, but none of these fits gave a significantly different value for the separation.

Initial test calculations showed that, once we used the correct masses as discussed above, the MBB, the MBB*, and the LF potentials reproduced our data set with standard deviations of 4.05, 0.79, and 1.81 cm^{-1} , respectively. These errors were considered too large to provide a good starting point for a rapidly convergent least-squares fit so we therefore scaled the constants $V_{2,0,0}$ and $V_{0,2,0}$ for each potential until they reproduced the known fundamental frequencies of H_3^+ . With these scalings the LF potential proved significantly better at reproducing our data set so it was used as the starting point for our fits.

As discussed above initial fits used unconverged calculations. These fits were used to refine the dataset to the one discussed above and to determine which constants in the potential expansion should be left free to vary in the fit. Initial calculations varied 6 potential constants and this was gradually increased, by trial and error, to 11 constants. In choosing which constants to vary we concentrated on ones with large initial values and ones which influenced levels with large residues. The latter levels were generally associated with $3\nu_2$.

An initial fit which varied 11 constants (see Table I) was performed with the unconverged basis and gave a standard deviation of 0.063 cm^{-1} . These refined constants were then used to start a final iteration with the converged basis. This gave a standard deviation of 0.053 cm^{-1} . It should be noted that in this final fit the constants $V_{0,4,0}$ and $V_{3,0,3}$ were found to be highly correlated.

This potential was used to generate revised estimates of the band origins for H_3^+ up to the fourth bending overtone (see Table II). In this case we have used the assignments of Carter and Meyer (35) which have been confirmed graphically by Sadovskii *et al.* (36). For comparison our estimates obtained using the MBB potential and the masses discussed above (see (37)) are also given.

To test this potential a series of calculations were performed on observed levels of the various deuterated forms of H_3^+ . The new potential gave satisfactory results, i.e., errors similar to those found for H_3^+ , for the rotational term values of the isotopomers. For example, the observed ground state term values of H_2D^+ (15), 19 levels with $J \leq 5$, were reproduced with a standard deviation of 0.046 cm^{-1} . However, it performed poorly for the vibrationally excited states of H_2D^+ and D_2H^+ . In particular, the fundamental frequencies of these mixed ions were found to be in error by up to 0.8 cm^{-1} .

One explanation for this discrepancy is that the fundamentals of the mixed isotopomers are sensitive to constants which were poorly determined in the H_3^+ fits. It was therefore decided to perform a further fit including these fundamentals in the data set.

TABLE I

 H_3^+ Potential Energy Surface; Constants $V_{n,2m,3k}$ for Eq. (1) in μ Hartree

n	2m	3k	LF	fitted	error
1	0	0	- 14.620	- 44.794	5.7
2	0	0	204613.180	204090.807	10
0	2	0	266482.250	266648.315	8.8
3	0	0	- 40228.030	- 39557.981	69
1	2	0	- 215815.560	- 211590.024	92
0	0	3	2111.470	2240.975	40
4	0	0	24945.540	a	
2	2	0	147173.310	134319.810	324
1	0	3	93087.320	90018.815	1039
0	4	0	45547.120	43919.340 ^b	68
5	0	0	109.030	a	
3	2	0	- 53083.250	a	
2	0	3	6097.420	a	
1	4	0	55215.860	a	
0	2	3	5750.940	a	
6	0	0	4422.260	a	
4	2	0	57593.050	a	
3	0	3	73537.630	88932.641 ^b	12750
2	4	0	36870.140	a	
1	2	3	88510.890	a	
0	6	0	15089.850	19429.894	103
0	0	6	841.300	a	
7	0	0	7.820	a	
5	2	0	- 27443.780	a	
4	0	3	- 11405.760	a	
3	4	0	17652.440	a	
2	2	3	2644.660	a	
1	6	0	- 2406.620	a	
1	0	6	- 29.470	a	
0	4	3	115.160	a	

^a Constant held fixed to the values of Lie and Frye (LF) (21) during fit.^b Constants highly correlated in fit.

A series of tests were performed to determine which, if any, constants influenced the fundamentals of H_2D^+ and D_2H^+ . It was rapidly found that the fundamentals were sensitive to constants of the type $V_{n,4,k}$. However, attempts to redetermine these constants showed that values which gave satisfactory results for the mixed isotopomers gave poor results for H_3^+ . Furthermore, the constants which reproduced the fundamentals of the mixed isotopomers showed unphysically large deviations from the ab initio starting values.

A closer inspection of this problem focused on the ν_2 and ν_3 fundamentals of the mixed isotopomers. In H_3^+ these fundamentals form the degenerate ν_2 mode which is

TABLE II

H_3^+ Band Origins, in cm^{-1} , Using the Corrected Potential of Meyer *et al.* (MBB*) and the New Potential from this Work (DMT)

ν_1	ν_2^l	MBB*	DMT
A ₁			
1	0 ⁰	3178.32	3178.16
0	2 ⁰	4777.02	4778.40
2	0 ⁰	6261.92	6261.65
0	3 ³	7282.52	7282.52
1	2 ⁰	7769.09	7769.06
0	4 ⁰	8996.73	9000.58
3	0 ⁰	9251.42	9252.08
1	3 ³	9964.03	9963.98
2	2 ⁰	10592.05	10590.51
0	5 ³	10913.37	10915.47
1	4 ⁰	11809.29	11808.06
A ₂			
0	3 ³	7493.69	7493.33
1	3 ³	10208.54	10206.76
0	5 ³	11525.75	11528.23
E			
0	1 ¹	2521.27	2521.40
0	2 ²	4997.41	4998.04
1	1 ¹	5553.67	5554.31
0	3 ¹	7003.49	7006.09
1	2 ²	7868.64	7869.09
2	1 ¹	8486.90	8487.20
0	4 ²	9107.74	9111.64
1	3 ¹	9650.72	9652.25
0	4 ⁴	9996.98	9996.67
2	2 ²	10642.57	10640.17
0	5 ¹	10853.52	10856.82
3	1 ¹	11321.39	11319.49
1	4 ²	11651.38	11650.02
0	5 ⁵	12073.51	12071.17

split by the lower symmetry of H_2D^+ and D_2H^+ . As the potential retains D_{3h} symmetry even for the asymmetric isotopomers, this splitting, within BO, is caused by the nuclear kinetic energy operator. Table III shows that the average values, $\frac{1}{2}(\nu_2 + \nu_3)$, of these fundamentals calculated using the potential fitted to the H_3^+ data are very close to the values obtained experimentally. But the same calculations for both H_2D^+ and D_2H^+ show the splitting between ν_2 and ν_3 is *underestimated* by about 0.9 cm^{-1} in H_2D^+ and *overestimated* by about 1.5 cm^{-1} in D_2H^+ .

TABLE III

Comparison of Fundamentals of H_2D^+ and D_2H^+ Calculated Using the ab initio Potentials of Meyer *et al.* (MBB) and Lie and Frye (LF), the Corrected Potential of MBB (MBB*), and the Potential of this Work (DMT) with the Observed Fundamentals (14-17)

H_2D^+					
	ν_1	ν_2	ν_3	$\frac{1}{2}(\nu_2 + \nu_3)$	$\nu_3 - \nu_2$
MBB	2992.5	2204.4	2332.8	2268.6	128.4
MBB*	2993.0	2206.2	2335.0	2270.6	128.7
LF	2995.8	2204.8	2333.5	2269.2	128.7
DMT	2992.7	2206.2	2334.9	2270.6	128.7
Obs	2992.5	2205.9	2335.4	2270.7	129.6
D_2H^+					
	ν_1	ν_2	ν_3	$\frac{1}{2}(\nu_2 + \nu_3)$	$\nu_3 - \nu_2$
MBB	2736.8	1966.2	2077.2	2021.7	111.0
MBB*	2737.4	1967.8	2079.2	2023.5	111.4
LF	2739.5	1967.3	2077.7	2022.5	110.4
DMT	2736.8	1967.5	2079.2	2023.3	111.7
Obs	2737.0	1968.2	2078.4	2023.3	110.2

Given that we are using a BO, but otherwise exact, kinetic energy operator, the only possible uncertainty in this operator is how exactly one defines the masses of the nuclei. Within the BO there is some uncertainty as to how electron masses should be included in the nuclear motion problem. We tested a range of plausible nuclear masses, but none of these altered the splittings discussed above by more than 0.1 cm^{-1} . Clearly these mass shifts are far too small to account for the observed discrepancy in the splitting and we are forced to conclude that the errors in the splittings are caused by a failure of the BO approximation.

4. DISCUSSION

As far as H_3^+ is concerned our fit to the observed energy levels is very satisfactory. The levels are reproduced with a standard deviation 35 times smaller than best ab initio estimates. Although a number of H_3^+ bands have now been observed, only the band origins for the fundamentals, 3178.3 (38) and 2521.31 (5), respectively, are known from experiment. The values given in Table II for the other vibrational states used in our fit ($2\nu_2(0)$, $2\nu_2(2)$, $\nu_1 + \nu_2$, and $3\nu_2(1)$) must therefore represent the best estimates of their band origins. Similarly we would expect our predictions for the higher vibrational states to be the best available.

The failure of the Born–Oppenheimer approximation is an interesting aspect of this work. This possibility was discussed by LF (21) who estimate that, while the nonadiabatic correction is probably very small, the adiabatic correction contributes about 5 cm^{-1} to the dissociation energy of H_3^+ . Of this they estimate a contribution of 1 cm^{-1} due to “potential shape” effects—presumably lowering of the zero point energy and hence also the vibrational frequencies due to the geometry dependence of the adiabatic correction. These numbers are similar to those found for H_2 (39).

A more detailed comparison may be obtained by considering the case of H_2^+ (40, 41), HD^+ (42, 43), and D_2^+ (40). Thus, for example, for HD^+ (42) the fundamental frequency is reduced by 0.5 cm^{-1} upon inclusion of the adiabatic correction. This effect is lower for higher vibrational levels—for example, the $v = 10$ –11 spacing is lowered by 0.1 cm^{-1} —and for rotational levels—the ground state $J = 1$ term value is only lowered by 0.02 cm^{-1} . For H_2^+ these shifts are larger but qualitatively similar; however, for D_2^+ BO- and adiabatic-corrected frequencies differ by only 0.26 cm^{-1} (44).

If one can extrapolate from these various pieces of information, it seems entirely possible that BO will cause errors in the fundamental frequencies of H_3^+ and its isotopomers of up to 1 cm^{-1} and that these effects should be stronger for the fundamentals than for either the higher bands or the rotational structure of the species. Although we are not aware of any systematic work on polyatomic molecules which study non-BO effects on the shape of potential surfaces, work by Handy *et al.* (45) studying the BO diagonal correction for a number of polyatomics, including H_2O , H_2O^+ , and H_3^+ , is not inconsistent with the magnitudes found here.

Clearly, because of the large mass change involved upon deuteration, non-BO effects can be expected to vary considerably between isotopomers. Why non-BO effects should have a particular influence on the splitting between the degenerate band is something that we intend to explore further by conducting separate fits for H_2D^+ and D_2H^+ .

5. CONCLUSIONS

We have developed a method of using high-accuracy variational calculations to parameterize potential energy surfaces using spectroscopic data. By applying this method to H_3^+ we have obtained a surface which reproduces a wide variety of rovibrational data with a standard deviation of 0.053 cm^{-1} . Superficially this surface thus represents the most accurate determination of the potential function for a polyatomic available. However, calculations on deuterated species, especially H_2D^+ and D_2H^+ , suggest that this surface is actually *more* accurate than the Born–Oppenheimer approximation. Thus it must be regarded as an *effective* H_3^+ surface and further work will be required to determine similar surfaces for the isotopomers.

ACKNOWLEDGMENT

We thank Dr. J. K. G. Watson and Dr. R. E. Moss for helpful discussions during the course of this work. We also thank Dr. M.-F. Jagod and Professor T. Oka for supplying results prior to publication. We thank NATO for supporting our collaboration with Professor Oka, and the Science and Engineering Research Council for support under various grants.

Note added in proof. Due to a programming mistake the errors in Table I are overestimated by a factor of about 5.

RECEIVED: June 21, 1993

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