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Asymmetric adiabatic correction to the rotation–vibration levels of H_2D^+ and D_2H^+

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Calculations on H_2D^+ and D_2H^+ have shown that the energy levels of these asymmetric isotopomers of H_3^+ cannot be reproduced using effective potential energy surfaces with D_{3h} symmetry. It is shown that for these ions the adiabatic correction to the Born–Oppenheimer approximation has an asymmetric component which can be expressed as a mass-independent surface multiplied by a mass factor. An expression for this function is obtained from *ab initio* calculations. Use of this adiabatic correction is found to resolve the discrepancy with the levels of H_2D^+ and D_2H^+ . The *ab initio* calculations reported reproduce the observed H_2D^+ transitions with an average error (obs–calc) of -8 MHz for the rotational transitions, -0.06 cm^{-1} for the ν_1 band, -0.13 cm^{-1} for ν_2 , and -0.19 cm^{-1} for ν_3 . These errors are nearly constant for all transitions within a vibrational band. This gives a very accurate *ab initio* framework for predicting unobserved transition frequencies. © 1995 American Institute of Physics.

I. INTRODUCTION

The H_3^+ molecular ion has been the focus of much recent attention because of its fundamental nature, its astrophysical importance, and its unassigned near dissociation spectrum. It has been the subject of a number of recent reviews.^{1–4}

Much of the spectroscopy of the low-lying levels of H_3^+ and its deuterated isotopomers is now understood; a situation which has only been achieved because of considerable interaction between *ab initio* theory and experiment.^{1,4} However there remain many unassigned lines both for H_3^+ ⁵ and the mixed isotopomers H_2D^+ and D_2H^+ .⁶

Recently calculations of H_3^+ spectra have made significant advances on two fronts. The use of electronic wave functions which explicitly include the electron–electron coordinate within the so-called Hylleraas-CI method have led to the calculation of potential energy surfaces very close to the Born–Oppenheimer (BO) limit of the system.^{7,8} Variational nuclear motion calculations have also been used to invert the wealth of spectroscopic data on, in particular, H_3^+ and D_3^+ to give very accurate effective potential energy surfaces for these ions.^{9–11}

Calculations using the *ab initio* potential energy surfaces have suggested that the largest outstanding error in the *ab initio* determination of the rotation–vibration states of H_3^+ and its isotopomers is the BO approximation on which these surfaces are based.^{8,11,12} Similarly calculations with the spectroscopically determined effective surfaces showed that surfaces optimized for one isotopomer performed significantly less well for the other isotopomers,¹⁰ a situation ascribed to the failure of the BO approximation.^{10,11}

The limited accuracy of the BO approximation for the light H_3^+ system is probably not too surprising. More unex-

pected was the discovery by Dinelli *et al.*¹⁰ that the asymmetric isotopomers H_2D^+ and D_2H^+ appeared to show an anomalously large non-BO effect. H_3^+ and D_3^+ only have two vibrational modes, a symmetric “breathing” mode, ν_1 , and a degenerate bending mode, ν_2 . The ν_2 mode is split in the mixed isotopomers H_2D^+ and D_2H^+ into a bending mode, ν_2 , and an asymmetric stretch, ν_3 . All three fundamentals have been observed^{13–16} for both isotopomers.

The rotational spectrum of H_2D^+ is particularly important for astrophysical observation,^{2,4} but only two transitions have been observed in the laboratory.^{17–19} Furthermore the infrared spectra of H_2D^+ and D_2H^+ are difficult to interpret with a number of reassignments having been made using effective Hamiltonians^{20,21} or *ab initio* calculations.²²

Dinelli *et al.*¹⁰ found that the splitting between the ν_2 and ν_3 modes predicted for H_2D^+ and D_2H^+ was significantly in error when computed using potentials obtained for the symmetric isotopomers. They argued that this splitting could only arise from terms in the Hamiltonian which are asymmetric in D_{3h} symmetry. As they used an exact nuclear kinetic energy operator within the BO approximation, they concluded that the effect was caused by non-BO terms which were asymmetric in D_{3h} symmetry and neglected in their calculations.

Recently Dinelli *et al.*¹² used a method proposed by Handy *et al.*²³ to obtain *ab initio* estimates of the mass dependent adiabatic correction for H_3^+ and D_3^+ . In this paper we show how the calculations of Dinelli *et al.* can be extended to give the asymmetric adiabatic correction. We show that this correction can be represented as a single surface, with an appropriate mass factor, for both H_2D^+ and D_2H^+ , and that use of this surface explains the unexpected $\nu_2 - \nu_3$ splittings in these systems.

II. SURFACES FOR THE ADIABATIC CORRECTION

Dinelli *et al.*¹² followed Handy *et al.*²³ and calculated a series of mass-independent integrals which, for each nucleus I , are given by

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$$f_I(\mathbf{Q}) = -\frac{1}{2} \langle \Psi | \nabla_I^2 | \Psi \rangle. \quad (1)$$

In Eq. (1), \mathbf{Q} are the internal coordinates and Ψ is the electronic wave function for which Dinelli *et al.* used wave functions of near-Hartree–Fock quality. From these integrals, and neglecting any effect of the electrons' translational motion, the adiabatic correction can be written as

$$\sum_{I=1}^3 \frac{f_I(\mathbf{Q})}{m_I}, \quad (2)$$

where the m_I are the nuclear masses.

We write the effective, mass dependent potential for the i th isotopomer as

$$V_i(\mathbf{Q}) = V_{\text{BO}}(\mathbf{Q}) + \frac{1}{\mu_i^S} \Delta V_{\text{ad}}^S(\mathbf{Q}) + \frac{1}{\mu_i^A} \Delta V_{\text{ad}}^A(\mathbf{Q}), \quad (3)$$

where V_{BO} is the Born–Oppenheimer potential. In this work we use the BO potential calculated *ab initio* by Röhse *et al.*⁸ $\Delta V_{\text{ad}}^S(\mathbf{Q})$ is the symmetric adiabatic correction which contributes to all the isotopomers of H_3^+ and which has already been studied by Tennyson and Polyansky,¹¹ and Dinelli *et al.*¹² $\Delta V_{\text{ad}}^A(\mathbf{Q})$ is the asymmetric adiabatic correction which is needed for H_2D^+ and D_2H^+ . The mass dependence of the potential is explicitly given in terms of the reduced masses μ_i^S and μ_i^A .

To obtain the functional form of the asymmetric adiabatic correction it is necessary to first correctly identify the symmetric portion of the adiabatic correction. For a general geometry, \mathbf{Q} , for which none of the atom-atom distances are equal, the integral f_I will be different at each nucleus. In this situation the symmetric adiabatic correction is obtained by considering the three possible cyclic permutations of the nuclei (the anticyclic permutations add nothing):

$$\frac{1}{\mu^S} \Delta V_{\text{ad}}^S(\mathbf{Q}) = \frac{1}{3} \left(\frac{f_1(\mathbf{Q})}{m_1} + \frac{f_2(\mathbf{Q})}{m_2} + \frac{f_3(\mathbf{Q})}{m_3} + \frac{f_1(\mathbf{Q})}{m_3} + \frac{f_2(\mathbf{Q})}{m_1} + \frac{f_3(\mathbf{Q})}{m_2} + \frac{f_1(\mathbf{Q})}{m_2} + \frac{f_2(\mathbf{Q})}{m_3} + \frac{f_3(\mathbf{Q})}{m_1} \right). \quad (4)$$

This expression simplifies to

$$\frac{1}{\mu^S} \Delta V_{\text{ad}}^S(\mathbf{Q}) = \left(\frac{1}{m_1} + \frac{1}{m_2} + \frac{1}{m_3} \right) \times \frac{1}{3} [f_1(\mathbf{Q}) + f_2(\mathbf{Q}) + f_3(\mathbf{Q})], \quad (5)$$

which clearly has the desired symmetry.

Consider the case where atom 1 has mass M , and atoms 2 and 3 both have mass m . From Eq. (4) the symmetric component of the adiabatic correction in the desired mass factored form is:

$$\frac{1}{\mu^S} \Delta V_{\text{ad}}^S(\mathbf{Q}) = \left(\frac{1}{M} + \frac{2}{m} \right) \times \frac{1}{3} [f_1(\mathbf{Q}) + f_2(\mathbf{Q}) + f_3(\mathbf{Q})]. \quad (6)$$

If one defines the remaining adiabatic correction as the asymmetric component, then

$$\frac{1}{\mu^A} \Delta V_{\text{ad}}^A(\mathbf{Q}) = \frac{f_1(\mathbf{Q})}{M} + \frac{f_2(\mathbf{Q})}{m} + \frac{f_3(\mathbf{Q})}{m} - \left(\frac{1}{M} + \frac{2}{m} \right) \times \frac{1}{3} [f_1(\mathbf{Q}) + f_2(\mathbf{Q}) + f_3(\mathbf{Q})]. \quad (7)$$

This can be simplified to

$$\frac{1}{\mu^A} \Delta V_{\text{ad}}^A(\mathbf{Q}) = \left(\frac{1}{M} - \frac{1}{m} \right) \times \frac{1}{3} [2f_1(\mathbf{Q}) - f_2(\mathbf{Q}) - f_3(\mathbf{Q})], \quad (8)$$

which, like the symmetric component, has the desired form of a mass-independent surface multiplied by a mass factor. In our form the reduced masses are given explicitly by

$$\frac{1}{\mu^S} = \frac{1}{M} + \frac{2}{m}, \quad (9)$$

$$\frac{1}{\mu^A} = \frac{1}{M} - \frac{1}{m}.$$

Fits to the computed adiabatic corrections were obtained in symmetry coordinates:

$$S_a = (\Delta R_{12} + \Delta R_{23} + \Delta R_{31}) / \sqrt{3},$$

$$S_x = (2\Delta R_{23} - \Delta R_{12} - \Delta R_{31}) / \sqrt{6} = S_e \cos(\phi),$$

$$S_y = (\Delta R_{12} - \Delta R_{31}) / \sqrt{2} = S_e \sin(\phi), \quad (10)$$

$$\Delta R_{jk} = R_{jk} - R_e,$$

where R_{jk} is the distance between atom j and atom k . Note that we do not employ the Morse transformed coordinates used previously.^{8,12} For the symmetric component we employed the expansion used previously for the potential:^{7,8,10,12}

$$\frac{1}{3} [f_1(\mathbf{Q}) + f_2(\mathbf{Q}) + f_3(\mathbf{Q})] = \sum_{n,m,k} V_{n,m,k}^S S_a^n S_e^{m+k} \cos(k\phi), \quad (11)$$

where $m = 0, 2, 4, \dots$ and $k = 0, 3, 6, \dots$

The functional form for the asymmetric component is less obvious. This function should have the property that it transforms as the x component of the E' representation in D_{3h} but is totally symmetric, A_1 , for the C_{2v} point group appropriate to H_2D^+ and D_2H^+ . In this case the appropriate expansion in symmetry coordinates has the form

$$\frac{1}{3} [2f_1(\mathbf{Q}) - f_2(\mathbf{Q}) - f_3(\mathbf{Q})] = \sum_{n,m,k} V_{n,m,k}^A S_a^n S_e^{m+k} \cos(k\phi), \quad (12)$$

where $m = 0, 2, 4, \dots$ and $k = 1, 2, 4, 5, \dots$

Fits were performed to the integrals calculated by Dinelli *et al.*¹² who copied the 69 geometries used by Röhse *et al.*⁸ The 58 geometries which are not equilateral triangles provide two items of data each for the fit of the asymmetric component which are obtained by permuting the atom labels. Nonisosceles triangle geometries, however, do not yield a third point as it is possible to generate this value simply by differencing the other two.

Least squares fits of the coefficients $V_{n,m,k}$, in Eqs. (11) and (12) to the *ab initio* data were performed for each of the

TABLE I. Fitted coefficients, $\mu_{\text{hartree}} m_e$, of the mass independent part of the adiabatic correction to Born–Oppenheimer potential, see expansions (11) and (12). The equilibrium bond length R_e was fixed at $1.6500a_o$.

n	m	k	$V_{n,m,k}^S$	n	m	k	$V_{n,m,k}^A$
0	0	0	288 247.444 82	0	0	1	223 801.880 75
1	0	0	−59 942.339 64	1	0	1	−92 523.084 44
2	0	0	21 223.889 60	0	0	2	781.062 17
0	2	0	62 708.85 37	2	0	1	26 399.575 43
3	0	0	−5 533.568 24	1	0	2	−8 774.550 23
1	2	0	−38 522.701 96	0	2	1	24 974.993 91
0	0	3	−1 838.680 68	3	0	1	−5 471.758 40
4	0	0	1 377.893 78	2	0	2	6 104.180 20
2	2	0	11 325.228 33	1	2	1	−19 868.596 56
1	0	3	−900.918 52	0	2	2	5 413.274 34
0	4	0	4 691.003 80	0	0	4	407.999 39
5	0	0	−410.967 94	4	0	1	341.307 35
3	2	0	−965.038 51	3	0	2	−1 661.197 49
2	0	3	1 410.276 78	2	2	1	7 993.452 48
1	4	0	−4 088.395 79	1	2	2	−5 688.303 48
0	2	3	631.881 52	1	0	4	−699.686 06
6	0	0	132.743 90	0	4	1	1 691.076 10
4	2	0	−666.110 43	0	0	5	−575.410 13
3	0	3	−318.094 57	5	0	1	96.169 95
2	4	0	1 127.105 40	4	0	2	26.850 75
1	2	3	−449.352 34	3	2	1	−1 124.265 01
0	6	0	276.936 70	2	2	2	1 645.902 01
0	0	6	−113.389 95	2	0	4	269.216 08
7	0	0	−22.618 54	1	4	1	−1 294.227 31
5	2	0	168.306 90	1	0	5	275.112 30

components separately using 25 terms in each expansion. For a mass factor appropriate for H₂D⁺, these fits give standard deviations of 0.008 and 0.002 cm^{−1} for the symmetric and asymmetric components, respectively. The coefficients are given in Table I.

TABLE II. Comparison of fundamentals of H₂D⁺ and D₂H⁺ calculated using the *ab initio* Born–Oppenheimer potential (BO) of Röhse *et al.* (Ref. 8), the spectroscopically determined potential of Dinelli *et al.* (DMT) (Ref. 10), and the BO potential plus mass dependent adiabatic correction of this work (nBO) with the observed fundamentals (Refs. 14, 20, and 21).

H ₂ D ⁺	ν_1	ν_2	ν_3	$\frac{1}{2}(\nu_2 + \nu_3)$	$\nu_3 - \nu_2$
BO	2993.756	2206.365	2335.067	2270.716	128.702
BO ^a	2993.279	2206.079	2334.714	2270.397	128.635
DMT ^a	2992.675	2206.209	2334.905	2270.557	128.696
nBO	2992.566	2206.081	2335.556	2270.819	129.475
Obs.	2992.505	2205.869	2335.449	2270.659	129.580
D ₂ H ⁺	ν_1	ν_2	ν_3	$\frac{1}{2}(\nu_2 + \nu_3)$	$\nu_3 - \nu_2$
BO	2737.840	1967.642	2079.231	2023.437	111.589
BO ^a	2737.446	1967.457	2078.977	2023.217	111.520
DMT ^a	2736.809	1967.480	2079.210	2023.345	111.730
nBO	2737.011	1968.262	2078.624	2023.443	110.362
Obs.	2736.981	1968.169	2078.430	2023.300	110.261

^aThese calculations were performed using atomic masses less one third of an electron mass. The other calculations used nuclear masses.

III. RESULTS AND DISCUSSION

Calculations were performed for H₂D⁺ and D₂H⁺ using previously optimized²⁴ basis functions and the TRIATOM program suite.²⁵ Because these calculations were considerably more accurate than any we have previously attempted on this system, it was necessary for us to test our basis sets so that we did not introduce any systematic effects due to lack of convergence. Test calculations showed that using energy selected basis sets comprising 1200 functions for the first, ‘vibrational’ step in the calculation and 350×(*J*+1) functions for the second step²⁵ was sufficient to converge the energy levels of interest to within 0.0001 cm^{−1}.

Initially calculations were performed with no rotational excitation, *J*=0, to obtain the band origins predicted by the new potentials. These calculations were performed using previously optimized²⁴ basis functions and the TRIATOM program suite.²⁵ Our results are summarized in Table II.

Table II also presents results for calculations using the *ab initio* Born–Oppenheimer (BO) potential of Röhse *et al.*⁸ and the spectroscopically determined effective H₃⁺ potential of Dinelli *et al.* (DMT).¹⁰ Neither of these potentials allow for the asymmetric component of the adiabatic correction and calculations which both give significant errors when compared with the observed band origins. Particularly notable are the errors in the splitting between the ν_2 and ν_3 band origins, which are large and systematic. These errors are greatly reduced with our *ab initio* non-Born–Oppenheimer (nBO) effective potentials. In particular the error in the $\nu_3 - \nu_2$ splitting is reduced by an order of magnitude.

It is interesting to note that our residual error in the $\nu_3 - \nu_2$ splitting is +0.01 cm^{−1} for H₂D⁺ and −0.01 cm^{−1} for D₂H⁺. The mass factors in the asymmetric adiabatic correction act to give an equal and opposite correction to these two isotopomers and these residual errors suggest that we may have underestimated this correction by about 10%.

The accuracy of these predictions encouraged us to undertake a more detailed comparison for H₂D⁺. We performed calculations using our nBO potential for *J* up to 7, the highest rotational level for which transitions have been observed.

Table III compares our calculations with the observed transitions. Overall our calculations reproduce the experimental data for the pure rotational transitions and the three fundamental bands with very high accuracy, typically about 3 parts in 10⁵. Furthermore the fundamental bands all show near uniform systematic errors of −0.06 cm^{−1} for the ν_1 band, −0.13 cm^{−1} for ν_2 , and −0.19 cm^{−1} for ν_3 , with remarkably little spread about these values. Detailed comparisons of individual transitions suggest that the previous reassignments^{20,22} are indeed correct and that three other transitions lie far enough away from our predicted transition frequencies to make their assignments very doubtful. These transitions are marked in Table III.

Table III shows that if due allowance is made for the systematic shift in a particular vibrational band, individual transitions can be predicted with an accuracy of better than

TABLE III. Comparison of observed and calculated transition frequencies for H₂D⁺. Data for the two observed rotational transitions (Refs. 17 and 19) is quoted in MHz, data for the ν_1 ro-vibrational band (Ref. 13), the ν_2 band (Ref. 14), and the ν_3 band (Ref. 14) are given in cm⁻¹.

ν_{obs}	ν_{calc}	Upper level	Lower level	Error	ν_{obs}	ν_{calc}	Upper level	Lower level	Error
15 5987.2	15 5995.1	2 2 0	2 2 1	-7.9	2 402.795	2 402.914	1 1 1	0 0 0	-0.119
37 2421.4	37 2431.8	1 1 0	1 1 1	-10.4	2 417.734	2 417.867	2 0 2	1 1 1	-0.133
					2 429.647 ^a	2 429.731	2 2 1	2 1 2	-0.084
ν_2 band					2 445.348	2 445.481	2 1 2	1 0 1	-0.133
1 837.573	1 837.742	6 1 5	7 1 6	-0.169	2 466.041	2 466.167	3 3 1	3 2 2	-0.126
1 837.688	1 837.856	6 2 5	7 2 6	-0.168	2 471.865	2 472.003	3 0 3	2 1 2	-0.138
1 892.541	1 892.712	5 0 5	6 0 6	-0.171	2 486.932	2 487.068	3 1 3	2 0 2	-0.136
1 892.558	1 892.731	5 1 5	6 1 6	-0.173	2 490.782	2 490.920	4 2 3	4 1 4	-0.138
1 895.995	1 896.170	5 1 4	6 1 5	-0.175	2 496.014	2 496.137	2 2 1	1 1 0	-0.123
1 896.345	1 896.520	5 2 4	6 2 5	-0.175	2 505.693	2 505.825	4 1 3	3 2 2	-0.132
1 952.024	1 952.206	4 1 3	5 1 4	-0.182	2 509.541	2 509.666	2 2 0	1 1 1	-0.125
2 012.621	2 012.807	3 0 3	4 0 4	-0.186	2 523.271	2 523.414	4 0 4	3 1 3	-0.143
2 013.010	2 013.195	3 1 3	4 1 4	-0.185	2 534.328	2 534.459	3 2 2	2 1 1	-0.131
2 053.211	2 053.409	2 1 1	3 1 2	-0.198	2 568.302	2 568.434	4 2 3	3 1 2	-0.132
2 060.684	2 060.880	2 2 1	3 2 2	-0.197	2 571.585	2 571.728	5 0 5	4 1 4	-0.143
2 066.958	2 067.151	2 0 2	3 0 3	-0.193	2 572.755	2 572.897	5 1 5	4 0 4	-0.142
2 068.680	2 068.872	2 1 2	3 1 3	-0.192	2 578.462	2 578.593	3 2 1	2 1 2	-0.131
2 081.851 ^a	2 082.282	4 1 4	3 3 1	-0.431	2 596.960	2 597.089	3 3 1	2 2 0	-0.129
2 102.488	2 102.690	1 1 0	2 1 1	-0.202	2 602.146	2 602.271	3 3 0	2 2 1	-0.125
2 115.046	2 115.245	1 0 1	2 0 2	-0.199	ν_1 band				
2 119.938	2 120.137	1 1 1	2 1 2	-0.199	2 839.387	2 839.450	3 1 3	4 1 4	-0.063
2 160.176	2 160.380	0 0 0	1 0 1	-0.204	2 840.962	2 841.024	2 1 1	3 1 2	-0.062
2 186.344	2 186.542	1 1 1	1 1 0	-0.198	2 871.897	2 871.960	2 0 2	3 0 3	-0.063
2 208.417	2 208.617	2 2 0	2 2 1	-0.200	2 874.811	2 874.879	2 1 2	3 1 3	-0.068
2 218.393	2 218.596	1 1 0	1 1 1	-0.203	2 887.370	2 887.433	1 1 0	2 1 1	-0.063
2 225.501	2 225.700	3 2 1	3 2 2	-0.199	2 904.657	2 904.720	2 0 2	2 2 1	-0.063
2 240.512	2 240.711	2 1 1	2 1 2	-0.199	2 906.523	2 906.589	1 0 1	2 0 2	-0.066
2 246.697	2 246.897	1 0 1	0 0 0	-0.200	2 911.635	2 911.699	1 1 1	2 1 2	-0.064
2 283.810	2 284.008	2 2 1	2 0 2	-0.198	2 946.802	2 946.865	0 0 0	1 0 1	-0.063
2 290.658 ^b	2 290.828	5 1 5	4 1 4	-0.170	2 952.940	2 953.002	2 1 2	2 1 1	-0.062
2 381.367	2 381.571	2 2 0	1 0 1	-0.204	2 963.513	2 963.572	3 2 2	3 2 1	-0.059
2 448.627	2 448.828	3 2 1	2 0 2	-0.201	2 975.064	2 975.118	3 3 1	3 3 0	-0.054
2 512.598	2 512.794	3 3 1	2 1 2	-0.196	2 978.045	2 978.105	1 1 1	1 1 0	-0.060
2 537.200	2 537.371	4 2 2	3 0 3	-0.171	2 978.492	2 978.547	3 3 0	3 3 1	-0.055
					2 979.987	2 980.046	2 2 1	2 2 0	-0.059
ν_3 band					2 991.162	2 991.221	2 2 0	2 2 1	-0.059
2 108.633	2 108.758	2 2 1	3 3 0	-0.125	3 003.276	3 003.339	1 1 0	1 1 1	-0.063
2 111.226	2 111.349	2 2 0	3 3 1	-0.123	3 009.123	3 009.183	3 2 1	3 2 2	-0.060
2 157.701	2 157.827	2 1 1	3 2 2	-0.126	3 028.263	3 028.326	2 1 1	2 1 2	-0.063
2 190.664	2 190.787	1 1 0	2 2 1	-0.123	3 038.177	3 038.241	1 0 1	0 0 0	-0.064
2 223.706	2 223.838	2 0 2	3 1 3	-0.132	3 063.006	3 063.070	3 1 2	3 1 3	-0.064
2 239.637	2 239.768	2 1 2	3 0 3	-0.131	3 068.845	3 068.908	2 1 2	1 1 1	-0.063
2 242.303	2 242.428	2 2 1	3 1 2	-0.125	3 072.190	3 072.252	2 2 1	2 0 2	-0.062
2 245.109	2 245.235	1 0 1	2 1 2	-0.126	3 077.611	3 077.674	2 0 2	1 0 1	-0.063
2 257.495	2 257.620	3 2 1	3 3 0	-0.125	3 094.671	3 094.732	2 1 1	1 1 0	-0.061
2 261.176	2 261.318	4 0 4	4 1 3	-0.142	3 104.207	3 104.267	3 1 3	2 1 2	-0.060
2 263.807	2 263.940	3 1 3	3 2 2	-0.133	3 109.645	3 109.706	3 0 3	2 0 2	-0.061
2 271.135	2 271.262	1 1 1	2 0 2	-0.127	3 121.202	3 121.261	3 2 2	2 2 1	-0.059
2 272.395	2 272.527	2 1 2	2 2 1	-0.132	3 137.007	3 137.066	4 1 4	3 1 3	-0.059
2 275.403	2 275.527	0 0 0	1 1 1	-0.124	3 139.197	3 139.255	4 0 4	3 0 3	-0.058
2 279.085 ^a	2 279.115	4 1 3	4 2 2	-0.030	3 140.044	3 140.105	3 2 1	2 2 0	-0.061
2 284.565	2 284.700	3 0 3	3 1 2	-0.135	3 141.131	3 141.193	3 1 2	2 1 1	-0.062
2 288.623	2 288.749	2 1 1	2 2 0	-0.126	3 160.971	3 161.030	4 2 3	3 2 2	-0.059
2 301.830	2 301.961	2 0 2	2 1 1	-0.131	3 168.702 ^c	3 168.761	5 0 5	4 0 4	-0.059
2 311.512	2 311.641	1 0 1	1 1 0	-0.129	3 178.973	3 179.030	4 1 3	3 1 2	-0.057
2 380.824	2 380.955	2 1 1	2 0 2	-0.131	3 193.963	3 194.022	4 2 2	3 2 1	-0.059
2 393.633	2 393.760	2 2 0	2 1 1	-0.127	3 208.187	3 208.243	5 1 4	4 1 3	-0.056

^aThese assignments are suspect.^bAs reassigned by Miller *et al.* (Ref. 22).^cAs reassigned by Kozin *et al.* (Ref. 20).

0.01 cm^{-1} . This value is close to experimental error and undoubtedly means that our method can resolve all remaining problems regarding assignments in the fundamental bands of H_2D^+ and D_2H^+ .

Dinelli *et al.*¹² found similar systematic errors for their nBO calculations on H_3^+ and D_3^+ . In particular, they found average errors for the ν_1 and ν_2 bands of H_3^+ of -0.08 and -0.15 cm^{-1} , respectively and -0.12 cm^{-1} for the ν_2 bands of D_3^+ . The similarity between the errors obtained for similar modes in different isotopomers suggests that the underlying error is due to the mass independent portion of the potential. From such a comparison it is not possible to distinguish between residual errors in the BO potential and other mass independent effects such as the relativistic correction. However we note that the calculations of Röhse *et al.*⁸ were about 1 cm^{-1} away from the exact BO energy of the system.

Careful analysis of the transitions within a band shows that there is a systematic variation in the error as a function of J . In particular, for the ν_2 and ν_3 bands the transitions involving higher J 's give smaller errors. It is likely that this reduction of error is actually fortuitous and due to some cancellation. In particular it is possible that the higher J levels are increasingly affected by nonadiabatic effects which are J dependent.^{26,27} However, one should first resolve the problems with the larger, systematic errors in the band origins before pursuing this hypothesis.

IV. CONCLUSIONS

We have constructed a mass dependent adiabatic correction to the Born–Oppenheimer (BO) potential of H_3^+ and its isotopomers which has lower symmetry than the purely BO potential. We have tested the resulting asymmetric effective potentials on the asymmetric isotopomers H_2D^+ and D_2H^+ , and found that this resolved the previously noted problem¹⁰ with the splitting between the ν_2 and ν_3 band origins of these ions. The adiabatic correction to the BO approximation was found to be the source of the discrepancy.

Detailed comparisons between our calculations and observed transition frequencies for H_2D^+ give excellent agreement, which solves the problem of assigning H_2D^+ and D_2H^+ transitions which has existed for many years. However, small systematic errors give pointers to how the *ab initio* computation of these transition frequencies might be further improved.

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