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# Non-Born-Oppenheimer correction to the $H_3{}^+$ potential from experimental data

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The spectrum of $D_3{}^+$ is analyzed using a spectroscopically determined effective $H_3{}^+$ potential [B. M. Dinelli, S. Miller, and J. Tennyson, J. Mol. Spectrosc. **163**, 71 (1994)] and an accurate *ab initio* potential [G. C. Lie and D. Frye, J. Chem. Phys. **96**, 6784 (1992)]. Calculations suggest that the major error in the potential of Lie and Frye is due to the Born-Oppenheimer approximation. $D_3{}^+$ spectroscopic data are used to construct both Born-Oppenheimer and mass-dependent adiabatic surfaces for the $H_3{}^+$ system by fitting only one parameter. These surfaces reproduce the fundamental rovibrational transitions of $H_3{}^+$ and $D_3{}^+$ to within 0.03 $\text{cm}^{-1}$. An accurate adiabatic surface has not previously been determined for a polyatomic molecule.

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The interpretation of nearly all molecular processes relies on potential energy surfaces which govern the motions of the interacting atoms. Yet the very existence of these surfaces is an approximation, based on the separation of the fast electronic and slow nuclear motion, generally called the Born-Oppenheimer (BO) approximation. Quantifying the accuracy of this approximation thus has implications for many areas of chemical physics.

That the BO approximation might fail is, in general, only considered when potential energy curves undergo (avoided) crossings. Mass considerations show that the BO is least reliable for hydrogenic species. For diatomic molecules, early experimental determinations of non-BO effects, for example Refs. [1] and [2], have been superseded by theoretical work which has quantified these effects for the diatomic $H_2$ and $H_2{}^+$ systems (see Refs. [3] and [4] and references therein). Conversely for polyatomic molecules only relatively crude [self consistent field (SCF level)] estimates of the BO diagonal correction have been calculated for a number of species [5, 6].

Recently, Dinelli *et al.* (DMT) [7] used high resolution spectroscopic data to determine an effective $H_3{}^+$ potential which reproduced their dataset of 243 energy levels up to 9000 $\text{cm}^{-1}$ with a standard deviation, $\sigma$, of only 0.053 $\text{cm}^{-1}$. Calculations on the isotopomers $H_2D^+$ and $D_2H^+$ forced DMT to conclude that their potential was better than the BO approximation. DMT started their $H_3{}^+$ potential determination from two accurate, *ab initio*, BO potentials due to Meyer *et al.* (MBB) [8] and Lie and Frye (LF) [6]. Comparison of the electronic structure calculations [8, 9] underlying these potentials with a quantum Monte Carlo determination of the electronic energy at the equilibrium structure [10] suggests that MBB's potential, which has been extensively used to assign spectra of $H_3{}^+$ [11], is about 164 $\text{cm}^{-1}$ above the BO limit but in the case of LF this error is only 9 $\text{cm}^{-1}$.

In this paper, we combine LF's BO potential and DMT's effective potential to determine BO and mass dependent adiabatic potentials for the $H_3{}^+$ system. This is done by simultaneously considering available spectroscopic data for both $H_3{}^+$ and $D_3{}^+$. We believe that a mass-dependent adiabatic surface has not previously been accurately determined for any polyatomic system. Of course these potentials provide a means of predicting and hence assigning the many unassigned transitions in this ion (see, for example, Table VI of Ref. [13]); they also provide the means of calculating partition functions and other temperature sensitive thermodynamic data of interest to astronomers and others (e.g., Ref. [12]). However, more generally the potentials presented here provide a target for *ab initio* theory. Recent calculations have obtained absolute BO energies for $H_3{}^+$ accurate to better than 0.2 $\text{cm}^{-1}$ [10, 14] and a proper treatment of non-BO effects does not appear too distant.

Generalizing from Schwartz and Le Roy [3] we write the effective potential for $H_3{}^+$ isotopomer $i$ with reduced mass $\mu_i$ as

$$V_i(\underline{R}) = V_{\rm BO}(\underline{R}) + \frac{1}{\mu_i}\Delta V_{\rm ad}(\underline{R}), \tag{1}$$

where $\underline{R}$ represents the three interparticle distances. We have only considered the adiabatic correction, $\Delta V_{\rm ad}$, to the BO potential, $V_{\rm BO}$, as this is known to be the dominant non-BO term [3, 4].

As a starting point we assume that LF's potential, $V_{\rm LF}$, represents the *exact* BO potential for $H_3{}^+$ and its isotopomers, and that DMT's potential, $V_{\rm DMT}$, represents the exact effective potential for $H_3{}^+$. In this case, the adiabatic correction is given by

$$\Delta V_{\rm ad}(\underline{R}) = \mu_{H_3{}^+}\,[V_{\rm DMT}\underline{R}) - V_{\rm LF}(\underline{R})] \tag{2}$$

and the effective potential for $D_3{}^+$ by

$$V_{D_3{}^+}(\underline{R}) = V_{\rm LF}(\underline{R}) + \frac{\mu_{H_3{}^+}}{\mu_{D_3{}^+}}\,[V_{\rm DMT}(\underline{R}) - V_{\rm LF}(\underline{R})]\,. \tag{3}$$

Although the reduced masses have not been unambigu-

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ously defined, all sensible definitions give a ratio of $m_H/m_D$.

Starting from this potential we have performed a series of rovibrational calculations on $D_3^+$ using the TRIATOM computer program suite [15] and, as there is only experimental data for the lowest two vibrational states, the smaller basis set is defined by DMT. The $D_3^+$ potential of (3) gives a value of 1834.655 $cm^{-1}$ for the $\nu_2$ fundamental compared to 1834.67 $cm^{-1}$ determined experimentally [16]; significantly better than 1834.86 $cm^{-1}$ obtained using DMT's potential. Furthermore, comparison of our calculations with the observed transitions of the $D_3^+$ fundamental band shows that, for low rotational levels, $J \leq 4$, these are reproduced by the potential with $\sigma \approx 0.05$ $cm^{-1}$ compared to $\sigma \sim 0.2$ $cm^{-1}$ using DMT's potential.

Superficially, this is a very satisfactory situation as we have constructed an effective potential which reproduces the known $H_3^+$ and $D_3^+$ data to the same accuracy. However, this is too simplistic as most of the error in DMT's $H_3^+$ fit comes from the levels of the second overtone band, $3\nu_2$. Indeed DMT's potential reproduces the rotational levels of the $H_3^+$ vibrational with $J \leq 8$ for the ground state with $\sigma = 0.014$ $cm^{-1}$ and the $\nu_2$ bending state with $\sigma = 0.026$ $cm^{-1}$. Moreover, our results for $D_3^+$ displayed a strong systematic error of $0.05 \pm 0.01$ $cm^{-1}$ for low $J$ which worsened to $\sim 0.1$ $cm^{-1}$ for $J = 5, 6$.

Clearly, LF's BO potential is not exact. Assuming that we should be able to reproduce the $\nu_2$ levels of $D_3^+$ to an accuracy similar to the equivalent levels in $H_3^+$, we can estimate the degree to which DMT's potential is correcting for errors in LF's BO potential. To do this we write

$$V_i(\underline{R}) = V_{\rm LF}(\underline{R}) + \frac{\mu_{{\rm H}_3^+} + \alpha(\mu_i - \mu_{{\rm H}_3^+})}{\mu_i} \times [V_{\rm DMT}(\underline{R}) - V_{\rm LF}(\underline{R})], \quad (4)$$

where $i$ labels the isotopomer. The parameter $\alpha$ is zero if the effective potential has the form of Eq. (3) and unity if the effective potential is given by $V_{\rm DMT}$ for all isotopomers.

A trial and error investigation showed that values of $\alpha$ in the range 0.16 – 0.20 satisfactorily reproduce the observed [16] bending fundamental transitions of $D_3^+$. For $\alpha = 0.20$ and the 89 available transitions (which involve $J \leq 8$) [16], the ground state combination differences are reproduced with $\sigma = 0.015$ $cm^{-1}$ and the transition frequencies with $\sigma = 0.028$ $cm^{-1}$. These standard deviations now completely mirror those for $H_3^+$. This suggests that only about 20% of the change to the LF potential introduced by DMT's fit of the $H_3^+$ spectroscopic data was to correct the BO behavior of $V_{\rm LF}$.

As a test of this procedure we used MBB's potential to represent the exact BO potential instead of LF's. In this case, the optimal value of $\alpha$ was about 0.9 suggesting that unlike LF, MBB's potential is still a long way from the true BO potential for the system.

Both $V_{\rm LF}$ and $V_{\rm DMT}$ were expressed using the same functional form

$$V = \sum_{n,m,k} V_{n,2m,3k} S_a^n S_e^{2m+3k} \cos(3k\phi); \qquad n + 2m + 3k \leq 7, \quad (5)$$

where the symmetry coordinates are given by

$$S_a = (\tilde{R}_{12} + \tilde{R}_{23} + \tilde{R}_{31})/\sqrt{3}, \quad (6)$$

$$S_x = (2\tilde{R}_{12} - \tilde{R}_{23} - \tilde{R}_{31})/\sqrt{6} = S_e \cos(\phi), \quad (7)$$

$$S_y = (\tilde{R}_{23} - \tilde{R}_{31})/\sqrt{2} = S_e \sin(\phi), \quad (8)$$

and the transformed atom-atom distances, $\tilde{R}$, are related to the actual atom-atom distances by

$$\tilde{R} = \left[1 - \exp\left(-\beta \frac{R - R_e}{R_e}\right)\right] \beta. \quad (9)$$

We use the functional form (5) for both $V_{\rm BO}$ and $\Delta V_{\rm ad}$ which can be expressed as

$$V_{\rm BO} = V_{\rm LF} + \alpha(V_{\rm DMT} - V_{\rm LF}), \quad (10)$$

$$\Delta V_{\rm ad} = \mu_{{\rm H}_3^+}(1 - \alpha)(V_{\rm DMT} - V_{\rm LF}). \quad (11)$$

Table I presents the parameters determined using $\alpha = 0.20$.

The difference between our $V_{\rm BO}$ and $V_{\rm LF}$ gives some measure of the quality of LF's potential. It must, however, be remembered that our "BO" potential will include contributions from the relativistic and radiative corrections which are also mass independent. By comparison with theoretical work on $H_2^+$ and its isotopomers [4, 17], we estimate that the relativistic and radiative contributions to the transition we consider here are $\sim$+0.03 $cm^{-1}$ and $\sim$−0.01 $cm^{-1}$, respectively, and that the terms should partially cancel. Again, by comparison [3] one would expect the adiabatic correction, which affects mass-dependent parts of the effective potentials, to be considerably smaller. Probably more serious is that in the absence of more extensive $D_3^+$ spectroscopic data we

TABLE I. Surfaces for the $H_3^+$ system: $V_{\rm BO}$ is the Born-Oppenheimer potential and $\Delta V_{\rm ad}$ the adiabatic correction. The constants $V_{n,2m,3k}$ for Eq. (5) are in $\mu$hartree. Constants not given were set to LF's values [6] for $V_{\rm BO}$ and zero for $\Delta V_{\rm ad}$.

| $n$ | $2m$ | $3k$ | $V_{\rm BO}$ | $\mu_{{\rm H}_3^+}^{-1}\Delta V_{\rm ad}$ |
|---|---|---|---:|---:|
| 1 | 0 | 0 | -20.655 | -24.139 |
| 2 | 0 | 0 | 204508.705 | -417.898 |
| 0 | 2 | 0 | 266515.460 | 132.852 |
| 3 | 0 | 0 | -40094.020 | 536.039 |
| 1 | 2 | 0 | -214970.453 | 3380.429 |
| 0 | 0 | 3 | 2137.371 | 103.604 |
| 2 | 2 | 0 | 144602.610 | -10282.800 |
| 1 | 0 | 3 | 92473.619 | -2454.804 |
| 0 | 4 | 0 | 45221.564 | -1302.224 |
| 3 | 0 | 3 | 76616.632 | 12316.009 |
| 0 | 6 | 0 | 15957.859 | 3472.035 |

have been forced to assume that the correction to LF's BO potential and $\Delta V_{\rm ad}$ have the same shape.

It is noteworthy that MBB's best *ab initio* BO potential actually gives very good estimates for the $\nu_1$ stretching fundamentals of $H_3{}^+$, $H_2D^+$ and $D_2H^+$, whereas LF's potential is 4.5 $\rm cm^{-1}$ for $\nu_1$ of $H_3{}^+$. Conversely, this and DMT's work shows that no reasonable BO potential can reproduce the bending fundamentals of $H_3{}^+$ and its isotopomers. This suggests that $V_{\rm BO}$ and $\Delta V_{\rm ad}$ should indeed behave differently for different modes and in particular that $\Delta V_{\rm ad}$ is larger for bending than stretching motion. For the case of diatomics, much attention has focussed on the behavior of equilibrium bondlength with isotopic substitution [1, 2]. In our parametrization this behavior is carried by the $V_{1,0,0}$ potential term. So far, we have not treated this term differently from others in the potential expansion.

In fact, our non-BO potential gives significantly larger residues for the higher rotational levels of both $H_3{}^+$ and $D_3{}^+$, which suggests that it may be possible to extract further information on $V_{\rm BO}$ and $\Delta V_{\rm ad}$ from these system. However, there is a much larger body of data available for the mixed isotopomers [18–21] which should clearly be used in any fit. For these systems, as shown by DMT, $\Delta V_{\rm ad}$ must contain terms with less than $C_{3v}$ symmetry. We are presently determining these terms and the results will be reported elsewhere.

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[1] P.R. Bunker, J. Mol. Spectrosc. **5**, 478 (1972).
[2] J.K.G. Watson, J. Mol. Spectrosc. **45**, 99 (1973).
[3] C. Schwartz and R.J. Le Roy, J. Mol. Spectrosc. **121**, 420 (1987).
[4] R.E. Moss, Mol. Phys. **78**, 371 (1993).
[5] N.C. Handy, Y. Yamaguchi, and H.F. Schaefer III, J. Chem. Phys. **84**, 4481 (1986).
[6] G.C. Lie and D. Frye, J. Chem. Phys. **96**, 6784 (1992).
[7] B.M. Dinelli, S. Miller, and J. Tennyson, J. Mol. Spectrosc. **163**, 71 (1994).
[8] W. Meyer, P. Botschwina, and P.G. Burton, J. Chem. Phys. **84**, 891 (1986).
[9] D. Frye, A. Preiskorn, G.C. Lie, and E. Clementi, J. Chem. Phys. **92**, 4230 (1990).
[10] J.B. Anderson, J. Chem. Phys. **96**, 3702 (1992).
[11] L. Kao, T. Oka, S. Miller, and J. Tennyson, Astrophys. J. Suppl. **77**, 317 (1991).
[12] K.S. Sidhu, S. Miller, and J. Tennyson, Astron. Astrophys. **255**, 453 (1992).
[13] L.-W. Xu, M. Rösslein, C.M. Gabrys, and T. Oka, J. Mol. Spectrosc. **153**, 726 (1992).
[14] R. Rohse, W. Klopper, and W. Kutzelnigg, J. Chem. Phys. **99**, 8830 (1993).
[15] J. Tennyson, S. Miller, and C.R. Le Sueur, Comput. Phys. Commun. **75**, 339 (1993).
[16] J.K.G. Watson, S.C. Foster, and A.R.W. McKellar, Can. J. Phys. **65**, 38 (1987).
[17] M.H. Howells and R.A. Kennedy, J. Chem. Soc. Faraday Trans. **86**, 3495 (1990).
[18] T. Amano and J.K.G. Watson, J. Chem. Phys. **81**, 2869 (1984).
[19] S.C. Foster, A.R.W. McKellar, I.R. Peterkin, J.K.G. Watson, F.S. Pan, M.W. Crofton, R.S. Altman, and T. Oka, J. Chem. Phys. **84**, 91 (1985).
[20] K.G. Lubic and T. Amano, Can. J. Phys. **62**, 1886 (1984).
[21] S.C. Foster, A.R.W. McKellar, and J.K.G. Watson, J. Chem. Phys. **85**, 664 (1986).