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Ab initio calculation of the rotation–vibration energy levels of H_3^+ and its isotopomers to spectroscopic accuracy

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Surfaces are fitted to the Born–Oppenheimer potential energy, electronic relativistic correction and adiabatic correction data calculated *ab initio* by Cencek *et al.* [J. Chem. Phys. **108**, 2831 (1998)]. These surfaces are used in calculations of the rotation–vibration energy levels of H_3^+, H_2D^+, D_2H^+, and D_3^+. Nonadiabatic corrections to the Born–Oppenheimer approximation are introduced following models developed for diatomics which involve the use of isotopomer independent scaled vibrational reduced masses. It is shown that for triatomics this approach leads to an extra term in the nuclear motion Hamiltonian. Our final calculations reproduce the known spectroscopic data for H_3^+ and its isotopomers to within a few hundredths of a cm^{-1}. © *1999 American Institute of Physics.* [S0021-9606(99)00811-9]

I. INTRODUCTION

H_3^+ is a system of importance in cool hydrogen plasmas such as those that occur in a variety of astrophysical environments. The spectrum of H_3^+ has been extensively studied in both the laboratory and astrophysical environments, see reviews.[1–6] In particular H_3^+ has recently been successful detected in the interstellar medium via its infrared absorption spectrum.[7]

H_3^+ is the electronically simplest polyatomic molecule and, therefore, has become a benchmark system for high accuracy studies.[8–12] By combining high accuracy Born–Oppenheimer (BO) electronic structure calculations[10] and *ab initio* estimates of the adiabatic correction to the BO approximation, *ab initio* spectra accurate to few tenths of a cm^{-1} have been achieved.[11,12] Very recently Cencek and coworkers have performed a series of calculations giving a submicrohartree accuracy potential-energy surface for H_3^+.[13,14] These workers performed exceptionally high accuracy electronic structure calculations which they augmented with an electronic relativistic correction, calculated for the first time for H_3^+, and mass-dependent adiabatic corrections to the Born–Oppenheimer (BO) approximation.[13] Fits to these surfaces used in nuclear motion calculations on H_3^+ and its isotopomers gave results which reproduced experiment within a ''few tenths of cm^{-1},'' similar to the accuracy of previous studies. In this work we show that with careful use of the calculations of Cencek *et al.*, plus allowance for the failure of the BO approximation, it is possible to obtain results which reproduce the experimental data for H_3^+ and its isotopomers to within a few hundredths of cm^{-1}.

Systematic studies of the effects of BO failure on the rotational and vibrational energy levels studies has been largely confined to diatomics. Since the classic paper of Kolos and Wolniewicz,[15] there have been a number of studies of non-BO effects on the rotation–vibration energy levels of diatomic systems. Of relevance to the present work are studies on the H_2^+ and H_2 systems a number of which[16–23] are considered in some detail in the following subsection. One particular feature of these works, which we employ here, is that nonadiabatic effects can be modeled effectively using different masses for vibrational and rotational motion. We test this approach for the H_3^+ system and show that, in contrast to diatomics, the choice of different vibrational and rotational masses leads to an extra term in the nuclear motion Hamiltonian. Calculations using vibrational masses taken from diatomic studies[17,22,23] and this extra term in the Hamiltonian give excellent agreement with observations for all isotopomers of H_3^+ for which spectra have been recorded.

II. THEORY

A. Diatomic molecules

Bunker and Moss[17] derived an effective vibration–rotation Hamiltonian for $^1\Sigma$ diatomic molecules which includes allowance nonadiabatic corrections to the BO approximation. Their Hamiltonian consists of three terms, the vibrational and rotational kinetic-energy operators, and the potential

$$\hat{H} = -\frac{\hbar^2}{2\mu^V R^2}\frac{\partial^2}{\partial R^2} + \frac{\hbar^2}{2\mu^R R^2}N(N+1) + (1+\gamma)W(R), \quad (1)$$

where R is the bond length and N the rotational quantum number. W is the sum of the mass-independent BO potential plus relativistic correction and the mass-dependent adiabatic correction. W is scaled by $(1+\gamma)$ to allow for nonadiabatic effects. The main means by which nonadiabatic effects are accounted for is via the two effective reduced masses. μ^V is the effective vibrational reduced mass and μ^R is the effective rotational reduced mass.

Hamiltonian (1) was recently used by Moss[22] for H_2^+ and D_2^+, and Moss and Jopling[23] for HD^+, who found that the spectra of all the isotopomers considered could be repro-

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duced to high accuracy with a single set of isotopomer independent parameters. Both Bishop and Shih,[16] and Bunker *et al.*[18] used a Hamiltonian similar to Eq. (1) for H_2 and D_2, again with satisfactory results. A feature of these studies is that the effective vibrational reduced mass, μ^V, was found to differ significantly from that given by nuclear masses, whereas the effective rotational reduced mass, μ^R, was found to be close to the nuclear reduced mass by Moss for the H_2^+ problem, and set equal to the nuclear mass in the studies of H_2.

It should be emphasized that calculations mentioned above do not represent the best available for the hydrogenic diatomics: Moss and co-workers have performed a series ultra high accuracy studies on H_2^+ as a three-body problem,[21] and Schwartz and Le Roy[20] have conducted an elaborate, but still approximate, treatment of nonadiabatic effects in H_2. However, it is beyond our present capabilities to perform calculations at this level for polyatomic systems.

B. Triatomic molecules

We wish to compute rotation–vibration spectra for H_3^+ to high accuracy. For this purpose we use the exact kinetic-energy operator approach of Sutcliffe and Tennyson who derived a number of Hamiltonians in internal coordinates expressed in terms of two distances and an included angle.[24–26] In this work we use atom–diatom scattering or Jacobi coordinate in which r_1 represents the distance between two atoms, the ''diatom,'' and r_2 the distance from the center-of-mass of the diatom to the third atom. θ is the angle between $\underline{r}_1$ and $\underline{r}_2$. Although it is not possible to represent the true symmetry of H_3^+ in these coordinates, they have been widely and successfully used for high-accuracy calculations on this system.[10,11,13,14,27]

Following Sutcliffe and Tennyson,[24] the body-fixed Hamiltonian can be written

$$\hat{H}=\hat{K}_V+\hat{K}_{VR}+V(r_1,r_2,\theta), \tag{2}$$

where V is the potential-energy surface, which is a function of internal coordinates only. In Jacobi coordinates, the vibrational kinetic-energy operator is

$$\hat{K}_V=-\frac{\hbar^2}{2}\left[\frac{1}{\mu_1^V}\frac{\partial^2}{\partial r_1^2}+\frac{1}{\mu_2^V}\frac{\partial^2}{\partial r_2^2}+\left(\frac{1}{\mu_1^V r_1^2}+\frac{1}{\mu_2^V r_2^2}\right)\right.$$
$$\left.\times\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\right]. \tag{3}$$

The vibration–rotation kinetic-energy operator, which is null when the rotational angular momentum, J, is zero, is

$$\hat{K}_{VR}=\frac{1}{2\mu_2^R r_2^2}(\Pi_x^2+\Pi_y^2)+\left(\frac{\cot^2\theta}{2\mu_1^R r_1^2}+\frac{\sin^{-2}\theta}{2\mu_2^R r_2^2}\right)\Pi_z^2$$
$$+\frac{\cot\theta}{2\mu_1^R r_1^2}(\Pi_x\Pi_z+\Pi_z\Pi_x)+\frac{\hbar}{i}\frac{1}{2\mu_2^R r_2^2}$$
$$\times\left(\frac{\partial}{\partial\theta}+\frac{\cot\theta}{2}\right)\Pi_y, \tag{4}$$

where Π_α is an angular momentum operator depending only on the Euler angles. In Eq. (4) it has been assumed that the z axis is placed along $\underline{r}_2$. An embedding with the body-fixed z axis placed along $\underline{r}_1$ is obtained by replacing μ_2^R with μ_1^R and r_2 with r_1.

For Jacobi coordinates the reduced masses used in Eqs. (3) and (4) are given by

$$\mu_1^{-1}=m_B^{-1}+m_C^{-1},\quad \mu_2^{-1}=m_A^{-1}+(m_B+m_C)^{-1}, \tag{5}$$

where m_B and m_C are the masses of the atoms comprising the diatom, and m_A is the mass of the atom. In line with the diatomic Hamiltonian (1), the reduced masses have been labeled V or R according to whether they are involved in vibrational or rotational motion.

The Hamiltonian (2) depends on the three internal coordinates and the three Euler angles, (α,β,γ), used to embed the axis system. The rotational motion of the system can be represented entirely in terms of Wigner rotation functions[28] $D_{k,M}^{J}{}^{\star}(\alpha,\beta,\gamma)=|J,M,k\rangle$, where M is the projection of the rotational motion on the space-fixed z axis and k is its projection on the body-fixed z axis. A standard step in the Sutcliffe–Tennyson procedure is to derive an effective internal coordinate Hamiltonian operator by multiplying from the left by $\langle J,M,k'|$, the right by $|J,M,k\rangle$ and integrating over all Euler angles. This gives[24,25]

$$\hat{H}=\delta_{k,k'}\hat{K}_V+\hat{K}_{VR}+\delta_{k,k'}V(r_1,r_2,\theta), \tag{6}$$

where the vibrational kinetic-energy operator and the potential do not depend on the Euler angles and are, therefore, not altered by the integration. The effective rotation–vibration operator is[25]

$$\hat{K}_{VR}=\delta_{k,k'}\hbar^2\left[\frac{(J(J+1)-2k^2)}{2\mu_2^R r_2^2}+\frac{k^2}{\sin^2\theta}\left(\frac{1}{2\mu_1^R r_1^2}+\frac{1}{2\mu_2^R r_2^2}\right)\right]$$
$$+\delta_{k',k\pm1}\frac{\hbar^2}{2\mu_2^R r_2^2}C_{Jk}^{\pm}\left(\mp\frac{\delta}{\delta\theta}+k\cot\theta\right), \tag{7}$$

where

$$C_{Jk}^{\pm}=(J(J+1)-k(k\pm1))^{1/2}. \tag{8}$$

In this form of $\hat{K}_{VR}$, it is clear that the term which depends on $\sin^{-2}\theta$ is potentially singular at linear geometries, i.e., $\theta=0$ or π. This singularity can be avoided by choice of angular basis functions: Associated Legendre polynomials,[29] $\Theta_{j,k}(\theta)=|j,k\rangle$, where k is explicitly coupled to the $|J,M,k\rangle$ used above.[24]

Multiply from left by $\langle j',k'|$, from the right by $|j,k\rangle$ and integrating over θ only gives a new effective, radial Hamiltonian:

$$\hat{H}=\delta_{k,k'}\hat{K}_V+\hat{K}_{VR}+\delta_{k,k'}\langle j',k|V(r_1,r_2,\theta)|j,k\rangle_\theta, \tag{9}$$

where

$$\hat{K}_V=\delta_{k,k'}\delta_{j,j'}\left[-\frac{\hbar^2}{2\mu_1^V}\frac{\partial^2}{\partial r_1^2}-\frac{\hbar^2}{2\mu_2^V}\frac{\partial^2}{\partial r_2^2}+j(j+1)\times\left(\frac{\hbar^2}{2\mu_1^V r_1^2}+\frac{\hbar^2}{2\mu_2^V r_2^2}\right)\right]-\delta_{k,k'}k^2\langle j',k|\sin^{-2}\theta|j,k\rangle\times\left(\frac{\hbar^2}{2\mu_1^V r_1^2}+\frac{\hbar^2}{2\mu_2^V r_2^2}\right), \tag{10}$$

$$\hat{K}_{VR}=\delta_{k,k'}\delta_{j,j'}\hbar^2\frac{(J(J+1)-2k^2)}{2\mu_2^R r_2^2}-\delta_{k',k\pm1}\delta_{j,j'}\frac{\hbar^2}{2\mu_2^R r_2^2}C_{Jk}^{\pm}C_{jk}^{\pm}+\delta_{k,k'}k^2\langle j',k|\sin^{-2}\theta|j,k\rangle\left(\frac{\hbar^2}{2\mu_1^R r_1^2}+\frac{\hbar^2}{2\mu_2^R r_2^2}\right). \tag{11}$$

Previous derivations of this effective radial Hamiltonian[24–26] have omitted the matrix element over $\sin^{-2}\theta$ as, when $\mu_i^V=\mu_i^R$, this part of the operator cancels between $\hat{K}_V$ and $\hat{K}_{VR}$. However, if $\mu_i^V\neq\mu_i^R$, a new term has to be considered in the Hamiltonian which has the form

$$\hat{K}_{\mathrm{NBO}}=\delta_{k,k'}k^2\langle j',k|\sin^{-2}\theta|j,k\rangle\left(\frac{\hbar^2}{2r_1^2}\left(\frac{1}{\mu_1^R}-\frac{1}{\mu_1^V}\right)+\frac{\hbar^2}{2r_2^2}\left(\frac{1}{\mu_2^R}-\frac{1}{\mu_2^V}\right)\right). \tag{12}$$

As μ_i^V is usually greater than μ_i^R, this extra term, which only occurs for $J>0$, is generally positive.

Matrix elements for the new operator have been included in both the program TRIATOM,[30] which works within a finite basis set representation, and DVR3D,[31] which employs as discrete variable representation (DVR). Within TRIATOM the extra matrix element $\langle j',k|\sin^{-2}\theta|j,k\rangle$ is calculated using M-point Gaussian quadrature based on the zeros of the associated Legendre polynomials Θ_{Mk}. Within DVR3D, the extra matrix elements implied by the new operator $\hat{K}_{\mathrm{NBO}}$ are simply computed with the quadrature approximation.[35] The angular integrals over $\sin^{-2}\theta$ are singular for basis functions with $k=0$. However, in this case the matrix element is zero, so such problems are avoided.

III. CALCULATIONS

A. Effective potential-energy surfaces

As for previous studies of H_3^+,[11,12,14] we write an effective potential-energy surface, $W(R)$, as a function of internal coordinates, Q, for the ith isotopomer as

$$W_i(Q)=V_{\mathrm{BO}}(Q)+V_{\mathrm{rel}}(Q)+\frac{1}{\mu_i^S}\Delta V_{\mathrm{ad}}^S(Q)+\frac{1}{\mu_i^A}\Delta V_{\mathrm{ad}}^A(Q), \tag{13}$$

where V_{BO} is the Born–Oppenheimer potential and V_{rel} is the electronic relativistic correction. The mass-dependent terms in Eq. (13) are due to the adiabatic correction to the BO approximation. For H_3^+ and D_3^+ only the symmetric adiabatic correction, ΔV_{ad}^S, is nonzero. The mass factor for this term is

$$(\mu_i^S)^{-1}=m_A^{-1}+m_B^{-1}+m_C^{-1}. \tag{14}$$

For H_2D^+ and D_2H^+ there is also an asymmetric adiabatic correction,[12] ΔV_{ad}^A, which has a mass factor

$$(\mu_i^A)^{-1}=m_A^{-1}-m_B^{-1}, \tag{15}$$

within a labeling scheme for which $m_B=m_C$.

The surfaces V_{BO}, V_{rel}, ΔV_{ad}^S, and ΔV_{ad}^A used here are all parameterized using the *ab initio* data of Cencek *et al.*[13] Analytic fits to the data of Cencek *et al.* have already been presented by Jaquet *et al.*,[14] however, as a cross check we have re-fitted the data.

Fits were performed using symmetry coordinates

$$S_a=(\tilde{R}_{12}+\tilde{R}_{23}+\tilde{R}_{31})/\sqrt{3},$$
$$S_x=(2\tilde{R}_{12}-\tilde{R}_{23}-\tilde{R}_{31})/\sqrt{6}=S_e\cos(\phi), \tag{16}$$
$$S_y=(\tilde{R}_{23}-\tilde{R}_{31})/\sqrt{2}=S_e\sin(\phi),$$

where for displacement coordinates

$$\tilde{R}_{jk}=R_{jk}-R_e, \tag{17}$$

and for Morse coordinates

$$\tilde{R}_{jk}=\left[1-\exp\left(-\beta\frac{R_{jk}-R_e}{R_e}\right)\right]\bigg/\beta. \tag{18}$$

In the above expressions R_{jk} is the distance between atom j and atom k, R_e is the equilibrium separation which was assumed to be $1.65a_o$ and the Morse parameter β was fixed at 1.3.[32]

Previous experience[11,12,14,27,32] has suggested that the BO potential, which of course shows dissociative behavior, is best represented using Morse coordinates; whereas the adiabatic and relativistic corrections are essentially polynomial functions which are best represented using displacement coordinates. In fact only the S_a coordinate is actually dissociative; tests showed that the best fits were obtained using Morse coordinates for S_a in V_{BO} and displacement coordinates in all other cases. The fits were performed using a function of the general form

$$V^{\mathrm{fit}}(Q)=\sum_{n,m,k}V_{n,m,k}S_a^nS_e^{m+k}\cos(k\phi), \tag{19}$$

where $m=0,2,4,\ldots$, and $k=0,3,6,\ldots$ for the symmetric functions V_{BO}, V_{rel}, and ΔV_{ad}^S, and $k=1,2,4,5,\ldots$ for ΔV_{ad}^A. Coefficients for the fits can be obtained from the EPAPS archive.[33]

The order of each fit, N, can be defined as the lowest number such that $n+m+k$ is always less than or equal to N. However, we did not retain all terms in expansion (19) for a given N. Instead constants which were poorly determined or strongly correlated were removed from the fits; such constants are given as blank entries.

For V_{BO} our tenth-order fit with 54 constants gives a standard deviation of $0.04\,\mathrm{cm}^{-1}$ compared with Jaquet *et al.* tenth-order fit which retained all 67 constants to fit 69 data points with a weighted standard deviation of $0.05\,\mathrm{cm}^{-1}$. Our fit to V_{rel}[34] required 28 out of the 31 seventh-order constants and gave a standard deviation of effectively zero compared

TABLE I. Parameters, in atomic units, for the Morse oscillatorlike functions used for the radial basis functions in TRIATOM (Ref. 30) and used to generate the radial grids in DVR3D (Ref. 31).

	r_1			r_2		
	r_e	D_e	ω_e	r_e	D_e	ω_e
H_3^+	2.1	0.1	0.0118	1.71	0.26	0.009
H_2D^+	1.71	0.1	0.0108	1.65	0.215	0.008 95
D_2H^+	1.83	0.09	0.0081	1.62	0.17	0.0105
D_3^+	1.78	0.12	0.009	1.48	0.2	0.009

to the $0.19\,\text{cm}^{-1}$ weighted standard deviation given by Jaquet *et al.* ninth-order fit. Our fit to ΔV_{ad}^{S} used a full seventh-order fit and gave a mass-weighted standard deviation similar to that of Jaquet *et al.* full ninth-order fit.

The only fit which gave significantly different results from the work of Jaquet *et al.* was to ΔV_{ad}^{A}. Our full sixth-order fit reproduces all 116 unique data points[36] with a mass-weighted standard deviation of $0.005\,\text{cm}^{-1}$. This fit used only half the number of constants used by Jaquet *et al.*

We believe our fits to be more compact and stable representations of the *ab initio* data of Cencek *et al.* However, calculations by us using Jaquet *et al.* best surfaces yielded results which differ by less than $0.01\,\text{cm}^{-1}$ from ones obtained with our fits, which we use for all results presented below. This suggests that the results presented are not sensitive to these high accuracy fits. Conversely our nuclear motion calculations using Jaquet *et al.* surfaces, their model and masses gave good agreement with their results for H_3^+ but results for the mixed isotopomers which differed by as much as $0.2\,\text{cm}^{-1}$. This suggests that the results are sensitive to the details of the nuclear motion calculations.

B. Nuclear motion calculations

As we are aiming for high accuracy in our calculations, we took considerable care to check the convergence of our rotation–vibration calculations. Convergence checks were performed for all four of the H_3^+ isotopomers discussed below. The calculations, including those which include the extra term $\hat{K}_{\text{NBO}}$, were cross checked by using adapted versions of both the finite basis representation program suite TRIATOM[30] and the discrete variable representation program suite DVR3D.[31] The two approaches give very similar results as can be seen by comparing Tables II and III, which present results computed using TRIATOM, with our subsequent results which used DVR3D.

Our final nuclear motion calculations used DVR3D. Parameters for the Morse oscillatorlike functions, which determined the radial grids, are given in Table I. These differ somewhat from the parameters used by Jaquet *et al.* who used a set optimized some time ago by Miller and Tennyson.[37] The main difference is that for our set the values for ω_e have been lowered to give a larger spread of radial grid points. Our DVR3D calculations used 21 grid points in r_2, 20 in r_1 and 36 angular grid points based on the zeros of Gauss-(associated) Legendre polynomials. For the vibrational step, a final Hamiltonian of dimension 2000 was used in all cases. For the rotational step a final Hamiltonian of dimension $350\times(J+1)$ was used. Comparing with Jaquet *et al.*, our vibrational calculations are somewhat larger but our rotational calculations are about 40% smaller. Tests suggested that our basis set is sufficient to converge all the energy levels considered to better than $0.005\,\text{cm}^{-1}$.

The aim of this work was to test a number of models for computing rotation–vibration spectra of H_3^+ and its isotopomers to accuracy well beyond that achievable within the BO approximation. The starting point for this was the BO potential energy, the electronic relativistic correction and the adiabatic correction surfaces fitted above.

There have been a number of studies exploring possible mass effects on the H_3^+ vibration–rotation spectrum,[14,38] however, we adopted a somewhat different approach guided by the various diatomic studies discussed above. To model nonadiabatic effects we followed the recipe of Bunker and Moss[17] and used separate masses for vibrational and rotational motions.

The rotational reduced masses, μ_i^R, were fixed to the values given by nuclear masses. There are two reasons for this choice: First the diatomic studies on both H_2^+[22] and H_2[16,18] set the rotational reduced mass at or near this value, second rotational nonadiabatic effects in triatomics are known to be related to rotational *g*-factors,[39] and the rotational *g*-factors for H_3^+ are known to be particularly small.[40]

We tested a number of possible vibrational reduced masses. In the end we used the hydrogenic vibrational reduced masses found optimal by Moss for H_2^+[22] and hence derived a deuterium vibrational reduced masses using the scaling relation of Bunker and Moss.[17] This yields $m_{\text{H}}=1.007\,537\,2$ u and $m_{\text{D}}=2.013\,814\,0$ u compared to values for the nuclear mass of $m_{\text{H}}=1.007\,276\,47$ u and $m_{\text{D}}=2.013\,553\,2$ u.[20] These values were used for all isotopomers. It is likely that even closer agreement with experiment could be obtained by adjusting these masses, but this was not attempted.

Table II compares our models for all the known band origins of the H_3^+ system whereas Table III just considers a few transition frequencies for the three known vibrational bands of H_2D^+. H_2D^+ is known to be particularly sensitive to non-BO effects.[42] The first column in each table shows the results obtained using only the Born–Oppenheimer (BO) potential-energy surface plus relativistic correction. This level of calculation shows errors of more than $1\,\text{cm}^{-1}$. The second column shows the effect of including the adiabatic correction to the BO approximation: This model, which is equivalent to the best *ab initio* one used by Jaquet *et al.*,[14] gives errors of a few tenths of cm^{-1}. All calculations in the first two columns used nuclear masses.

In the third column of both tables we used the effective vibrational reduced masses discussed above. This results in a very significant improvement in the $J=0$ calculations: The errors are reduced by almost an order of magnitude to hundredths of cm^{-1}. However, for the results including rotational excitation, Table III, the improvement is not so great. There is another notable difference between the results of column 2 and the results of column 3 in Table III: The residues for the BO, relativistic plus adiabatic correction calcu-

TABLE II. $J=0$ band origins,[a] in cm^{-1}, for H_3^+ and its observed isotopomers. Results, which are given as observed–calculated, for various models[b] calculated with TRIATOM.

		E_{obs}	BO	$+\Delta V_{\mathrm{ad}}$	$\mu^V \neq \mu^R$
H_3^+					
	01^1	2521.409	−0.11	−0.24	0.056
	10^0	3178.290	−1.30	−0.40	0.025
	02^0	4778.350	0.00	−0.50	0.020
	02^2	4998.045	−0.30	−0.64	0.010
	11^1	5554.155	−1.40	−0.50	0.000
H_2D^+					
	ν_1	2992.505	−1.46	−0.36	−0.020
	ν_2	2205.869	0.47	−0.25	−0.050
	ν_3	2335.449	0.47	−0.14	0.090
D_2H^+					
	ν_1	2736.981	−1.04	−0.28	0.001
	ν_2	1968.169	0.58	−0.11	0.023
	ν_3	2078.430	−0.74	−0.18	−0.004
D_3^+					
	01^1	1834.670	⋯	⋯	0.015

[a] Experimentally derived data (Ref. 43).

[b] Models defined as follows: BO: *Ab initio* BO potential+relativistic surface. $+\Delta V_{\mathrm{ad}}$: As BO plus adiabatic correction surface, ΔV_{ad}. $\mu^V \neq \mu^R$: As $+\Delta V_{\mathrm{ad}}$ with $\mu^V \neq \mu^R$.

lation (column 2) are systematic and smooth; those for the $\mu_i^V \neq \mu_i^R$ calculation are not. In the final column of Table III we show the effect of including the extra term in Hamiltonian, $\hat{K}_{\mathrm{NBO}}$, which arises when $\mu_i^V \neq \mu_i^R$. Including this term reduces the magnitude of the errors and recovers the situation whereby the residues, which are now a few hundredths of cm^{-1}, are systematic and smooth. Systematic and smooth residues are important as they can be accounted when using the results for spectroscopic assignments,[41] and indeed can be easily corrected by fitting to experimental data. Furthermore, these residues are pointers on how the *ab initio* model can be further improved. Clearly this extra term, while not large, is important.

TABLE III. Sample transition frequencies, in cm^{-1}, for H_2D^+. Results, which are given as observed–calculated, were calculated using TRIATOM for various models.[a]

JK_aK_c	JK_aK_c	ν_{obs} (Refs. 44 and 45)	BO	$+\Delta V_{\mathrm{ad}}$	$\mu^V \neq \mu^R$	$+\hat{K}_{\mathrm{NBO}}$
ν_2						
2 2 0	2 2 1	2208.417	−0.435	−0.242	−0.050	−0.068
3 2 1	3 2 2	2225.501	−0.385	−0.245	−0.062	−0.044
2 2 1	2 0 2	2283.810	−0.521	−0.239	+0.030	−0.059
2 2 0	1 0 1	2381.367	−0.573	−0.250	+0.008	−0.060
3 2 1	2 0 2	2448.627	−0.521	−0.259	−0.011	−0.076
3 3 1	2 1 2	2512.598	−0.647	−0.250	+0.075	−0.099
ν_3						
2 0 2	3 1 3	2223.706	−0.418	−0.163	+0.050	+0.068
2 2 1	3 1 2	2242.303	−0.753	−0.151	+0.140	+0.095
2 1 2	2 2 1	2272.395	−0.420	−0.168	+0.035	+0.099
2 2 0	2 1 1	2393.633	−0.320	−0.162	+0.140	+0.087
3 3 1	3 2 2	2466.041	−0.224	−0.164	+0.190	+0.080
3 3 1	2 2 0	2596.960	−0.185	−0.177	+0.167	+0.077
3 3 0	2 2 1	2602.146	−0.203	−0.172	+0.167	+0.080
ν_1						
2 0 2	2 2 1	2904.657	−1.364	−0.357	−0.073	+0.009
3 2 2	3 2 1	2963.513	−1.487	−0.355	+0.001	−0.012
3 3 1	3 3 0	2975.064	−1.438	−0.356	−0.020	−0.018

[a] Models defined as follows: BO: *Ab initio* BO potential+relativistic surface. $+\Delta V_{\mathrm{ad}}$: As BO plus adiabatic correction surface, ΔV_{ad}. $\mu^V \neq \mu^R$: As $+\Delta V_{\mathrm{ad}}$ with $\mu^V \neq \mu^R$, no additional kinetic-energy term. $+\hat{K}_{\mathrm{NBO}}$: As $\mu^V \neq \mu^R$, but with the additional kinetic-energy term, $\hat{K}_{\mathrm{NBO}}$.

By allowing for nonadiabatic effects via scaled vibrational masses and the extra term in the Hamiltonian we obtain results which approach spectroscopic accuracy for all isotopomers. The diatomic procedure proposed by Bunker and Moss[17] contained one further parameter, γ, which they used to scale the potential. Moss' studies[22,23] on the H_2^+ system found that values of γ about -0.5×10^{-5} was appropriate for this system. Tests on the H_3^+ system with γ set to this value showed that the scaling was too small to make a noticeable difference to the results. This line of work was, therefore, not pursued.

Tables IV compares our final results generated for H_2D^+ with experimental data[44,45]; a corresponding comparison with experimental data[44,46] for D_2H^+ can be obtained from the EPAPS archive.[33] Table V presents some final results for H_3^+; a fuller set of H_3^+ results have been placed in the EPAPS archive.[33] All calculations were performed using our best model which includes adiabatic effects, vibrational mass scaling and $\hat{K}_{\mathrm{NBO}}$. These tables show that the excellent results obtained in our test calculations are generally true for the range of energy levels considered. Our final results have improved the accuracy of the *ab initio* predictions by an order of magnitude.

For the mixed isotopomers, for which only rather limited spectral information is available, we compare with all transition frequencies. These results show similar systematic deviations for a particular vibrational band to the ones noted above. These deviations are small, less than a tenth of wave number in all cases, but real. At this stage it is not possible to say for certain whether they arise from small, residual errors in the BO or adiabatic surfaces or from the approximate way we correct the BO approximation. However, it should be noted that the largest systematic errors are for transitions involving the ν_2 and ν_3 states. These are known from previous studies[12,27,42] to be the states most sensitive to non-BO effects. The influence of the adiabatic correction to the BO approximation on the calculated energy levels appears insensitive to the level of theory used to calculate it.[13] It is, therefore, most likely that these residual problems are due to our relatively crude treatment of the vibrational nonadiabatic problem.

For H_3^+ there are too many assigned transitions for a compilation and instead Table V compares our results with energy levels for $1 \leqslant J \leqslant 3$ derived from experimental data[43] (a comparison for $J \leqslant 5$ can be obtained from the EPAPS archive[33]). Also given for comparison are results obtained by Dinelli *et al.*[43] using the Dinelli, Polyansky, and Tennyson (DPT)[27] spectroscopically determined, effective potential-energy surface. The table includes predictions of H_3^+ energies up to the region where assigning quantum number labels becomes arbitrary for this molecule.[43] The H_3^+ observations cover a much wider range of energies than for the mixed isotopomers; it is therefore, not surprising that there are cases where our calculations give larger residues. It is notable that

TABLE IV. Comparison of observed (Refs. 44 and 45) and calculated transition frequencies for H_2D^+ in cm^{-1}. Δ is obs−calc.

ν_{obs}	ν_{calc}	$J''K_a''K_c''$	$J'K_a'K_c'$	Δ
ν_2 band				
1837.573	1837.582	6 1 5	7 1 6	−0.009
1837.688	1837.696	6 2 5	7 2 6	−0.008
1892.541	1892.553	5 0 5	6 0 6	−0.012
1892.558	1892.572	5 1 5	6 1 6	−0.014
1895.995	1896.011	5 1 4	6 1 5	−0.016
1896.345	1896.360	5 2 4	6 2 5	−0.015
1952.024	1952.050	4 1 3	5 1 4	−0.026
2012.621	2012.653	3 0 3	4 0 4	−0.032
2013.010	2013.041	3 1 3	4 1 4	−0.031
2053.211	2053.260	2 1 1	3 1 2	−0.049
2060.684	2060.732	2 2 1	3 2 2	−0.048
2066.958	2067.003	2 0 2	3 0 3	−0.045
2068.680	2068.723	2 1 2	3 1 3	−0.043
2102.488	2102.543	1 1 0	2 1 1	−0.055
2115.046	2115.101	1 0 1	2 0 2	−0.055
2119.938	2119.993	1 1 1	2 1 2	−0.055
2160.176	2160.238	0 0 0	1 0 1	−0.062
2186.344	2186.394	1 1 1	1 1 0	−0.050
2208.417	2208.481	2 2 0	2 2 1	−0.064
2218.393	2218.460	1 1 0	1 1 1	−0.067
2225.501	2225.573	3 2 1	3 2 2	−0.072
2240.512	2240.582	2 1 1	2 1 2	−0.070
2246.697	2246.755	1 0 1	0 0 0	−0.058
2283.810	2284.889	2 2 1	2 0 2	−0.079
2381.367	2381.446	2 2 0	1 0 1	−0.079
2448.627	2448.716	3 2 1	2 0 2	−0.089
2512.598	2512.679	3 3 1	2 1 2	−0.081
2537.200	2537.245	4 2 2	3 0 3	−0.045
ν_3 band				
2108.633	2108.550	2 2 1	3 3 0	0.082
2111.226	2111.142	2 2 0	3 3 1	0.084
2157.701	2157.637	2 1 1	3 2 2	0.064
2190.664	2190.586	1 1 0	2 2 1	0.078
2223.706	2223.664	2 0 2	3 1 3	0.042
2239.637	2239.592	2 1 2	3 0 3	0.045
2242.303	2242.231	2 2 1	3 1 2	0.072
2245.109	2245.048	1 0 1	2 1 2	0.061
2257.495	2257.434	3 2 1	3 3 0	0.061
2261.176	2261.132	4 0 4	4 1 3	0.044
2263.807	2263.753	3 1 3	3 2 2	0.054
2271.135	2271.073	1 1 1	2 0 2	0.062
2272.395	2272.337	2 1 2	2 2 1	0.058
2275.403	2275.304	0 0 0	1 1 1	0.099
2284.565	2284.513	3 0 3	3 1 2	0.052
2288.623	2288.560	2 1 1	2 2 0	0.063
2301.830	2301.773	2 0 2	2 1 1	0.057
2311.512	2311.449	1 0 1	1 1 0	0.063
2380.824	2380.780	2 1 1	2 0 2	0.044
2393.633	2393.571	2 2 0	2 1 1	0.062
2402.795	2402.727	1 1 1	0 0 0	0.068
2417.734	2417.689	2 0 2	1 1 1	0.045
2445.348	2445.302	2 1 2	1 0 1	0.046
2466.041	2465.987	3 3 1	3 2 2	0.054
2471.865	2471.836	3 0 3	2 1 2	0.029
2486.932	2487.897	3 1 3	2 0 2	0.035
2490.782	2490.784	4 2 3	4 1 4	−0.002
2496.014	2495.955	2 2 1	1 1 0	0.059
2505.693	2505.672	4 1 3	3 2 2	0.021
2509.541	2509.488	2 2 0	1 1 1	0.053
2523.271	2523.256	4 0 4	3 1 3	0.015
2534.328	2534.286	3 2 2	2 1 1	0.042
2568.302	2568.269	4 2 3	3 1 2	0.033
2571.585	2571.581	5 0 5	4 1 4	0.004
2572.755	2572.749	5 1 5	4 0 4	0.006
2578.462	2578.436	3 2 1	2 1 2	0.026
2596.960	2596.910	3 3 1	2 2 0	0.050
2601.146	2602.095	3 3 0	2 2 1	0.051
ν_1 band				
2839.387	2839.445	3 1 3	4 1 4	−0.058
2840.962	2841.006	2 1 1	3 1 2	−0.044
2871.897	2871.953	2 0 2	3 0 3	−0.056
2874.811	2874.872	2 1 2	3 1 3	−0.061
2887.370	2887.418	1 1 0	2 1 1	−0.048
2904.657	2904.688	2 0 2	2 2 1	−0.031
2906.523	2906.579	1 0 1	2 0 2	−0.056
2911.635	2911.692	1 1 1	2 1 2	−0.057
2946.802	2946.855	0 0 0	1 0 1	−0.053
2952.940	2952.980	2 1 2	2 1 1	−0.040
2963.513	2963.554	3 2 2	3 2 1	−0.041
2975.064	2975.114	3 3 1	3 3 0	−0.050
2978.045	2978.093	1 1 1	1 1 0	−0.048
2978.492	2978.545	3 3 0	3 3 1	−0.052
2979.987	2980.037	2 2 1	2 2 0	−0.050
2991.162	2991.217	2 2 0	2 2 1	−0.055
3003.276	3003.335	1 1 0	1 1 1	−0.049
3009.123	3009.184	3 2 1	3 2 2	−0.061
3028.263	3028.329	2 1 1	2 1 2	−0.066
3038.177	3038.232	1 0 1	0 0 0	−0.055
3063.006	3063.082	3 1 2	3 1 3	−0.076
3068.845	3068.897	2 1 2	1 1 1	−0.052
3072.190	3072.257	2 2 1	2 0 2	−0.067
3077.611	3077.663	2 0 2	1 0 1	−0.052
3094.671	3094.729	2 1 1	1 1 0	−0.058
3104.207	3104.253	3 1 3	2 1 2	−0.046
3109.645	3109.691	3 0 3	2 0 2	−0.046
3121.202	3121.258	3 2 2	2 2 1	−0.056
3137.007	3137.048	4 1 4	3 1 3	−0.041
3139.197	3139.237	4 0 4	3 0 3	−0.040
3140.044	3140.108	3 2 1	2 2 0	−0.064
3141.131	3141.190	3 1 2	2 1 1	−0.059
3160.971	3161.024	4 2 3	3 2 2	−0.053
3168.702	3168.737	5 0 5	4 0 4	−0.035
3178.973	3179.022	4 1 3	3 1 2	−0.049
3193.963	3194.025	4 2 2	3 2 1	−0.062
3208.187	3208.229	5 1 4	4 1 3	−0.042

our *ab initio* calculations reproduce the H_3^+ energy levels with a standard deviation very similar to that given by the fitted DPT surface and that levels which are relatively poorly reproduced in our present calculations are also those for which DPT gives poorer results. In particular this is true for levels of the $\nu_1+2\nu_2$ states which were originally assigned by Dinelli *et al.*[43] from the hot band data of Oka and co-workers.[47,48] These findings are consistent with the assumption that the main residual problem with our calculations is the treatment of the nonadiabatic correction to the BO approximation which, of course, cannot be properly modeled using a single potential-energy function.

We suspect, given the excellence of the *ab initio* electronic structure data that these calculations are based on, it would be difficult to greatly improve on these results *ab initio* without using a significantly more complicated model for the nonadiabatic effects. Besides BO breakdown there are other terms which might be important at the sub $0.1\,cm^{-1}$

TABLE V. H_3^+ energy levels in cm^{-1} relative to the $J=0$ ground state. E_{calc} are the results of this work, E_{DPT} are due to Dinelli *et al.* (Ref. 43) and E_{obs} are derived from experiment (see Ref. 43). Δ is obs−our calc. A fuller tabulation can be found in the electronic archive (Ref. 33).

$\nu_1\nu_2^l$	J	G	U	E_{calc}	E_{DPT}	E_{obs}	Δ
00^0	1	1	0	64.1248	64.126	64.126	⋯
00^0	1	0	0	86.9683	86.963	86.963	⋯
01^1	1	2	1	2548.1305	2548.176	2548.169	0.039
01^1	1	1	1	2609.5170	2609.552	2609.557	0.040
01^1	1	0	−1	2616.6567	2616.694	2616.648	−0.008
10^0	1	1	0	3240.8468	3240.744	3240.735	−0.111
10^0	1	0	0	3263.2301	3263.122	3263.006	−0.230
02^0	1	1	0	4842.5900	4842.567	4842.573	−0.017
02^0	1	0	0	4870.3388	4870.312	4870.242	−0.097
02^0	1	0	0	4870.3388	4870.312	4870.242	−0.097
02^2	1	3	2	4994.8507	4994.829	4994.832	−0.018
02^2	1	2	2	5087.6602	5087.626	5087.622	−0.038
02^2	1	1	2	5125.3383	5125.301	5125.313	−0.025
11^1	1	2	1	5584.1709	5584.235	5584.256	−0.025
11^1	1	1	1	5640.4473	5640.503	5640.486	0.039
11^1	1	0	−1	5644.6814	5644.745	⋯	
20^0	1	1	0	6323.0017	6323.283	⋯	
20^0	1	0	0	6345.0081	6345.284	⋯	
03^1	1	2	1	7046.9693	7046.854	7046.859	−0.110
03^1	1	0	−1	7083.2190	7083.095	⋯	
03^1	1	1	1	7103.1990	7103.078	7103.090	−0.109
03^3	1	4	3	7325.3785	7325.514	⋯	
03^3	1	3	3	7381.1558	7381.347	⋯	
03^3	1	2	3	7572.1611	7572.244	⋯	
12^0	1	1	0	7839.7435	7840.562	⋯	
12^0	1	0	0	7857.6292	7858.509	⋯	
12^2	1	3	2	7872.1364	7872.971	⋯	
12^2	1	2	2	7958.3098	7959.172	⋯	
12^2	1	1	2	7988.9721	7989.897	⋯	
21^1	1	2	1	8519.0331	8520.304	⋯	
21^1	1	1	1	8571.9037	8573.222	⋯	
21^1	1	0	1	8573.4696	8574.839	⋯	
00^0	2	2	0	169.2915	169.302	169.311	0.020
00^0	2	1	0	237.3682	237.359	237.356	−0.012
01^1	2	3	1	2614.2276	2614.283	2614.275	0.047
01^1	2	2	1	2723.9419	2723.971	2723.970	0.029
01^1	2	1	−1	2755.5402	2755.577	2755.559	0.019
01^1	2	1	1	2790.3263	2790.352	2790.330	0.004
01^1	2	0	1	2812.8440	2812.869	2812.843	−0.001
10^0	2	2	0	3343.2385	3343.146	3343.195	−0.043
10^0	2	1	0	3409.9427	3409.832	3409.823	−0.120
02^0	2	2	0	4942.7472	4942.733	4942.719	−0.028
02^0	2	1	0	5023.4992	5023.470	5023.459	−0.040
02^2	2	4	2	5032.4035	5032.399	5032.400	−0.004
02^2	2	3	2	5181.2147	5181.189	5181.184	−0.030
02^2	2	2	2	5266.4797	5266.435	5266.427	−0.052
02^2	2	0	2	5286.9580	5286.920	5286.895	−0.063
02^2	2	1	2	5305.0164	5304.969	5304.966	−0.050
11^1	2	3	1	5653.9361	5654.009	5653.983	0.047
11^1	2	2	1	5755.9587	5756.008	5756.063	0.104
11^1	2	1	−1	5778.9399	5779.009	5778.986	0.046
11^1	2	1	1	5815.8179	5815.862	5815.857	0.039
11^1	2	0	1	5835.3011	5835.345	5835.225	−0.076
20^0	2	2	0	6422.6758	6422.972	⋯	
20^0	2	1	0	6488.2490	6488.531	⋯	
03^1	2	3	1	7122.6770	7122.635	7122.638	−0.039
03^1	2	1	−1	7208.4654	7208.350	7208.337	−0.128
03^1	2	2	1	7235.8426	7235.725	7235.761	−0.083
03^1	2	1	1	7301.5250	7301.438	7301.424	−0.101
03^1	2	0	1	7328.3377	7328.244	7328.119	−0.218
03^3	2	5	3	7368.9322	7368.995	⋯	
03^3	2	4	3	7514.6723	7514.820	⋯	
00^3	2	1	3	7702.9887	7703.345	⋯	
03^3	2	2	3	7752.0014	7752.085	7751.836	−0.165
03^3	2	3	3	7758.9880	7759.016	7758.878	−0.110
12^2	2	4	2	7914.5711	7915.369	⋯	
12^0	2	2	0	7963.2742	7963.926	⋯	
12^0	2	1	0	8013.4771	8014.294	⋯	
12^2	2	3	2	8056.8704	8057.661	8057.335	0.465
12^2	2	2	2	8135.2052	8136.059	⋯	
12^2	2	0	2	8141.4552	8142.467	⋯	
12^2	2	1	2	8167.6239	8168.538	⋯	
21^1	2	3	1	8589.5143	8590.737	⋯	
21^1	2	2	1	8687.4849	8688.750	⋯	
21^1	2	1	−1	8703.0024	8704.420	⋯	
21^1	2	1	1	8743.3275	8744.640	⋯	
21^1	2	0	1	8760.4418	8761.792	⋯	
00^0	3	3	0	315.3353	315.351	315.342	0.007
00^0	3	2	0	428.0315	428.024	428.039	0.007
00^0	3	1	0	494.7973	494.771	494.774	−0.023
00^0	3	0	0	516.9207	516.885	516.879	−0.042
01^1	3	4	1	2719.4145	2719.488	2719.466	0.042
01^1	3	3	1	2876.8132	2876.848	2876.839	0.026
01^1	3	2	−1	2931.3321	2931.380	2931.386	0.054
01^1	3	2	1	2992.4228	2992.443	2992.467	0.044
01^1	3	1	−1	3002.8901	3002.909	3002.897	0.007
01^1	3	0	−1	3025.9618	3025.965	3025.940	−0.022
01^1	3	1	1	3063.4774	3063.481	3063.476	−0.001
10^0	3	3	0	3485.3835	3485.308	3485.280	−0.103
10^0	3	2	0	3595.8505	3595.744	3595.773	−0.077
10^0	3	1	0	3661.2187	3661.090	3661.077	−0.141
10^0	3	0	0	3682.8684	3682.730	3682.610	−0.258
02^0	3	3	0	5078.9349	5078.933	5078.925	−0.010
02^2	3	5	2	5105.2679	5105.284	5105.311	0.043
02^0	3	2	0	5210.8302	5210.794	5210.797	−0.033
02^0	3	1	0	5282.3792	5282.315	5282.299	−0.078
02^2	3	4	2	5299.2553	5299.233	5299.249	−0.006
02^0	3	0	0	5305.6346	5305.583	5305.608	−0.026
02^2	3	3	2	5431.1736	5431.118	5431.119	−0.055
02^2	3	1	−2	5486.4840	5486.458	5486.447	−0.037
02^2	3	2	2	5533.7950	5533.738	5533.747	−0.048
02^2	3	0	2	5567.4027	5567.403	5567.370	−0.033
02^2	3	1	2	5573.8250	5573.767	5573.754	−0.071
11^1	3	4	1	5764.7880	5764.873	5764.849	0.061
11^1	3	3	1	5910.0479	5910.105	5910.079	0.029
11^1	3	2	−1	5949.3658	5949.454	5949.352	−0.014
11^1	3	2	1	6015.9046	6015.945	6015.990	0.085
11^1	3	1	−1	6023.7099	6023.772	6023.755	0.045
11^1	3	0	−1	6047.4949	6047.543	6047.424	−0.070
11^1	3	1	1	6080.9447	6080.969	6080.965	0.020
20^0	3	3	0	6560.9737	6561.293	⋯	
20^0	3	2	0	6669.5919	6669.886	⋯	
20^0	3	1	0	6733.7638	6734.048	⋯	
20^0	3	0	0	6754.9818	6755.282	⋯	
03^1	3	4	1	7229.8922	7229.819	⋯	
03^1	3	2	−1	7362.2861	7362.213	7362.221	−0.065
03^1	3	3	1	7394.1063	7394.007	⋯	
03^3	3	6	3	7418.4465	7418.485	7418.421	−0.025
03^1	3	1	−1	7460.1394	7460.014	⋯	
03^1	3	2	1	7498.1707	7498.056	⋯	
03^1	3	0	−1	7525.7318	7525.654	⋯	
03^1	3	1	1	7597.1284	7597.114	⋯	
03^3	3	5	3	7659.5443	7659.577	⋯	
03^3	3	4	3	7796.5703	7796.715	7796.601	0.031
03^3	3	3	3	7854.3313	7854.569	7854.413	0.082
03^3	3	0	3	7866.1204	7866.782	7866.287	0.167
03^3	3	1	3	7977.8011	7978.186	⋯	
03^3	3	2	3	7991.1503	7991.928	⋯	
12^0	3	5	0	8017.8451	8017.963	8017.719	−0.126
12^0	3	3	0	8138.8933	8139.345	8139.053	0.160
12^2	3	4	2	8176.4463	8177.246	⋯	

TABLE V. (*Continued.*)

$\nu_1\nu_2^l$	J	G	U	E_{calc}	E_{DPT}	E_{obs}	Δ
12^0	3	2	0	8220.5622	8221.193	⋯	
12^0	3	1	0	8259.8055	8260.620	⋯	
12^0	3	0	0	8274.3487	8275.225	⋯	
12^2	3	3	2	8301.5470	8302.413	8302.090	0.543
12^2	3	1	−2	8334.5939	8335.708	⋯	
12^2	3	2	2	8399.9457	8400.798	⋯	
12^2	3	0	2	8424.8200	8425.805	8425.297	0.477

level, such as the radiative correction. Bishop and Cheung[19] studied this effect *ab initio* for H_2 and found that it altered the vibrational spacings by $\sim 0.02\,\text{cm}^{-1}$. This is probably too small to worry about in the context of H_3^+.

It is unlikely that the small errors given by our present comparisons will extend to studies involving either more highly excited vibrational states or high rotational states. Moss and Bunker[17] show that scaling the vibrational mass accounts for some vibrational nonadiabatic effects, but suggest that the scaling should itself be a function of R. Such an approach can be identified in the very detailed calculations performed by Schwartz and Le Roy,[20] who used five parameters to represent the vibrational reduced mass for each isotopomer of hydrogen. It would be surprising if the use of a constant scaled vibrational mass would give good results for highly excited vibrational states which sample a large range of coordinate values.

Our calculations do not include any allowance for nonadiabatic effects in the rotational motion. As argued above, there are reasons for suspecting that such effects might be relatively small in H_3^+, nonetheless inspection of the errors shown in our calculations suggest some systematic variations with J. We will study higher J states and associated nonadiabatic effects in a future work.

IV. CONCLUSIONS

We have performed first principles rotation–vibration calculations on H_3^+ and its isotopomers. These calculations used the very high accuracy electronic structure calculations data of Cencek *et al.*;[13] the accuracy of our results is a testimony to the accuracy of these electronic structure calculations.

Using Cencek *et al.* data we have been able to test various levels of approximation for computing vibration–rotation spectra. As was known previously,[11] calculations performed entirely with the BO approximation give frequencies 1 cm^{-1} or more in error for the H_3^+ system. Inclusion of the adiabatic correction to the Born–Oppenheimer (BO) approximation, sometimes also known as the BO diagonal correction, reduces the errors to a few tenths of cm^{-1}.[11,12,14] Modeling nonadiabatic corrections to the BO approximation by using different reduced masses for vibrational and rotational motion reduces these errors still further: To a few hundredths of cm^{-1}. However, using different vibrational and rotational masses also introduces an extra term into the Hamiltonian used here. This term, and similar ones we would expect to arise in other internal coordinate bent molecule Hamiltonians, is found to be important for obtaining accurate results for rotationally excited molecules. Altogether we have achieved near spectroscopic accuracy from first principles for this important benchmark system.

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