13 January 1995

ELSEVIER

Chemical Physics Letters 232 (1995) 295-300

CHEMICAL
PHYSICS
LETTERS

Ab initio ro-vibrational levels of H_3^+ beyond the Born–Oppenheimer approximation

Bianca M. Dinelli [a], C. Ruth Le Sueur [a], Jonathan Tennyson [a], Roger D. Amos [b]

[a] *Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK*

[b] *University Chemical Laboratories, Lensfield Road, Cambridge CB2 1EW, UK*

Received 8 September 1994; in final form 26 October 1994

Abstract

The value of the adiabatic correction to the Born–Oppenheimer electronic energy is calculated as a function of geometry for H_3^+ using SCF wavefunctions. A mass-dependent adiabatic function is combined with the near-Born–Oppenheimer electronic structure calculations of Röhse, Kutzelnigg, Jaquet and Klopper and the rotation–vibration energy levels of H_3^+ and D_3^+ are calculated. The levels for H_3^+ are significantly better than any previous ab initio estimates but are less accurate than those obtained by recent spectroscopically determined effective H_3^+ potentials. The adiabatic correction is less important for the heavier D_3^+. For both ions rotational levels are obtained to near experimental accuracy. Small, systematic shifts in the vibrational bands may be attributable to residual errors in the Born–Oppenheimer potential.

1. Introduction

The rotation–vibration spectrum of H_3^+ has excited much interest since its original detection by Oka [1], both because of its fundamental nature and its astrophysical importance, see recent reviews by Oka [2] and McNab [3]. The electronic simplicity of H_3^+ makes it a natural target for ab initio electronic structure calculations; Anderson [4] tabulates the results of 43 electronic structure calculations on this system.

Very recently Röhse et al. [5] have published an ab initio H_3^+ potential energy surface of unprecedented accuracy for a triatomic molecule. This surface was constructed using wavefunctions which explicitly included the electron–electron distance and is within about 1 cm^{-1} of the Born–Oppenheimer (BO) limit over its entire range. Nuclear motion calculations performed by Röhse et al. suggest that the Born–Oppenheimer approximation itself was the major source of error when comparisons were made with vibrational band origins inferred from experiment. Similar conclusions concerning other higher accuracy potential energy surfaces have been made previously [6-8].

As far as we know, no-one has attempted to calculate ab initio rotation–vibration energy levels for a triatomic molecule beyond the Born–Oppenheimer approximation for what is essentially a single surface problem. Several such studies have been performed on molecular hydrogen [9-11]. These studies show that the major correction to the BO approximation is due to the mass-dependent adiabatic correction, ΔV_{ad}. H_3^+, which has no low-lying electronic excited states, is expected to be similar; a view supported by previous ab initio estimates [8].

Handy et al. [12] calculated the adiabatic correction, or BO diagonal correction as they called it, for a number of molecules, including H_5^+ but not H_3^+,

0009-2614/95/$09.50
SSDI 0009-2614(94)01301-2

at their equilibrium geometries. The purpose of that study was to estimate the contribution of this leading non-BO term to the dissociation, ionisation or electronic excitation energy for the systems in question. Handy et al. found that electronic wavefunctions computed within the self consistent field (SCF) approximation were perfectly adequate for this purpose. Furthermore Handy et al. showed that, using standard analytic derivative theory, it was relatively straightforward to compute the adiabatic correction at the SCF or MCSCF level.

In this Letter, we follow methodology advocated by Handy et al. and compute the adiabatic correction for H_3^+ as a function of geometry. This correction is then combined with the BO potential energy surface of Röhse et al. [5] and the rotation-vibration energy levels of H_3^+ and D_3^+ computed. The resulting levels are the most accurate ab initio estimates obtained for these systems.

2. Electronic calculations

Following Handy et al. [12], the Born–Oppenheimer diagonal correction is given by the expression

$$\langle\Psi| -\frac{1}{2}\sum_I \frac{1}{M_I}\nabla_I^2|\Psi\rangle = \sum_I \frac{1}{2M_I}\langle\nabla_I\Psi|\nabla_I\Psi\rangle. \qquad (1)$$

The summation in (1) runs over all $3N$ nuclear coordinates and thus could contain a contribution from the translational motion of the molecule not included in more elaborate treatments of the adiabatic correction [9,13,14]. However these integrals are invariant to translations. Thus, for example, when we use this expression to repeat the calculation of Bardo and Wolfsberg [13], who used a much more complicated formalism which removes the effects of centre of mass motion in the adiabatic correction, we exactly reproduce their value of 103.35 cm^{-1} for the adiabatic correction of equilibrium H_3^+.

For a closed-shell SCF determinant each of the integrals $\langle\nabla_I\Psi|\nabla_I\Psi\rangle$ in (1) can be written in terms of the occupied molecular orbitals as

$$2\sum_i\langle\phi_i'|\phi_i'\rangle + 2\sum_i\sum_j\langle\phi_i|\phi_j'\rangle\langle\phi_j|\phi_i'\rangle, \qquad (2)$$

where the ϕ_i' are the derivatives with respect to a nuclear coordinate of the molecular orbitals ϕ_i. In terms of the basis set and molecular orbitals (MO) coefficients,

$$\phi_i = \sum_\mu c_{\mu i}\eta_\mu, \qquad (3)$$

and therefore

$$\phi_i' = \frac{\partial\phi_i}{\partial x} = \sum_\mu c_{\mu i}\frac{\partial\eta_\mu}{\partial x} + \sum_\mu \frac{\partial c_{\mu i}}{\partial x}\eta_\mu = \phi_i^x + \sum_r U_{ri}^x\phi_r, \qquad (4)$$

where the first term contains basis function derivatives and the second term contains the derivatives of the MO coefficients. After some manipulation the expression for the integral $\langle\nabla_I\Psi|\nabla_I\Psi\rangle$ becomes

$$\sum_i 2\langle\phi_i^x|\phi_i^x\rangle - \tfrac{1}{2}\sum_{ij}[\langle\phi_i|\phi_j^x\rangle - \langle\phi_j|\phi_i^x\rangle]^2 + \sum_{ri}[2(U_{ri}^x)^2 + 4\langle\phi_i^x|\phi_r\rangle U_{ri}^x], \qquad (5)$$

where in the summations i and j denote occupied orbitals, and r is any molecular orbital i.e. occupied or virtual. The coefficients U_{ri}^x are found by coupled perturbed Hartree-Fock (CPHF) theory [15] which is a standard technique found in many programs. The integrals $\langle\phi_i|\phi_j^x\rangle$ are related to derivatives of the overlap matrix and are easy to evaluate. The above formula has been implemented in the CADPAC [16] program, where it was convenient to evaluate the diagonal Born–Oppenheimer correction at the end of a calculation of the harmonic vibrational frequencies.

In order to decide which basis set to use, nine of the CADPAC library H-atom basis sets were used for a randomly selected asymmetric point geometry. These were STO3G, 3-21G, 6-31G, 6-31G*, 6-311G*, 6-31G extended, 3s2p, 6s3p and 6s3p1d. The results are summarised in Table 1. The 6s3p basis set was chosen as a reasonable compromise between speed and convergence. Calculations were then performed on the grid of 69 geometries used by Röhse et al. and originally designed by Meyer et al. [17].

Having computed the adiabatic correction at each nucleus as a function of geometry it is necessary to fit this to an appropriate function form. In the case

Table 1
The adiabatic or Born-Oppenheimer diagonal correction (BODC), in cm^{-1}, for H_3^+ as calculated using CADPAC for several library basis functions. CPU times in s are quoted for calculations performed on an IBM RS6000 250T. The calculations are for an arbitrary geometry for which the atom-atom distances are 2.6088, 2.6088 and 2.0877 a_0

Basis set	BODC	CPU time
STO3G	109.1137	1.77
3-21G	96.3240	3.38
6-31G	101.0601	5.41
6-31G*	96.8426	7.68
6-311G*	90.3571	11.17
6-31G ext	86.9070	20.32
3s2p	87.0285	21.05
6s3p	86.2358	118.21
6s3p1d	86.0286	308.69

considered here, where all three nuclei are the same, the effective potential for system i can be written as

$$V_i(\underline{Q}) = V_{\mathrm{BO}}(\underline{Q}) + \frac{1}{\mu_i}\Delta V_{\mathrm{ad}}(\underline{Q}), \tag{6}$$

where V_{BO} is the Born-Oppenheimer potential, $\underline{Q}$ are suitable internal coordinates and the reduced mass, μ_i, is $m/3$ where m is the appropriate nuclear mass.

$(1/\mu_i)\Delta V_{\mathrm{ad}}(\underline{Q})$ was expressed in the functional form used in previous fits to the ab initio data [5,8,17],

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

where the symmetry coordinates are given by

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

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

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

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

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

A least-squared fit to our computed points is given in Table 2. This fit reproduced our data with a standard deviation of 5×10^{-8} E_h (≈ 0.01 cm^{-1}).

Table 2
Fitted coefficients, μhartree, of the adiabatic correction to Born-Oppenheimer potential, $(1/\mu_i)\Delta V_{\mathrm{ad}}$, for H_3^+. The parameters β and R_e were fixed at Röhse et al.'s values of 1.30 and 1.6500 a_0 [5]

n	$2m$	$3k$	$V_{n,2m,3k}$
0	0	0	470.92
1	0	0	−161.49
2	0	0	34.42
0	2	0	220.86
3	0	0	−2.31
1	2	0	119.17
0	0	3	115.12
4	0	0	0.35
2	2	0	18.96
1	0	3	91.30
0	4	0	73.96
5	0	0	10.28
3	2	0	36.74
2	0	3	39.67
1	4	0	79.74
0	2	3	58.23
6	0	0	3.02
4	2	0	137.25
3	0	3	296.92
2	4	0	591.90
1	2	3	480.90
0	6	0	184.83
0	0	6	18.79
7	0	0	−11.55
5	2	0	36.93
4	0	3	402.85
3	4	0	774.94
2	2	3	1036.52
1	6	0	617.12
1	0	6	65.99
0	4	3	235.40

3. Results and discussion

This surface gives an adiabatic correction for equilibrium H_3^+ of 103.31 cm^{-1}. Using our procedure we obtain an adiabatic correction for H_2 at $R = 1.4$ a_0 of 101.22 cm^{-1} which can be compared with the accurate value of 115 cm^{-1} quoted by Kołos and Wolniewicz [9]. Thus the adiabatic correction to the dissociation energy of H_3^+ would appear to be about 2 cm^{-1}. H_3^+ and H_2 adiabatic corrections similar to ours are quoted by Lie and Frye [8]. However, they conclude that the adiabatic correction to the H_3^+ dissociation energy is ≈ 6 cm^{-1}. Röhse et al. [5] obtained a contribution to the dissociation energy of 16 cm^{-1}, but their H_3^+ adi-

Table 3
Comparison of rotation-vibration term values for H_3^+ in cm^{-1} for the Born-Oppenheimer (BO) potential of Röhse et al. [5] and adiabatic corrected potential of this work. ν gives the calculated band origin for each band. $\langle \delta E \rangle = \langle E_{obs} - E_{calc} \rangle$ is the average error and σ the standard deviation, both in cm^{-1}, in reproducing the n observed term values in that band

(ν_1, ν_2^ℓ)	n	V_{BO}			$V_{BO} + (1/\mu)\Delta V_{ad}$		
		ν	$\langle \delta E \rangle$	σ	ν	$\langle \delta E \rangle$	σ
$(0, 0^0)$	35	0.00	−0.532	0.626	0.00	0.015	0.018
$(0, 1^1)$	89	2521.59	−0.784	0.894	2521.58	−0.148	0.149
$(1, 0^0)$	14	3179.35	−1.483	1.500	3178.35	−0.078	0.081
$(0, 2^0)$	14	4778.39	−0.321	0.351	4778.58	−0.227	0.227
$(0, 2^2)$	62	4998.40	−1.007	1.116	4998.41	−0.361	0.367
$(1, 1^1)$	24	5555.49	−1.427	1.434	5554.62	−0.365	0.371
$(0, 3^1)$	12	7006.22	−0.199	0.237	7006.63	−0.458	0.460

abatic correction was only estimated from mass scaling effects. None of these corrections are sufficient to account for the discrepancy between theory and experiment for the H_3^+ dissociation energy [5].

Rotation-vibration energy levels were calculated for H_3^+ and D_3^+ using the TRIATOM program suite [18] and basis sets developed previously [6]. Nuclear masses from Schwartz and Le Roy [10] were used in all calculations which considered rotational levels up to $J = 9$.

For H_3^+ there are extensive lists of experimentally derived rotation-vibration energy levels ('term values' denoted E) available [19,20]. Detailed comparison with the 250 term values with $J \leqslant 9$ and undisputed assignments gives a clear picture of the quality of the potentials used. The results of these comparisons are summarized in Table 3.

Table 3 shows that calculations performed with the BO potential of Röhse et al. [5] are indeed very accurate, with errors of about 1 cm^{-1}. By comparison previous ab initio potentials typically gave an error of 3 cm^{-1} for the $3\nu_2^1$ band [20]. Inclusion of the adiabatic correction greatly improves the results, reducing typical errors to about 0.2 cm^{-1}. Furthermore, for the non-BO calculations, comparison of the absolute mean error, $| \langle E_{obs} - E_{calc} \rangle |$ and standard deviation, σ, for each band shows that these parameters never differ by more than 0.006 cm^{-1}. This means that each vibrational band shows a systematic error which is nearly independent of the rotational energy level occupied. This systematic behaviour will allow the missing term values in each band to be predicted with near experimental accuracy.

Although Amano et al. [21] have recently greatly extended the number of measured D_3^+ transition frequencies, there is still not a reliable set of D_3^+ term values for us to compare with. For comparison, therefore, we have computed frequencies for the 342 transitions between states with $J \leqslant 9$ tabulated by Amano et al. Combinational differences have also been used to analyse the level structures of the three vibrational bands about which there is most information: the vibrational ground state, ν_2^1 and $2\nu_2^2$.

Unsurprisingly, given the greater mass of D, the BO potential of Röhse et al. performs better for D_3^+ and reproduces these transitions with a standard deviation of only 0.148 cm^{-1}. Using the BO potential plus adiabatic correction, however, reduces this standard deviation to 0.102 cm^{-1}. In the course of this work we also performed calculations using the atomic masses, adjusted for the lost electron, which have been used recently in calculations performing fits to spectroscopic data [6,7,22]. This calculation gives excellent agreement with experiment and a standard deviation of only 0.049 cm^{-1} or one part in 40000 for a typical measured transition frequency.

Impressive as this result undoubtedly is, careful analysis suggests it is somewhat fortuitous. Our adiabatic corrected calculations give combination differences of near experimental accuracy and transition frequencies where the magnitude of the average error $| \langle \nu_{obs} - \nu_{calc} \rangle |$ and the standard deviation, σ, are nearly the same. Thus again our non-BO calculations are reproducing the rotational structure of the vibrational bands to very high accuracy, giving only a systematic shift in the band origins.

Table 4

Comparison of rotation–vibration transition frequencies and combinational differences for D_3^+ in cm^{-1}. Results are for the Born–Oppenheimer (BO) potential of Röhse et al. [5], adiabatic corrected potential of this work and the BO potential using atomic rather than nuclear masses. $\langle \delta\nu \rangle = \langle \nu_{obs} - \nu_{calc} \rangle$ is the average error in the transition frequency or combination difference and σ the standard deviation, both in cm^{-1}, in reproducing the n observed values for that band. Final standard deviations include results for 4 other bands also observed by Amano et al. [21]

	n	V_{BO}		$V_{BO} + (1/\mu)\Delta V_{ad}$		V_{BO}[a]	
		$\langle \delta\nu \rangle$	σ	$\langle \delta\nu \rangle$	σ	$\langle \delta\nu \rangle$	σ
transition frequencies							
$\nu_2^1 \leftarrow 0$	138	−0.177	0.183	−0.122	0.124	0.003	0.017
$2\nu_2^{0,2} \leftarrow 0$	115	−0.246	0.252	−0.206	0.210	0.055	0.070
$2\nu_2^{0,2} \leftarrow \nu_2^1$	77	−0.142	0.168	−0.062	0.085	0.047	0.090
combination differences							
ground state	99	−0.043	0.052	0.005	0.011	−0.006	0.011
ν_2^1	153	−0.046	0.055	0.007	0.014	−0.010	0.019
$2\nu_2^{0,2}$	177	−0.040	0.076	0.007	0.046	−0.004	0.058
all data			0.148		0.102		0.049

[a] Calculation performed using a mass of $(3M_D - m_e)/3$ per heavy particle.

Superficially the significantly better results for D_3^+ than H_3^+ would suggest that the major error in the H_3^+ calculations is still due to non-BO effects. However one must be careful as the D_3^+ measurements are dominated by the ground, ν_2^1 and $2\nu_2^2$ states for which the errors in the H_3^+ calculations are small. Furthermore the use of transition frequencies for D_3^+ rather than term values may lead to a systematic cancellation of errors as, for H_3^+ anyway, all the predicted band origins are systematically below the observed values.

Comparing the H_3^+ and D_3^+ results for the calculation including the adiabatic corrections, one notes that the systematic errors in the ν_2^1 and $2\nu_2^2$ term values/frequencies are similar in magnitude but slightly reduced for the heavier D_3^+ ion. This suggests that these are due to some mass-independent effect which, given the approximately 1 cm^{-1} error in the BO potential employed, may well be still caused by the underlying potential energy surface.

The rotation–vibration levels computed here are undoubtedly of an accuracy never previously achieved for a triatomic by ab initio calculation. However, the predictions remain not only less accurate than the observations, which is hardly surprising given the accuracy of high-resolution spectroscopy, but are also less accurate than results obtained using potentials derived from fits to spectroscopic data [6,7,22,23]. This may also appear unsurprising, but for H_2 ab initio non-BO calculations [10,11] have proved more accurate than attempts to derive effective H_2 potentials from the observed data. Our analysis suggests that more work is still required on the Born–Oppenheimer electronic potential energy surface before this situation can be achieved for H_3^+.

Finally we have not considered the mixed isotopomers H_2D^+ and D_2H^+, for which extensive experimental data is also available. For these systems the adiabatic correction no longer has D_{3h} symmetry and therefore the simple functional form used here is not sufficient. We are presently working on extending the above analysis to these ions; our results will be published elsewhere.

Acknowledgement

We would like to thank Professor N.C. Handy for encouraging us to perform these calculations and Dr. J.K.G. Watson for supplying results prior to publication. This work was supported by the UK Engineering and Physical Science Research Council.

References

[1] T. Oka, Phys. Rev. Letters 45 (1980) 531.

[2] T. Oka, Rev. Mod. Phys. 45 (1992) 1141.

[3] I.R. McNab, Advan. Chem. Phys. 89 (1994) 1.

[4] J.B. Anderson, J. Chem. Phys. 96 (1992) 3702.

[5] R. Röhse, W. Kutzelnigg, R. Jaquet and W. Klopper, J. Chem. Phys. 101 (1994) 2231.

[6] B.M. Dinelli, S. Miller and J. Tennyson, J. Mol. Spectry. 163 (1994) 71.

[7] J. Tennyson and O.L. Polyansky, Phys. Rev. A 50 (1994) 314.

[8] G.C. Lie and D. Frye, J. Chem. Phys. 96 (1992) 6784.

[9] W. Kołos and L. Wolniewicz, J. Chem. Phys. 41 (1964) 3663.

[10] C. Schwartz and R.J. Le Roy, J. Mol. Spectry. 121 (1987) 420.

[11] W. Kołos and J. Rychlewski, J. Chem. Phys. 98 (1993) 3960.

[12] N.C. Handy, Y. Yamaguchi and H.F. Schaefer III, J. Chem. Phys. 84 (1986) 4481.

[13] R.D. Bardo and M. Wolfsberg, J. Chem. Phys. 68 (1978) 2686.

[14] B.T. Sutcliffe, J. Chem. Soc. Faraday Trans. 89 (1993) 2321.

[15] J. Gerratt and I. M. Mills, J. Chem. Phys. 49 (1968) 1719.

[16] The Cambridge Analytic Derivatives Package (CADPAC), Issue 5, Cambridge 1992. A suite of quantum chemistry programs developed by R.D. Amos with contributions from I.L. Alberts, J.S. Andrews, S.M. Colwell, N.C. Handy, D. Jayatilaka, P.J. Knowles, R. Kobayashi, N. Koga, K.E. Laidig, P.E. Maslen, C.W. Murray, J.E. Rice, J. Sanz, E.D. Simandiras, A.J. Stone and M.-D. Su.

[17] W. Meyer, P. Botschwina and P.G. Burton, J. Chem. Phys. 84 (1986) 891.

[18] J. Tennyson, S. Miller and C.R. Le Sueur, Comput. Phys. Commun. 75 (1993) 339.

[19] L.-W. Xu, M. Rosslein, C.M. Gabrys and T. Oka, J. Mol. Spectry. 153 (1992) 726, and references therein.

[20] B.F. Ventrudo, D.T. Cassidy, Z.Y. Gou, S. Joo, S.S. Lee and T. Oka, J. Chem. Phys. 100 (1994) 6263.

[21] T. Amano, M-C. Chan, S. Civiš, A.R.W. McKellar, W.A. Majewski, D. Sadovski and J.K.G. Watson, Can. J. Phys., in press.

[22] J.K.G. Watson, Can. J. Phys. 72 (1994) 238.

[23] B.M. Dinelli, O.L. Polyansky and J. Tennyson, to be published.