Spectroscopically determined Born–Oppenheimer and adiabatic surfaces for H_3^+, H_2D^+, D_2H^+, and D_3^+

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Spectroscopically determined Born–Oppenheimer and adiabatic surfaces for H_3^+, H_2D^+, D_2H^+, and D_3^+

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High resolution spectroscopic data for H_3^+, H_2D^+, D_2H^+, and D_3^+ is used to determine effective, mass-dependent potential energy surfaces for each isotopomers. These surfaces are expressed as a sum of the mass-independent Born–Oppenheimer (BO) potential and a mass dependent adiabatic correction. For H_3^+ and D_3^+ the adiabatic correction is a single surface of the same symmetry and functional form as the BO surface. For H_2D^+ and D_2H^+ a second, lower symmetry surface is required. Fits to all three surfaces were started from recent, high quality *ab initio* calculations. The standard deviations for fits using all the available data with $J \leqslant 9$ are 0.015 cm^{-1} for H_3^+, 0.010 cm^{-1} for H_2D^+ and D_2H^+ combined, and 0.015 cm^{-1} for D_3^+. These values are close to the intrinsic experimental error of much of the data and improve on the corresponding *ab initio* surfaces by at least an order of magnitude. The fits are very compact: nearly 1600 data are fitted by adjusting 36 constants and freezing 51 at their *ab initio* values. *© 1995 American Institute of Physics.*

I. INTRODUCTION

Hydrogen is not only the lightest and simplest atom but also the most common in the Universe. Molecules made out of hydrogen are therefore of great importance in many applications and of fundamental importance when studying the failure of the Born–Oppenheimer (BO) approximation which allows the motions of electrons and nuclei to be decoupled.

Molecular hydrogen can thus be thought as the most fundamental diatomic molecule. The two decades after Kolos and Wolniewicz's benchmark calculations[1] on the H_2 saw a concerted attack on the nuclear motion states of this system. This work led to the construction of Born–Oppenheimer and adiabatic surfaces for H_2 and its isotopomers. It also saw the detailed consideration of non-adiabatic effects including, for example, the realization that for mixed isotopomers such as HD interactions not present in H_2 or D_2 also had to be considered. Information for these studies came both from *ab initio* calculation[2,3] and from detailed fitting to high resolution infrared spectra.[4]

The molecular ion H_3^+, the most stable triatomic form of hydrogen, can be thought as playing a similar role for triatomic species as H_2 does for diatomics. H_3^+ has been the subject of several of recent reviews.[5–9] The ion and its deuterated isotopomers have well documented infrared spectra covering several vibrational bands in each case; H_3^+ has also been the subject of numerous electronic structure calculations of increasing accuracy, see Anderson[10] for a tabulation and Röhse *et al.*[11]

Recent advances have allowed attention to focus on the validity of the BO approximation for the H_3^+ system. Fits to spectroscopic data for H_3^+ were found to behave significantly worse for the other isotopomers.[12] We then demonstrated that both BO and adiabatic potentials could be extracted from spectroscopic data by combining fits for H_3^+ and D_3^+.[13] Subsequent *ab initio* calculations[14,15] have confirmed the need for significant mass-dependent, adiabatic correction to the BO potential for this system. Interestingly this adiabatic correction was found to be particularly important for the asymmetric isotopomers, H_2D^+ and D_2H^+, for which it introduces symmetry lowering terms not present in the BO potential.[15]

In this work we present a systematic, simultaneous fit to the available high resolution spectroscopic data for all four observed isotopomers of H_3^+. This procedure means that rather than developing effective potentials for each isotopomer in turn, we obtain a Born–Oppenheimer potential and both symmetric and asymmetric adiabatic surfaces. The effective potential energy surfaces of all[16] isotopomers of H_3^+ are obtained using these three surfaces with appropriate mass-scaling factors. These surfaces give a compact and very accurate representation of the spectroscopic data which substantially improve on present *ab initio* estimates. As such they provide a goal for *ab initio* calculations.

II. METHOD

A. Variational calculations

All fits were performed in scattering coordinates using the TRIATOM program suite[17] which uses a two-step variational procedure for solving the rotation-vibration problem. For the first, "vibrational" step, basis functions were taken from previous calculations[18] and 1200 functions, selected by energy ordering, were used in each calculation. For the final calculation for a state with rotational angular momentum J we used $N \times (J+1)$ functions selected on energy ordering from the first step. For H_3^+ and D_3^+, for which overtone, fundamental and hot bands have been observed, N was taken to be 600. For H_2D^+ and D_2H^+, N equals 350 was previously found to give convergence to 0.0001 cm^{-1} for levels belonging to the ground state and vibrational fundamentals.[15]

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Nuclear masses, $m_{\mathrm{H}}=1836.152\,724$ m_e and $m_{\mathrm{D}}=3670.483\,058$ m_e,[3] were used for all calculations. Derivatives of constants to be varied during a fit were evaluated using the Hellmann–Feynman theorem[19] in common with other workers performing spectroscopic determination of potentials.[20] Previous tests with our programs[21] have shown this to be of comparable accuracy to and computationally much more efficient than numerical evaluation of the derivatives.

B. Surfaces

Following our previous work,[15] we write the effective, mass dependent potential for the ith isotopomer as

$$V_i(\underline{Q})=V_{\mathrm{BO}}(\underline{Q})+\frac{1}{\mu_i^S}\,\Delta V_{\mathrm{ad}}^S(\underline{Q})+\frac{1}{\mu_i^A}\,\Delta V_{\mathrm{ad}}^A(\underline{Q}). \qquad (1)$$

V_{BO} is the Born–Oppenheimer potential, which, once fitted, may contain contributions from any other mass independent effects such as relativistic terms. $\Delta V_{\mathrm{ad}}^S(\underline{Q})$ is the symmetric adiabatic correction which contributes to all the isotopomers of H_3^+. $\Delta V_{\mathrm{ad}}^A(\underline{Q})$ is the asymmetric adiabatic correction which is needed for H_2D^+ and D_2H^+.

The mass dependence of the effective potential, $V_i(\underline{Q})$, is contained entirely in the reduced masses. Considering the case where atom 1 has mass M, and atoms 2 and 3 both have mass m, then the appropriate reduced masses are defined by[15]

$$\begin{aligned}\frac{1}{\mu^S}&=\frac{1}{M}+\frac{2}{m},\\ \frac{1}{\mu^A}&=\frac{1}{M}-\frac{1}{m}.\end{aligned} \qquad (2)$$

Following both previous *ab initio* and fitting work, the surfaces were expressed in symmetry coordinates

$$\begin{aligned}S_a&=(\tilde{R}_{12}+\tilde{R}_{23}+\tilde{R}_{31})/\sqrt{3},\\ S_x&=(2\tilde{R}_{23}-\tilde{R}_{12}-\tilde{R}_{31})/\sqrt{6}=S_e\cos(\phi),\\ S_y&=(\tilde{R}_{12}-\tilde{R}_{31})/\sqrt{2}=S_e\sin(\phi).\end{aligned} \qquad (3)$$

For the symmetric surfaces, V_{BO} and $\Delta V_{\mathrm{ad}}^S(\underline{Q})$, $\tilde{R}$ was defined using a Morse transformation[22]

$$\tilde{R}_{jk}=\left[1-\exp\left(-\beta\,\frac{R_{jk}-R_e}{R_e}\right)\right]\bigg/\beta, \qquad (4)$$

where R_{jk} is the distance between atom j and atom k. For these surfaces we adopted the values $R_e=1.6500$ a_o and $\beta=1.30$ used previously.[11,14] As before,[15] we used simple displacement coordinates for the asymmetric adiabatic correction, $\Delta V_{\mathrm{ad}}^A(\underline{Q})$

$$\tilde{R}_{jk}=R_{jk}-R_e, \qquad (5)$$

with R_{jk} and R_e defined as above.

In all cases the surfaces were expressed as polynomial expansions in the symmetry coordinates.

$$V(\underline{Q})=\sum_{n,m,k}V_{n,m,k}S_a^nS_e^{m+k}\cos(k\phi), \quad m=0,2,4,\ldots. \qquad (6)$$

Symmetry considerations mean that for the symmetric functions, V_{BO}, $\Delta V_{\mathrm{ad}}^S(\underline{Q})$ and the effective H_3^+ and D_3^+ potentials discussed below, $k=0,3,6,\ldots$. Conversely for the asymmetric adiabatic correction, $\Delta V_{\mathrm{ad}}^A(\underline{Q})$, $k=1,2,4,5,\ldots$.

An expansion of order N is defined as one including all terms given by $N\geqslant n+m+k$. This work used entirely $N=7$ which gives 31 terms in the expansions with $k=0,3,6$ and 25 in the expansion with $k=1,2,4,5,7$. As discussed below, less than half this number of terms were allowed to vary in our fits.

C. Spectroscopic data

At each stage of the fitting process described below, a number of exploratory fits were made using reduced datasets or only band origins. All fits presented here were based upon use of all the available experimental data for H_3^+, H_2D^+, D_2H^+ and D_3^+ with $J\leqslant 9$. Specifically for H_3^+ we used the 246 energy levels used in our first fit of the H_3^+ surface[12] supplemented by the 310 new transitions with $J\leqslant 9$ recently presented by Majewski *et al.*[23] Our H_3^+ datasets contains information on the ground vibrational state, the fundamentals (ν_1 and ν_2), overtones ($2\nu_2$ and $3\nu_2$) and the combination band $\nu_1+\nu_2$, see Table IV.

For D_3^+ Amano *et al.*[24] have recently provided a sixfold increase in the available data. We fitted the 342 transitions with $J\leqslant 9$. These give extensive information on the ν_2 and $2\nu_2$ bands with a few transitions also involving other bands. The fit was augmented by 429 combination differences for the ground, ν_2 and $2\nu_2$ vibrational states, see Table V.

It is worth noting that there is experimental data for H_3^+ up to $J=16$,[23] and for D_3^+ up to $J=20$.[24] This higher rotational data was not included in the fits because there is relatively little of it and reproducing it is computationally expensive. In practice using this data would have meant fundamentally changing our method of calculation to allow us to treat the H_3^+ problem above the barrier to linearity. Furthermore our previous work[15] has suggested that higher rotational states show significant nonadiabatic effects. If this is so, then including these states might actually degrade fits performed within the adiabatic approximation.

For H_2D^+ and D_2H^+ information is only available for the ground state and the vibrational fundamentals. Our fits used the two measured pure rotational transitions[26–28] and the data on the ν_1, ν_2, and ν_3 bands,[29–32] with assignments as tabulated in Polyansky *et al.*[15] These were augmented by ground state combination differences and the band origins for the 6 vibrational fundamentals. This gave a dataset containing 157 observables with $J\leqslant 7$ for H_2D^+ (see Table VI) and 177 observables with $J\leqslant 5$ for D_2H^+ (see Table VII).

In our fits all data were weighted equally. Of course the rotational transitions observed for H_2D^+ are of much higher accuracy than the infrared data. However there is so little of this data that it did not merit special treatment.

A further issue that had to be addressed in performing the fits is whether all the published data is as accurate as it is claimed. Spectra of H_3^+ and its isotopomers are very hard to assign and there is a long history of misassignments. Furthermore, recent analysis by Watson[25] has pointed to a number of mismeasurements in the H_3^+ system.

It is important that our fits do not get degraded by spurious data. To combat this problem we adopted a procedure whereby any data which were more than 3 standard deviations away in a particular fit were omitted from the subsequent iteration. This criterion was relaxed for data involving the highest vibrational state in our fit (H_3^+ $3\nu_2$), which will be discussed further below. Data which fell below this threshold was reincorporated into the fit. Tables IV–VII show that for some bands quite a lot of the data was indeed omitted in our final fits.

III. FITS

A. H_3^+ and D_3^+

Initial fits were performed separately for the H_3^+ and D_3^+ ions. In this case we fitted the effective potential, V_i of Eq. (1), directly for each ion. The fits were started from potentials defined by the *ab initio* BO potential of Röhse *et al.*[11] and the appropriately mass weighted *ab initio* symmetric adiabatic correction of Dinelli *et al.*[14] These *ab initio* potentials gave a standard deviation of 0.244 cm^{-1} and 0.105 cm^{-1} for H_3^+ and D_3^+, respectively, when tested against the datasets detailed above.

From these *ab initio* effective potentials we adjusted 16 constants for H_3^+ and 14 for D_3^+. The results of the fits are given in Table I. The resulting standard deviations 0.015 cm^{-1} for H_3^+ and 0.017 cm^{-1} for D_3^+.

In the case of H_3^+ this fit represents our final effective potential for this ion; it is not altered in any of the fits described below.

As we performed further fits for the D_3^+, the effective D_3^+ potential described in Table I is *not* our final potential for this ion. Although the greatly increased amount of spectroscopic data available for D_3^+ has allowed us to determine many more constants for this ion than our previous attempt,[13] there is still insufficient data to properly characterize the potential in the direction of the ν_1 breathing mode. We return to this problem below.

Using the fits to H_3^+ and D_3^+ one can derive our initial estimates of the BO and symmetric adiabatic correction surfaces as

$$\Delta V^S_{\mathrm{ad}}(\underline{Q})=\left(\frac{1}{\mu_{H_3^+}}-\frac{1}{\mu_{D_3^+}}\right)^{-1}(V_{H_3^+}(\underline{Q})-V_{D_3^+}(\underline{Q})), \quad (7)$$

$$V_{\mathrm{BO}}(\underline{Q})=V_{H_3^+}(\underline{Q})-\frac{1}{\mu_{H_3^+}}\Delta V^S_{\mathrm{ad}}(\underline{Q}). \quad (8)$$

B. H_2D^+ and D_2H^+

The next step in our fitting procedure was to determine the asymmetric adiabatic correction which is particularly important in treating the splitting of the ν_2 bending mode, degenerate in H_3^+ and D_3^+, into the ν_2 and ν_3 modes in H_2D^+ and D_2H^+. The evidence from the *ab initio* calculations is that the asymmetric adiabatic correction, $\Delta V^A_{\mathrm{ad}}(\underline{Q})$, term of Polyansky *et al.*[15] is about 10% too small.[34]

TABLE I. Fitted coefficients, in μhartree, for the effective H_3^+ and D_3^+ potentials, see the text for details.

n	m	k	$V_{H_3^+}$	$V_{D_3^+}$
0	0	0	470.5153[a]	235.1745[a]
1	0	0	186.3259	−23.8205
2	0	0	204452.1615	204544.5011
0	2	0	266609.0054	266330.4915
3	0	0	−48869.9169	−50471.6014
1	2	0	−237802.4271	−239845.5904
0	0	3	−5549.3727	−5750.4815
4	0	0	25296.3030[a]	25296.1266[a]
2	2	0	129245.8210	143101.1994
1	0	3	90829.6061	90629.0133
0	4	0	45399.5443	47533.2894
5	0	0	−3016.4330[a]	−3021.5690[a]
3	2	0	−71848.6567	−64723.5231
2	0	3	−31135.9134	−31155.7369
1	4	0	−31425.5946	−29306.6760
0	2	3	−5959.9035	−5246.2579
6	0	0	3898.6848[a]	3897.17315[a]
4	2	0	64894.0441	46880.3873[a]
3	0	3	56410.9346[a]	56262.5460[a]
2	4	0	178371.7793	116957.9669[a]
1	2	3	72815.3785[a]	72575.0486[a]
0	6	0	14717.3034	8121.3843
0	0	6	−1525.2457	−4593.7125
7	0	0	261.5186[a]	267.2914[a]
5	2	0	8684.3773[a]	8665.9228[a]
4	0	3	18148.6162[a]	17947.2931[a]
3	4	0	42218.5234[a]	41831.2441[a]
2	2	3	117188.5624[a]	116670.5585[a]
1	6	0	46713.6348[a]	46405.2256[a]
1	0	6	−2919.8205[a]	−2952.7989[a]
0	4	3	11942.1197[a]	11824.4783[a]

[a] These constants were frozen at their *ab initio* values.

To start the spectroscopic determination of $\Delta V^A_{\mathrm{ad}}(\underline{Q})$ we used effective potentials defined using the $V_{\mathrm{BO}}(\underline{Q})$ and $\Delta V^S_{\mathrm{ad}}(\underline{Q})$ potentials determined above and a $\Delta V^A_{\mathrm{ad}}(\underline{Q})$ determined from the *ab initio* data of Polyansky *et al.* This starting point gave a standard deviation of 0.038 cm^{-1} for our combined H_2D^+ and D_2H^+ datasets. This should be compared with a standard deviation of 0.110 cm^{-1} obtained using the best *ab initio* surfaces.

Trial fits showed that our dataset contained only limited information on the asymmetric adiabatic correction — the most important being the splitting between the band origins discussed above. However fits with fewer than 6 parameters varied were generally unsatisfactory. By adjusting 6 parameters in the expansion of $\Delta V^A_{\mathrm{ad}}(\underline{Q})$, we were able to reduce the standard deviation to 0.014 cm^{-1}. However analysis of this fit showed that it performed significantly worse for levels of the stretching mode, ν_1, of both H_2D^+ and D_2H^+ than for other data included in the fit. In particular the standard deviations for the ν_1 data were 0.035 and 0.019 cm^{-1} respectively, whereas all other bands were fitted by a standard deviation of less than 0.010 cm^{-1}.

This relatively large error in the ν_1 data could be ascribed to the method used to determine the initial BO and symmetric adiabatic surfaces. For H_3^+ the effective potential was determined using data from a variety of vibrational

TABLE II. Fitted coefficients for the Born–Oppenheimer (BO) potential, in μhartree, and the mass independent part of the symmetric adiabatic correction, in μhartree m_e^{-1}.

n	m	k	V_{BO}	ΔV_{ad}^S
0	0	0	−0.4000[a]	288224.1001[a]
1	0	0	106.9020	−179470.3649
2	0	0	204545.6396	−57213.3827
0	2	0	266097.5142	313058.6688
3	0	0	−51098.7672	1364169.8172
1	2	0	−241977.2030	2555175.3154
0	0	3	−6025.8748	291643.5795
4	0	0	25295.9500[a]	216.0510[a]
2	2	0	153072.3745	−14583063.1013
1	0	3	90645.4518	112711.8078
0	4	0	50181.8121	−2926991.2436
5	0	0	−3026.7100	6290.0361
3	2	0	−61871.2107	−6106704.6178
2	0	3	−31175.5800	24277.9614
1	4	0	−16188.8423	−9325667.7003
0	2	3	−3726.3535	−1367046.2444
6	0	0	3895.6600[a]	1851.3203[a]
4	2	0	28848.8348[b]	22061502.0970[b]
3	0	3	56114.0100[a]	181732.9370[a]
2	4	0	55483.1426[b]	75214098.4478[b]
1	2	3	72334.4800[a]	294334.3365[a]
0	6	0	−5703.8322	12498774.0273
0	0	6	−8001.1692	3963594.6754
7	0	0	273.0700[a]	−7070.0415[a]
5	2	0	8647.4500[a]	22601.3582[a]
4	0	3	17745.7700[a]	246562.3750[a]
3	4	0	41443.5800[a]	474304.7691[a]
2	2	3	116152.0400[a]	634404.4566[a]
1	6	0	46096.5100[a]	377711.7842[a]
1	0	6	−2985.8100[a]	40388.9576[a]
0	4	3	11706.7200[a]	144076.6008[a]

[a] These constants were frozen at their *ab initio* values.

[b] These constants varied in the H_3^+ fit only.

TABLE III. Coefficients, in μhartree m_e^{-1}, of the mass independent part of the asymmetric adiabatic correction, ΔV_{ad}^A, to the Born–Oppenheimer potential.

n	m	k	ΔV_{ad}^A
0	0	1	230475.323
1	0	1	−84659.650
0	0	2	10718.349
2	0	1	−1998.382
1	0	2	−390058.009
0	2	1	24974.99391[a]
3	0	1	−5471.75840[a]
2	0	2	6104.18020[a]
1	2	1	−19868.59656[a]
0	2	2	439144.398
0	0	4	407.99939[a]
4	0	1	341.30735[a]
3	0	2	−1661.19749[a]
2	2	1	7993.45248[a]
1	2	2	−5688.30348[a]
1	0	4	−699.68606[a]
0	4	1	1691.07610[a]
0	0	5	−575.41013[a]
5	0	1	96.16995[a]
4	0	2	26.85075[a]
3	2	1	−1124.26501[a]
2	2	2	1645.90201[a]
2	0	4	269.21608[a]
1	4	1	−1294.22731[a]
1	0	5	275.11230[a]

[a] These constants were frozen at their *ab initio* values.

states including both the bending (ν_2) and symmetric breathing (ν_1) fundamentals. Conversely for D_3^+ there is no direct observations of the breathing fundamental and little data on any states which have more than zero quanta of breathing vibration in our dataset. This means that for D_3^+ portions of the potential dependent on the symmetric S_a coordinate are not particularly well determined by the spectroscopic data.

C. Final fits

To combat the problem with the stretching modes of the mixed isotopomers it was decided to perform fits which used information on these ions to determine not only the asymmetric adiabatic correction but also the BO and symmetric adiabatic correction. We made some attempts to fit simultaneously both the BO and symmetric adiabatic correction surfaces. However even when we used data from all four isotopomers, these attempts all showed very strong correlation effects between the surfaces and they were not pursued.

Although the standard deviation of our fit to our H_3^+ dataset (0.015 cm^{-1}) obtained above was similar to those quoted for the other ions, this comparison is not strictly fair. In the case of H_3^+ there are considerable data on overtone vibrational states and, as shown in Table IV, the standard deviation is dominated by transitions and levels involving $3\nu_2$. An H_3^+ standard deviation evaluated by considering only data equivalent to that used in the H_2D^+/D_2H^+ fit gives a significantly lower value. Furthermore, as already mentioned, the H_3^+ dataset includes data on all the vibrational states below $2\nu_1$, which is not true for any of the other ions. We therefore decided to do a combined fit for H_2D^+, D_2H^+ and D_3^+ which froze the effective H_3^+ potential at the values given in Table I.

To do this we varied 14 parameters in the BO potential, $V_{BO}(\underline{Q})$. Because the effective H_3^+ potential was held constant, varying $V_{BO}(\underline{Q})$ implied a corresponding variation in the symmetric adiabatic correction given by

$$\Delta V_{ad}^S(\underline{Q}) = \mu_{H_3^+}(V_{H_3^+}(\underline{Q}) - V_{BO}(\underline{Q})). \tag{9}$$

This new fit reduced the D_3^+ standard deviation to 0.015 cm^{-1} and the H_2D^+/D_2H^+ combined fit to 0.011 cm^{-1}. The new fit also lowered the standard deviation of the ν_1 data of the mixed isotopomers by about a third, although they remain the worst determined of all the fundamental bands in our dataset, see Tables IV–VII.

This fit gave our final values of the parameters of the BO potential, $V_{BO}(\underline{Q})$, and the symmetric adiabatic correction, $\Delta V_{ad}^S(\underline{Q})$. These are presented in Table II.

To check whether the adjustment of the symmetric surfaces affected the asymmetric adiabatic correction, we performed a final fit for the H_2D^+/D_2H^+ combined dataset. In this fit the same 6 parameters were allowed to vary. This final step in the fit made minor modifications to the surface and reduced the standard deviation for the mixed isotopomers to

TABLE IV. Detailed breakdown of our final fit for H_3^+. Available data refers to the number of items included in our initial dataset and fitted data to the number included in our final fit. Standard deviations and average errors for each category are given in cm^{-1}.

State	Available data	Fitted data	Standard deviation	Average error
Ground state levels	37	37	0.007	0.0008
ν_1 levels	14	14	0.014	−0.0002
ν_2 levels	81	80	0.012	−0.0001
$2\nu_2(l=2)$ levels	43	41	0.013	0.0014
$2\nu_2(l=0)$ levels	29	29	0.015	−0.0016
$3\nu_2(l=1)$ levels	12	10	0.022	−0.0020
$\nu_1+\nu_2$ levels	30	22	0.015	−0.005
$\nu_1\leftarrow 0$	13	13	0.012	−0.0004
$\nu_2\leftarrow 0$	86	84	0.013	0.0052
$2\nu_2\leftarrow 0$	11	8	0.019	0.0015
$2\nu_2\leftarrow \nu_2$	91	77	0.013	0.0005
$3\nu_2\leftarrow 0$	15	13	0.024	−0.0067
$3\nu_2\leftarrow 2\nu_2$	4	2	0.098	0.0033
$\nu_1+\nu_2\leftarrow \nu_2$	46	34	0.016	−0.0001
$\nu_1+\nu_2\leftarrow \nu_1$	44	37	0.017	0.0052

0.010 cm^{-1}. Our final surface for the asymmetric adiabatic correction, $\Delta V_{ad}^{A}(Q)$, is given in Table III. Tables IV–VII present band by band standard deviations for all 4 isotopomers using our final spectroscopically determined surfaces.

IV. DISCUSSION

The fitted potentials described above represent a very significant improvement on their *ab initio* starting point. For example the effective H_3^+ potential reproduces the observed data with a standard deviation a factor of about 16 better than the *ab initio* estimates. Similar results are obtained for the other isotopomers.

Our fits also perform significantly better than previous spectroscopically determined effective potentials. Our H_3^+ standard deviation of 0.015 cm^{-1} should be compared with 0.137 cm^{-1} obtained by Watson,[33] 0.053 by Dinelli *et al.*[12] and 0.118 cm^{-1} by Majewski *et al.*,[23] all using broadly similar datasets. The improvement for D_3^+ is similar: our standard deviation of 0.015 cm^{-1} should be compared with 0.059 cm^{-1} reported by Amano *et al.*[24] All the previous fits started from *ab initio* BO potentials.[22,35] It is likely that a large part of our improvement is due to the better starting point provided by the improved *ab initio* BO potential of Röhse *et al.*[11] augmented by the *ab initio* adiabatic corrections.

TABLE V. Detailed breakdown of our final fit for D_3^+. Available data refers to the number of items included in our initial dataset and fitted data to the number included in our final fit. Standard deviations and average errors for each category are given in cm^{-1}.

State	Available data	Fitted data	Standard deviation	Average error
$\nu_2\leftarrow 0$	138	138	0.011	0.0020
$2\nu_2\leftarrow 0$	115	114	0.012	−0.0013
$2\nu_2\leftarrow \nu_2$	77	68	0.021	−0.0056
$3\nu_2\leftarrow 2\nu_2$	3	3	0.010	−0.0031
$\nu_1+\nu_2\leftarrow \nu_1$	4	4	0.055	−0.0004
$\nu_1+\nu_2\leftarrow \nu_2$	4	3	0.095	−0.0097
$\nu_1+2\nu_2\leftarrow \nu_1+\nu_2$	1	1	-	0.058
Ground state comb. diff.	99	99	0.009	−0.0009
ν_2 comb. diff.	153	152	0.009	0.0003
$2\nu_2$ comb. diff.	177	172	0.019	−0.0006

TABLE VI. Detailed breakdown of our final fit for H_2D^+. Available data refers to the number of items included in our initial dataset and fitted data to the number included in our final fit. Standard deviations and average errors for each category are given in cm^{-1}.

State	Available data	Fitted data	Standard deviation	Average error
Ground state comb. diff.	49	49	0.003	−0.0012
$\nu_1\leftarrow 0$	36	35	0.013	0.0026
$\nu_2\leftarrow 0$	31	30	0.005	0.0008
$\nu_3\leftarrow 0$	41	40	0.006	0.0013

The fits to the available spectroscopic data for H_3^+ family have allowed us to determine surfaces which reproduce these data to an accuracy of close to 0.01 cm^{-1}. It is interesting to ask whether it is possible to improve on this figure. To answer this question it is probably necessary to consider two aspects of the problem: the intrinsic accuracy of the data being used in the fit and the validity of the Born–Oppenheimer approximation plus adiabatic correction model employed.

For the data used here in our fits, the experimental errors are generally claimed to be in the vicinity of 0.002 cm^{-1}, an error which would be doubled in the case of combination differences used in some of our fits. Watson[25] has recently performed a detailed test of these claims by analyzing combination differences for H_3^+. His conclusion, after omitting 7 lines whose inclusion degraded the standard deviation to 0.03 cm^{-1}, was that the intrinsic error in the data was about 0.004 cm^{-1}, or about twice that generally claimed. This would imply an error of 0.008 cm^{-1} in our combination differences and suggest that there is only limited further information that could be extracted from our dataset.

Polyansky *et al.*[15] give an *ab initio* treatment of the spectra of H_2D^+ and D_2H^+ within the adiabatic approximation. They noted small systematic changes in their errors as a function of rotational excitation. They ascribed these errors to nonadiabatic effects which were omitted from their calculations. It is notable that we had difficulty reproducing data associated with the $3\nu_2$ vibrational state of H_3^+. It is at least possible that this problem is associated with J-independent nonadiabatic effects. Unlike the adiabatic correction, nonadiabatic effects cannot be treated in terms of simple surfaces, so their contribution cannot be properly taken account of within the scheme presented here. It would be unwise to push our fitting of the surfaces too far without some consideration of the nonadiabatic contribution, particularly for higher rotational levels. This is a topic we plan to pursue in future work.

Tables IV–VII show that 62 transitions were not used in our final fits. Already we have some tentative reassignments for some of these transitions. However this issue, combined with analysis of still unassigned observed transitions (see Xu

TABLE VII. Detailed breakdown of our final fit for D_2H^+. Available data refers to the number of items included in our initial dataset and fitted data to the number included in our final fit. Standard deviations and average errors for each category are given in cm^{-1}.

State	Available data	Fitted data	Standard deviation	Average error
Ground state comb. diff.	56	56	0.002	0.0009
$\nu_1 \leftarrow 0$	33	33	0.025	−0.0041
$\nu_2 \leftarrow 0$	53	53	0.007	−0.0038
$\nu_3 \leftarrow 0$	35	35	0.006	−0.0055

et al.,[36] for example) and treatment of rotational levels up to $J=20$ will be a subject of a future paper.[38]

V. CONCLUSIONS

We have fits to the great majority of the available spectroscopic data for H_3^+, H_2D^+, D_2H^+, and D_3^+. Starting from accurate *ab initio* estimates of mass dependent potential surfaces for each system, we have fitted 1586 data items covering some 18 vibrational states to an accuracy close to 0.01 cm^{-1} by varying only 36 constants. This has allowed us to derive a spectroscopically determined Born–Oppenheimer potential energy surface and adiabatic correction surfaces for this system. The accuracy achieved in these calculations is very close to the intrinsic accuracy of the observations. These surfaces will provide a reliable means of making further and future assignments, always a major problem in this floppy system.

Our representation is very compact. It may appear that one could derive effective surfaces for each ion and therefore we have only reduced four surfaces to three. However the asymmetry of H_2D^+ and D_2H^+ means that these four surfaces would require exactly twice as many constants as ours to achieve fits of the same accuracy. Furthermore, our surfaces are perfectly general and should, for example, provide predictions for the spectra of tritium containing isotopomers of H_3^+ of much higher accuracy than any previous method.

The spectroscopy of H_3^+ is a topic of major astronomical interest.[6,8] For this reason tabulations of accurate transition frequencies and linestrengths (see, for example, Kao *et al.*[37]) are of great importance for both observational and modelling work. The surfaces presented here are being used to improve our understanding of H_3^+ spectroscopy[38] as well as provide thermodynamic and opacity data for astronomical studies.[39]

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