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Spectroscopy of H_3^+ based on a new high-accuracy global potential energy surface

By Oleg L. Polyansky[1,2,*], Alexander Alijah[3], Nikolai F. Zobov[1], Irina I. Mizus[1], Roman I. Ovsyannikov[1], Jonathan Tennyson[2], Lorenzo Lodi[2], Tamás Szidarovszky[4] and Attila G. Császár[4]

[1] *Institute of Applied Physics, Russian Academy of Sciences, Ulyanov Street 46, Nizhny Novgorod 603950, Russia*
[2] *Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK*
[3] *Groupe de Spectrométrie Moléculaire et Atmosphérique, GSMA, UMR CNRS 7331, Université de Reims Champagne-Ardenne, Reims, France*
[4] *Laboratory of Molecular Structure and Dynamics, Institute of Chemistry, Eötvös University, 1518 PO Box 32, Budapest 112, Hungary*

The molecular ion H_3^+ is the simplest polyatomic and poly-electronic molecular system, and its spectrum constitutes an important benchmark for which precise answers can be obtained *ab initio* from the equations of quantum mechanics. Significant progress in the computation of the ro–vibrational spectrum of H_3^+ is discussed. A new, global potential energy surface (PES) based on *ab initio* points computed with an average accuracy of $0.01\,\mathrm{cm}^{-1}$ relative to the non-relativistic limit has recently been constructed. An analytical representation of these points is provided, exhibiting a standard deviation of $0.097\,\mathrm{cm}^{-1}$. Problems with earlier fits are discussed. The new PES is used for the computation of transition frequencies. Recently measured lines at visible wavelengths combined with previously determined infrared ro–vibrational data show that an accuracy of the order of $0.1\,\mathrm{cm}^{-1}$ is achieved by these computations. In order to achieve this degree of accuracy, relativistic, adiabatic and non-adiabatic effects must be properly accounted for. The accuracy of these calculations facilitates the reassignment of some measured lines, further reducing the standard deviation between experiment and theory.

Keywords: H_3^+; spectroscopy; potential energy surface; ro–vibrational calculations

1. Introduction

In a paper entitled ‘Quantum mechanics of many-electron systems’, Dirac [1, p. 714] famously wrote that ‘The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. It therefore becomes desirable that approximate practical methods of applying quantum mechanics

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*Author for correspondence (oleg@theory.phys.ucl.ac.uk).

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should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation'.

It is relevant to the present paper to summarize two developments since Dirac's seminal paper was published. First, the underlying physical laws have been altered slightly, mostly as a result of the development of quantum electrodynamics (QED). Second, many approximate methods have indeed been developed, taking advantage of the rapid development of computers. When these methods are applied to small (few-body) systems, they give very accurate results, rivalling the accuracy of the best measurements.

More approximate methods applicable to complex (many-body) systems give reasonable and highly useful but not highly accurate results when compared with experiments. It is one of the aims of molecular physics and quantum chemistry to develop new methods capable of providing better accuracy when applied to many-body systems. Quantum theory, in the form of non-relativistic quantum mechanics and of its QED extension, is arguably the most successful theory in the history of science. When applied to small quantum systems with less than about four particles, very accurate calculations are possible and, for selected physical properties, the agreement with experiment has reached eight or nine significant digits [2–6].

The hydrogen molecular ion H_2^+ and the hydrogen molecule H_2, along with their isotopologues, have received much attention, and recent studies including non-adiabatic and QED effects up to α^4 obtained ro–vibrational energy levels with accuracies of the order of 1 MHz (about $3\times10^{-5}\,\mathrm{cm}^{-1}$) all the way to dissociation [6–8]. However, such a global *ab initio* solution for any polyatomic system remains elusive; if, by complete solution, we mean obtaining all energy levels up to ionization or dissociation to a high accuracy, then no polyatomic system can be classified as solved.

There are at least two compelling reasons to try to find such solutions. First, attempts to find the limit of applicability of quantum mechanics as applied to ever larger systems remains an important scientific objective, as scientists always strive to find the limits of applicability of their best theories. Second, the ability to obtain accurate solutions for larger and larger systems is a major driving force for scientific developments, when the basic laws are already in place. In either case, the ability to provide a complete and accurate solution to polyatomic systems is an important and interesting challenge.

The simplest and most fundamental polyatomic system, H_3^+, is the subject of this issue and of this paper. The polyatomic nature of H_3^+ is the key here, as diatomic two-electron systems are very well characterized, and outstanding accuracy has been achieved globally for these systems. For the polyatomic H_3^+ system, our benchmark accuracy for ro–vibrational energy levels is set to $0.1\,\mathrm{cm}^{-1}$. For energies below the barrier to linearity, which lies at around $10\,000\,\mathrm{cm}^{-1}$, an accuracy of $0.1\,\mathrm{cm}^{-1}$ was first achieved semi-empirically by Dinelli *et al.* [9] and subsequently *ab initio* by Polyansky & Tennyson [10]. Further progress in reaching this accuracy globally, up to dissociation (about $35\,000\,\mathrm{cm}^{-1}$) or at least above the barrier to linearity, proved to be hard to achieve.

In the study by Pavanello *et al.* [11], the most recent steps towards the goal of achieving $0.1\,\mathrm{cm}^{-1}$ accuracy globally are described. This work not only prepared the way for ro–vibrational energy level predictions of the H_3^+ molecular ion with global accuracy of $0.01\,\mathrm{cm}^{-1}$, but may even lead to an improved accuracy of 0.01 cm^{-1}, as major components of energy level calculations—potential energy surface (PES) and adiabatic and relativistic corrections already have this increased accuracy, and only the corresponding QED and non-adiabatic corrections need still to be provided. Such improved accuracy would not only describe experimental spectroscopic lines within their observed widths, but would also allow automated assignment of experimental lines by simple comparison with an *ab initio* generated line list. This will finally provide the accuracy required to understand and interpret the rich and complicated [12] predissociation spectrum. The failure to explain this 30 year old spectrum recorded for such a fundamental and seemingly simple molecule is an embarrassment for molecular quantum theory.

This paper is organized as follows. The field of H_3^+ spectroscopy leading to the present work is reviewed in §2. A detailed account about the *ab initio* computation of the 42 000 energy points, with an accuracy of 0.01 cm^{-1} [11], used in this work is given by Pavanello & Adamowicz [13] elsewhere in this issue. In §3, we give details about a fit to these points leading to a global analytical form of the PES. In §4, we describe the nuclear motion computation of H_3^+ spectra. Comparison of our computed spectrum with previous measurements as well as the recent optical region experiments [11], described in detail by Petrignani *et al.* [14] elsewhere in this issue, is also given. We demonstrate that an accuracy of 0.1 cm^{-1} is achieved for the first time for all known lines of H_3^+, including optical lines that probe states well above the barrier to linearity. The prospects for further work resulting from this paper and the results presented by Pavanello *et al.* [11] are described in §5.

2. A historical perspective of the global H_3^+ potential energy surface

For quite some time, the *ab initio* H_3^+ PES due to Meyer *et al.* [15] (MBB) remained the most accurate H_3^+ PES and was used for many studies of the H_3^+ spectrum. Lie & Frye [16], performing Hylleraas configuration interaction (CI) calculations, went beyond the accuracy of these calculations and concluded, by comparison with experimental data, that further improvement would require the inclusion of the adiabatic correction. On the basis of their work, Dinelli *et al.* [9] constructed the first accurate semi-empirical surface. Their PES, which was obtained by adjusting some of the expansion coefficients of Lie and Frye, can be used to reproduce the observed energy levels with a standard deviation of about 0.05 cm^{-1}. At the about the same time, Röhse *et al.* [17] reported an MBB-type potential energy surface with microhartree accuracy obtained fully *ab initio* with the CISD-R12 method. The results of both papers pointed to the importance of going beyond the Born–Oppenheimer (BO) approximation if experimental accuracy was to be obtained. Tennyson & Polyansky [18] constructed the first accurate polyatomic adiabatic, i.e. beyond the BO surface from the empirical PES of Dinelli *et al.* and the BO PES of Lie and Frye. They demonstrated that the discrepancy between *ab initio* and experimental results was indeed due to adiabatic effects and reproduced D_3^+ data with a standard deviation of 0.03 cm^{-1} using their mass-dependent surface without any fitting to D_3^+ data.

Dinelli *et al.* [19] computed *ab initio* adiabatic corrections using the method of Handy *et al.* [20], see also Kutzelnigg [21]. Polyansky *et al.* [22] gave symmetry rules for this correction with respect to the different isotopologues of H_3^+ and calculated the adiabatic surfaces for all deuterated isotopologues of H_3^+ *ab initio*. On the basis of these *ab initio* surfaces, they constructed semi-empirical PESs for all isotopologues with close to experimental accuracy of about $0.01\,\mathrm{cm}^{-1}$ [23]. This accuracy, though obtained via the use of a semiempirical PES, still proved to be useful, as calculations based on this PES yielded assignments for 85 per cent of then unassigned H_3^+ lines [24].

The PES by Röhse *et al.* [17] was the basis for accurate ro–vibrational calculations for H_3^+ by Jaquet & Röhse [25] and Wolniewicz & Hinze [26] and for the isotopologues by Alijah *et al.* [27,28] and Alijah & Beuger [29]. The latter calculations yield transition frequencies close to experimental accuracy after applying empirical shifts to the vibrational band origins to account for non-BO (n-BO) effects.

These developments prepared the way for the very accurate and completely *ab initio* computation of the energy levels of all H_3^+ isotopologues. The main component missing was a high-accuracy, *ab initio* BO PES of H_3^+. Cencek *et al.* [30] recalculated the 69 MBB points with the method of exponentially correlated Gaussians [31] and obtained an accuracy of $0.02\,\mathrm{cm}^{-1}$, an improvement by one order of magnitude. They also calculated, to the same accuracy, the adiabatic and relativistic corrections at each grid point.

Polyansky & Tennyson [10] used these *ab initio* points, refitted them as well as the adiabatic and relativistic points of Cencek *et al.* [30], and generalized the non-adiabatic model of Moss [32], developed for H_2^+ to the polyatomic case. They were able to reproduce the existing experimental data on all H_3^+ isotopologues with a standard deviation of only $0.01\,\mathrm{cm}^{-1}$. This model proved excellent not only for the calculation of existing line centres and energy levels. Spectra of asymmetric isotopologues were computed for new measurements, and all the new line centres were predicted with an accuracy better than $0.2\,\mathrm{cm}^{-1}$ [33,34]. This approach for the *ab initio* determination of high-resolution spectra prompted Mielke *et al.* [35] to claim that the spectrum of H_3^+ was among the very few completely solved quantum chemical problems.

In fact, the H_3^+ problem is far from being solved. To formulate the remaining problems in a few words, we note that the complete solution would include the determination of an accurate global PES, treating the nBO corrections, and performing accurate nuclear motion computations up to and above the first dissociation limit. In particular, there are problems not only with calculations close to dissociation, but also with attempts to calculate lines above the barrier to linearity, which is around $10\,000\,\mathrm{cm}^{-1}$ for H_3^+. In this region, calculations gave inaccurate results: errors were up to a few cm^{-1}. Alternative methods have been suggested, in particular, those of hyperspherical harmonics [36], where no extra problem arises. With this method, Schiffels *et al.* [37] obtained consistent accuracy of the calculations below and above the barrier using the PES by Cencek *et al.* [30]. They also provided labels for the calculated states, not only in terms of the exact symmetry quantum numbers, but also of the approximate spectroscopic quantum numbers commonly used to characterize spectra. Non-adiabatic shifts were accounted for empirically in these calculations.

Several attempts have been made to produce an accurate *ab initio* global PES for the electronic ground state of H_3^+ and its isotopologues. Polyansky *et al.* [38] computed about 130 *ab initio* points above 25 000 cm^{-1} and used them in the fit, together with the 69 points at the MBB geometries of Cencek *et al.* [30] and a lot of considerably less accurate points close to dissociation. The energy levels close to dissociation resulting from the use of this PES differ even qualitatively from those corresponding to the MBB PES. Thus, this PES was a step forward but far from the accuracy one would consider appropriate for the H_3^+ system. Further determinations of the global H_3^+ PES have been made [39–43], but the results were still not completely satisfactory (see also §3).

Several authors have published energy levels calculated just above the barrier to linearity: Schiffels *et al.* [37], Bachorz *et al.* [43], Neale *et al.* [44], Jaquet [45] and Alijah [46] (see also the experimental paper by Morong *et al.* [47] and references therein). The typical accuracy of these calculations was 0.5–1 cm^{-1} and thus inferior to that achieved by calculations below the barrier. This is mainly due to shortcomings of the PESs. Even though the three major advances in the H_3^+ PES determinations, due to Meyer *et al.* [15], Röhse *et al.* [17] and Cencek *et al.* [30], each resulted in an improved highly accurate BO surface, as we will show below, the sparseness of the grid, which was common to all these studies, does not allow accurate nuclear motion calculation at higher energies.

Experimental observation of lines involving energy levels above the barrier to linearity proved to be difficult [47] as well. Thus, improvements in the accurate calculation of ro–vibrational energies above the barrier to linearity awaited experimental progress, so that comparisons could be made. Simultaneous progress in *ab initio* electronic structure calculations and ro–vibrational energy determinations, as well as observation of weak lines up to the orange optical region, high above the barrier to linearity, changed this situation [11]. In the remainder of this paper, we will describe the first-principles calculation of all the known spectral lines of H_3^+, on the basis of the *ab initio* computations of Pavanello *et al.* [11].

3. Fitting of the *ab initio* points

For the construction of a global PES of the ground electronic state of H_3^+ and its isotopologues, one should bear in mind that this state is not isolated. In fact, avoided crossings occur between the ground state and the first excited singlet state, which in turn becomes degenerate, at equilateral triangular configurations, with the second excited singlet state. One thus faces a three-state problem. The most promising procedure for the construction of the ground state surface therefore starts from a three-dimensional diabatic presentation of the three lowest states, such as provided by the diatomics-in-molecules (DIM) approach [48]. The potential energy surfaces of these states are then obtained by diagonalization of the DIM matrix. Such a strategy has recently been implemented by Viegas *et al.* [41] and is followed here. The 3 × 3 DIM matrix is expressed as

$$\mathbf{H}(\mathbf{R}) = \begin{bmatrix} E(R_1)+\epsilon(R_2,R_3) & \varDelta(R_3) & \varDelta(R_2) \\ \varDelta(R_3) & E(R_2)+\epsilon(R_3,R_1) & \varDelta(R_1) \\ \varDelta(R_2) & \varDelta(R_1) & E(R_3)+\epsilon(R_1,R_2) \end{bmatrix}, \quad (3.1)$$

where

$$E(R_i) = V_{[\mathrm{H}_2, X^1\Sigma_g^+]}(R_i), \tag{3.2}$$

$$\begin{aligned}\epsilon(R_j, R_k) = \frac{1}{2}[\,&V_{[\mathrm{H}_2^+, X^2\Sigma_g^+]}(R_j) + V_{[\mathrm{H}_2^+, A^2\Sigma_u^+]}(R_j) \\ &+ V_{[\mathrm{H}_2^+, X^2\Sigma_g^+]}(R_k) + V_{[\mathrm{H}_2^+, A^2\Sigma_u^+]}(R_k)] - 2E_\mathrm{H}\end{aligned} \tag{3.3}$$

and

$$\Delta(R_k) = \frac{1}{2}[\,V_{[\mathrm{H}_2^+, X^2\Sigma_g^+]}(R_k) - V_{[\mathrm{H}_2^+, A^2\Sigma_u^+]}(R_k)]. \tag{3.4}$$

In these equations, V denotes potential energy curves of H_2 and H_2^+, and E_H is the non-relativistic BO energy of the 1s state of H, $E_\mathrm{H} = -0.5\,E_\mathrm{h}$. i, j and k are the particle indices understood as cyclic permutations of (1,2,3). R_1, for example, is the distance between particles 2 and 3. $\mathbf{R}$ is a three-element vector with coordinates R_1, R_2 and R_3.

In our approach, we use the H_2 and H_2^+ potentials of Viegas *et al.* [41], which are based on the accurate *ab initio* energies of Wolniewicz [49,50] ($H_2(X^1\Sigma_g^+)$), Bishop & Wetmore [51] ($H_2^+(X^2\Sigma_g^+)$) and Peek [52] ($H_2^+(A^2\Sigma_u^+)$).

The 3×3 DIM matrix describes correctly any near or exact degeneracies between the states as well as their dissociation channels. At a short distance, it is not accurate because only a limited number of diatomic states were used for its construction and overlaps were ignored [48]. To increase the accuracy of the representation, either the dimension of the matrix should be augmented or three-body terms, i.e. terms depending on the three distances, should be added, either before [53] or after diagonalization [54]. Following Viegas *et al.* [41], we chose to add diagonal and off-diagonal terms to the DIM matrix before diagonalization. Such an insertion must respect the permutation invariance of the DIM matrix and also the negativeness of the off-diagonal terms, see equation (3.4). A consistent choice is

$$H_{ii} \to H_{ii} + V^{(3)}(R_1, R_2, R_3) \tag{3.5}$$

and

$$H_{ij} = \Delta(R_k) - \tfrac{1}{2}[\tilde{V}^{(3)}(R_1, R_2, R_3)]^2, \tag{3.6}$$

where the three-body terms, $V^{(3)}$ and $\tilde{V}^{(3)}$, are represented as polynomials of integrity basis functions. These are formed from the usual symmetry coordinates in such a way that any combination of them transforms as the totally symmetric representation of the three-particle permutation group [55,56]. At large distances, as the DIM becomes accurate, the polynomials are damped by a range-determining factor. For details of the specific parametrization of the expansion functions, see Pavanello *et al.* [57].

What is different in our present approach from the one by Viegas *et al.* [41] is our use of a grid of *ab initio* points of both unprecedented accuracy [58] and density, and the restriction to only the ground state. The ultra-dense grid in hyperspherical coordinates, of 7840 points, which by symmetry corresponds to $6 \times 7840 = 47\,040$ points spanning the whole surface, allows the use of high-order polynomials, a 15th-order diagonal and a 13th-order off-diagonal one, while minimizing problems with unphysical oscillations. We used *ab initio* points up to $6000\,\mathrm{cm}^{-1}$ above dissociation, omitting only some asymptotic configurations with

Table 1. The number of PES points, N, in different energy regions, ΔE and the fitting error of the PES in those different regions.

ΔE (cm^{-1})	n	r.m.s. (cm^{-1})	$\varDelta_{\max}$ (cm^{-1})
≤5000	443	0.029	0.093
5000–10 000	573	0.044	0.125
10 000–15 000	700	0.040	0.159
15 000–20 000	831	0.043	0.187
20 000–25 000	851	0.043	0.152
25 000–30 000	955	0.095	0.117
30 000–35 000	1069	0.054	0.219
35 000–40 000	1574	0.141	0.967
≥40 000	844	0.191	1.153
≥0	7840	0.097	1.153

at least two internuclear distances larger than 9 bohr, as they would spoil the fit. The 7840 points were least-squared fitted with 297 parameters with an overall root mean square (r.m.s.) deviation of 0.097 cm^{-1}. Table 1 shows r.m.s. and maximum ($\varDelta_{\max}$) deviations for energy regions given in the 5000 cm^{-1} interval. Many more *ab initio* points were generated during the course of this work [57]. They correspond to high-energy configurations and will be needed for studies of the metastable states of H_3^+ located above the first dissociation limit.

(*a*) *Further assessment of the quality of the fit*

Besides the data presented in table 1, the ultimate proof of the accuracy of the fit is the demonstration of predictability by this analytical PES of interpolated points. We can show this by comparison with *ab initio* points not used in the fit. To this end, we have checked our fit against the 16 collinear configurations plus the corresponding envelope points from the paper by Bachorz *et al.* [43]. This set, D, comprises 144 points, of which 122 are below 30 000 cm^{-1}, the energy region of interest to this paper. To our surprise, we found an r.m.s. deviation of 7.34 cm^{-1} and a maximum deviation of 10.91 cm^{-1} for these 122 points. Further analysis showed that only some of the points in the main subset of points, D1-5 to D16-5, were reproduced accurately by our fit. In particular, for each of those points, only two close configurations in which one of the small distances was conserved, i.e. the points (Di-4,6) were reproduced. The reason for this behaviour became clear once we recalculated some of the critical points: a large portion of the envelope points are incorrect. Table 2 illustrates this conclusion and shows our findings for the first three points of the D set.

(*b*) *Comparison of various potential energy surfaces of* H_3^+

In order to fully appreciate the quality of the PES presented by Pavanello *et al.* [11] and given in more detail in §3*a*, we present here the comparison of various PESs with our PES, which we call GLH3P. This comparison can be made using calculations of energy values of these PESs on a very dense grid, which would represent practically the whole surface. The comparison of surfaces at the values

Table 2. Comparison of *ab initio* electronic energies at selected linear geometries: energies in E_h and internuclear distances in a_0.

point	R_{12}	R_{13}	R_{23}	fit	Bachorz *et al.* [43]	recalculated
$D1$-1	1.22	2.44	1.22	−1.247173565	−1.247126742	−1.2471732158
$D1$-2	1.22	2.47	1.25	−1.250492860	−1.250445580	−1.2504925325
$D1$-3	1.22	2.50	1.28	−1.253281412	−1.253233664	−1.2532811131

of coordinates used in the *ab initio* calculations only gives information on the quality of these *ab initio* calculations. When this is repeated on a very dense grid, we compare also the quality of the fit of the analytical surfaces to *ab initio* points. There are two surfaces worth comparing with here. The first one is the PES [10], which represents the fit of 69 points of Cencek *et al.* [30]. The second one is the global surface of Polyansky *et al.* [38], where about 130 high-accuracy points at higher energies were additionally calculated and fitted together with a bulk of much less-accurate points close to dissociation.

When we compare the accuracy of ro–vibrational calculations using the GLH3P PES with that of other surfaces, as described in detail in §4, the calculations are performed with nBO corrections. We supplemented these test ro–vibrational calculations with those performed using purely BO surfaces. The results of these calculations were counterintuitive and surprised us. The differences for some $J = 0$ levels are very small; however, for many levels, there are differences of a few tenths of a wavenumber for levels up to the barrier to linearity and between a few wavenumbers to tens of wavenumbers for the levels above it. This was unexpected for PESs based on *ab initio* calculations, which were different by no more than $0.1\,\mathrm{cm}^{-1}$. A possible explanation lies in significant differences in the interpolation between the points by the fitted surfaces due to the different density of the original grids, upon which the *ab initio* electronic structure computations were performed. In order to confirm, a comparison of the earlier-mentioned PESs was made using a grid with a step size of 0.01 bohr. PT99 deviates from GLH3P with a standard deviation of $4.62\,\mathrm{cm}^{-1}$. A much smaller deviation of $1.1\,\mathrm{cm}^{-1}$ is observed between PPKT and GLH3P.

We might conclude from the above analysis that a much denser grid than the one provided by the 69 ‘standard’ geometries is necessary to produce an accurate surface, even below the barrier to linearity. In the work of Pavanello *et al.* [11], 1700 points are below the barrier to linearity, and this number is enough for the accurate interpolation between the *ab initio* points. This conclusion is also confirmed by the fact that when we predict the energy values of points at geometries not used in the fit using our GLH3P PES, the values coincide with the subsequent *ab initio* calculations within our standard deviation.

Thus, our GLH3P surface is the only existing surface that is accurate to within $0.1\,\mathrm{cm}^{-1}$, not only at the geometries used for the *ab initio* calculations, but everywhere up to designated energies. Strong support to this conclusion comes from §4, where we use the GLH3P PES for comparison with the published experimental data below the barrier to linearity and also with the data in the optical region, above this barrier [11,14].

4. Computation of ro–vibrational lines of H_3^+ and their comparison with experiment

To make direct comparison with the extensive ro–vibrational lines and levels available from high-resolution molecular spectroscopy [33,34,47,59–61], a series of variational rotation–vibration computations were performed using the adiabatic PESs of this study and exact kinetic energy operators. These computations used the DVR3D program suite [62] and previously tested basis sets, the D^2FOPI code [63–65] with appropriate basis sets to deal with singularities, and the hyperspherical harmonics code [36,26]. DVR3D and D^2FOPI were adapted to allow for non-adiabatic effects.

The first set of nuclear motion calculations used nuclear masses, the preferred choice when mass-dependent adiabatic surfaces are available. The variational approach used, without non-adiabatic corrections, has previously been shown by Polyansky *et al.* [66] to give energies that agree to within $0.01\,\mathrm{cm}^{-1}$ with other procedures for treating the nuclear motion problem [67]. The three sets of results of this study were found to be identical to better than $0.001\,\mathrm{cm}^{-1}$ for the energies up to $25\,000\,\mathrm{cm}^{-1}$ and $J=0$ (see supplementary material to Pavanello *et al.* [57]).

After comparing the accuracy of nuclear motion computation using our three programs in the BO approximation using nuclear masses, we used the DVR3D and D^2FOPI programs to allow for the nBO effect. As it is well known [10], to achieve spectroscopic accuracy, adiabatic, relativistic and non-adiabatic effects must be included in the nuclear motion computation. Adiabatic effects were allowed for by the addition of a mass-weighted adiabatic surface to the analytical BO PES. Relativistic effects were allowed for as follows. Bachorz *et al.* [43] determined a set of relativistic corrections. We fitted these points with a standard deviation of $0.007\,\mathrm{cm}^{-1}$ using an analytical surface with 31 constants as given by Polyansky & Tennyson [10], and added the relativistic surface to the adiabatic PES. Both adiabatic and relativistic surfaces were fitted for the points with coordinates corresponding to BO energies up to $30\,000\,\mathrm{cm}^{-1}$. We were able to achieve highly accurate results of ro–vibrational level calculations using the simple model by Polyansky & Tennyson [10], namely using constant (though different) vibrational and rotational masses. Clearly, further improvement in the accuracy of non-adiabatic calculations requires more sophisticated models, as the example of the H_2 molecule shows [68–71].

Comparison with the newly measured visible wavelength transitions has already been given elsewhere [11]; for these lines, the discrepancy between observed and calculated values is better than $0.1\,\mathrm{cm}^{-1}$. The comparison with the other data [47] also confirms much higher accuracy of the present calculations. The lines from Morong *et al.* [47] belong to the levels with lower vibrational energies, but higher values of the rotational quantum number J. The accuracy of our calculations allowed us to make a few reassignments (table 3). The standard deviation of these discrepancies is $0.15\,\mathrm{cm}^{-1}$, which is a significant improvement over the previous theoretical predictions.

The other set of data that are worth comparing with our calculations are given in table 5 of Bachorz *et al.* [43]. The lines between $10\,000$ and $13\,000\,\mathrm{cm}^{-1}$ are presented there and the accuracy of prediction is about $1\,\mathrm{cm}^{-1}$. Special attention should be given to the last line of this table. The transition at $13\,676\,\mathrm{cm}^{-1}$ was

Table 3. Difference between observed [47] and calculated line frequencies states of H_3^+ that were reassigned on the basis of new calculations.

line	band v_1,v_2,l_2	exp. cm^{-1}	calc. cm^{-1}	calc. this work cm^{-1}	obs.–calc. this work cm^{-1}	obs.–calc. [47] old assignment
tR(3,0)	(2,2,2)	10935.358	10935.113	0.25	−0.12	Q(3, 0)
Q(3,0)	(0,5,1)	10935.631	10935.477	0.15	0.52	tR(3, 0)
P(4,3)	(0,5,5)	11494.835	11494.892	−0.06	−1.33	P(3,3)
P(3,3)	(0,5,3)	11496.055	11496.162	−0.11	1.16	P(4,3)

reproduced so badly by previous calculations (up to $3\,cm^{-1}$) that Bachorz *et al.* [43] concluded that the reason of such discrepancy is not yet known. In our calculations, all these lines including the last one are reproduced with a standard deviation of about $0.1\,cm^{-1}$.

The results described earlier show a significant improvement in the accuracy of the present work in comparison with previous calculations. This improvement is of one order of magnitude, or even more in some cases. A similar comparison for the deuterated isoptopologues of H_3^+, which provide a particular test of effects beyond the BO approximation [19], is presented elsewhere [57].

5. Conclusions

A significant step towards achieving experimental accuracy from *ab initio* calculations for the ro–vibrational line centres of the H_3^+ molecular ion over an extended frequency range is presented. A global BO PES calculated *ab initio* on an extremely dense grid by Pavanello *et al.* [11] and Pavanello & Adamowicz [13] is represented with a standard deviation of $0.097\,cm^{-1}$ up to energies $7000\,cm^{-1}$ higher then the first dissociation limit of H_3^+. Adiabatic and relativistic correction surfaces are used together with the BO PES and the non-adiabatic model of Polyansky & Tennyson [10] for the ro–vibrational levels calculation. Lines in the optical region [11,14] are reproduced with an accuracy close to the experimental linewidth. The higher accuracy of these calculations allowed us to reassign some high-J lines and reproduced a ‘problematic’ line observed by Morong *et al.* [47] with an accuracy of about $0.1\,cm^{-1}$.

This work lays the foundation for significant new studies. Dipole moment points have been determined as part of the *ab initio* calculations; an analytical dipole moment surface (DMS) is being produced that should allow extremely accurate H_3^+ intensities to be computed and the calculation of extensive line lists. H_3^+ line lists of transitions [44,72], partition functions [73] and cooling functions [74,75] are all of great importance for applications in astrophysics and elsewhere [76]. Intensity calculations can also help with the detection of high-frequency lines of H_3^+ by guiding experimental search that would otherwise require prohibitively long scans.

The production of a high-accuracy global PES, and the associated high-accuracy ro–vibrational calculations, opens the way for further improvement of the accuracy of global non-BO corrections in analogy to those already developed for the diatomic hydrogen species. For instance, much higher accuracy of QED calculations should be possible for H_3^+, than for larger systems, where they have already been studied by Pyykkö *et al.* [77]. We hope that such improvements will lead to an accuracy approaching 0.01 cm^{-1} for calculations of energy levels close to and above the first dissociation limit, allowing an *ab initio* interpretation of the near dissociation spectrum. We note that several of us have already performed such a study for the simpler, above-dissociation ro–vibrational spectrum of water [78].

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