QED correction for H₃⁺

Lorenzo Lodi,[1] Oleg L. Polyansky,[1,2,*] Jonathan Tennyson,[1] Alexander Alijah,[3] and Nikolai F. Zobov[2,4]

[1]*Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, United Kingdom*
[2]*Lobachevsky State University of Nizhny Novgorod, 23 Prospekt Gagarina, 603950, Nizhny Novgorod, Russia*
[3]*Groupe de Spectrométrie Moléculaire et Atmosphérique, GSMA, UMR CNRS 6089, Université de Reims Champagne-Ardenne, Reims, France*
[4]*Institute of Applied Physics, Russian Academy of Sciences, Ulyanov Street 46, Nizhny Novgorod, Russia 603950*

A quantum electrodynamics (QED) correction surface for the simplest polyatomic and polyelectronic system H₃⁺ is computed using an approximate procedure. This surface is used to calculate the shifts to vibration-rotation energy levels due to QED; such shifts have a magnitude of up to 0.25 cm⁻¹ for vibrational levels up to 15 000 cm⁻¹ and are expected to have an accuracy of about 0.02 cm⁻¹. Combining our H₃⁺ QED correction surface with existing highly accurate Born-Oppenheimer, relativistic, and adiabatic components suggests that deviations of the resulting *ab initio* energy levels from observed ones are largely due to nonadiabatic effects.

PACS number(s): 31.30.jf, 31.15.ac, 33.20.Vq, 33.20.Ea

I. INTRODUCTION

Ab initio studies of diatomic and triatomic systems containing less than ten electrons are now able to produce rotation-vibrational energy levels with better than spectroscopic accuracy, i.e., with errors of less than 1 cm⁻¹. To improve on this accuracy one needs to account for several small effects which are routinely neglected, including electronic relativistic and adiabatic corrections, as well as, most notably for this work, nonadiabatic effects and corrections due to quantum electrodynamics (QED). General discussions of relativistic and QED effects in molecular physics and quantum chemistry can be found in several recent reviews [1–7] and textbooks [8,9]. In this study we follow the convention of calling "relativistic effects" corrections to the nonrelativistic Schrödinger equation of second order in the fine-structure constant α (i.e., all effects correctly described by the many-electron no-pair Dirac-Coulomb-Breit equation), while so-called radiative corrections due to the quantization of the electromagnetic field and appearing in higher powers of α are referred to as QED effects.

The hydrogen molecular ion H₂⁺ is the simplest physical system with a rotational-vibrational spectrum and serves as an important benchmark. Rotational-vibrational energy levels for H₂⁺ were notably presented by Moss [10] with an estimated accuracy of 10^{-4} cm⁻¹ and included nonadiabatic, relativistic, and leading QED corrections. More recent studies have considerably improved the achievable accuracy, and for selected rotation-vibrational transitions, QED corrections up to α^5 have been computed [11–13], leading to uncertainties of about 2×10^{-6} cm⁻¹.

Next in terms of size and complexity is the hydrogen molecule H₂, for which an accuracy of 10^{-4} cm⁻¹ has recently been achieved *ab initio* [14–16] by careful inclusion of nonadiabatic corrections and of QED corrections to order α^4. Studies of H₂⁺ and H₂ represent the current state of the art for calculations of molecular rotational-vibrational energy levels; for larger systems the achievable accuracy is considerably lower.

In particular, for H₃⁺ the highest accuracy achieved so far is 0.10 cm⁻¹ for all known energies up to 17 000 cm⁻¹ [17], which is therefore several orders of magnitude worse than for H₂⁺ and H₂. Higher-accuracy energy levels are necessary for proper analysis of H₃⁺ experimental spectra. More specifically, about 30 years ago Carrington and coworkers [18–20] measured very dense near-dissociation spectra of H₃⁺ and its isotopologs with an average line spacing of less than 0.01 cm⁻¹; these spectra, which remain unassigned and substantially uninterpreted [21], clearly require very high accuracy to be analyzed from theoretical calculation.

Another source of motivation is provided by the recent studies by Wu *et al.* [22] and Hodges *et al.* [23], who have concentrated on high-precision and high-accuracy frequency measurements on the H₃⁺ ν_2 fundamental band. Measurements were made by both groups at the submegahertz (3×10^{-5} cm⁻¹) level but currently do not agree with each other within the claimed uncertainties.

The assigned H₃⁺ experimental data have recently been the subject of an analysis using the procedure described in Ref. [24], producing a comprehensive set of rotation-vibration energy levels [25,26] which we use for comparison throughout this study.

Given the present experimental situation, it is therefore very desirable to improve the accuracy of theoretical H₃⁺ energy levels beyond the 0.1 cm⁻¹ level. The main nonrelativistic, clamped nuclei Born-Oppenheimer (BO) potential energy surface (PES) from Pavanello *et al.* [17,27] and the associated relativistic and adiabatic surfaces, all of which we use in this work, are probably sufficiently well determined to predict energy levels with an accuracy of about 10^{-2} cm⁻¹ for low-lying levels up to about 15 000 cm⁻¹. There are currently two factors limiting the accuracy in H₃⁺ to the 0.1 cm⁻¹ level, namely, a proper treatment of (i) nonadiabatic and (ii) QED effects.

Nonadiabatic effects in H₃⁺ and its isotopologs are known to affect line positions by up to 1.0 cm⁻¹ [28] and therefore must be accounted for accurately. Polyansky and Tennyson (PT) [28] introduced a simple model based on the use of fixed effective vibrational and rotational masses taken from Moss's [29] studies on H₂⁺; PT were able to improve the accuracy of calculations from 1 to 0.1 cm⁻¹. Further improvements require more sophisticated treatments of nonadiabatic effects;

---

*o.polyansky@ucl.ac.uk

a step in this direction has been made by Diniz *et al.* [30], who obtained nonadiabatic rotational-vibrational energies for the ν_2 band with an accuracy of 0.01 cm^{-1} but did not consider higher vibrational states.

The second factor limiting the final accuracy of H$_3^+$ energy levels is QED effects. As discussed above, QED effects have been computed accurately for H$_2^+$ [29] and H$_2$ [14–16] and have an effect on the corresponding rotation-vibration energy levels in the region 0.1–0.2 cm^{-1}. In the case of H$_3^+$, QED effects have so far been entirely neglected but must clearly be taken into account to achieve accuracies better than 0.1 cm^{-1}.

Pyykkö *et al.* [28] suggested a simple scheme for describing leading QED effects in molecules (see Sec. III for details). This scheme has already been applied to the water molecule [28,31], for which QED corrections are of the order of 1 cm^{-1}, and was instrumental in recent studies achieving an accuracy of 0.1 cm^{-1} for levels up to 15 000 cm^{-1} [32] and of 1 cm^{-1} for the dissociation energy [33]. In this study we use the model of Pyykkö *et al.* [28] to provide a QED correction surface for H$_3^+$. This correction energy surface, when combined with the existing nonrelativistic, relativistic, and adiabatic surfaces from previous studies [17,27] and with a future accurate treatment of nonadiabatic effects, is expected to provide rotation-vibration energy levels with a typical accuracy of 0.01 cm^{-1}.

This paper is organized as follows. Section II presents a comparison of the Born-Oppenheimer PES computed using explicitly correlated Gaussians [17,27] and surfaces computed using standard quantum chemistry methods based on full configuration interaction (FCI) and Gaussian basis sets. We show that available basis sets provide an accuracy between 0.1 and 1 cm^{-1} for rotation-vibration energy levels. Section III compares results of accurate QED calculations for H$_2$ [14–16] with our calculations using the approximate method of Pyykkö *et al.* [28]. QED corrections for H$_3^+$ using the same methodology are presented. Section IV presents results of nuclear motion calculations using a BO PES, relativistic and adiabatic corrections [17,27], and our QED correction surface. Nuclear motion calculations are given both without nonadiabatic corrections and with a simple nonadiabatic treatment based either on the PT model [28] or on the model by Diniz *et al.* [30]. Analysis of the residual deviations between theory and experiment is given. Section V presents a final discussion and conclusions.

II. ERRORS DUE TO BASIS-SET INCOMPLETENESS FOR H$_2$ AND H$_3^+$

Before discussing QED corrections we briefly discuss errors in vibrational energy levels computed from nonrelativistic BO energy surfaces obtained using standard quantum chemistry methods. We find this discussion appropriate because practical application of the method of Pyykkö *et al.* [28] for QED correction also relies on standard electronic structure methods. All calculations used the electronic structure program MOLPRO [34] using the configuration interaction single and doubles (CISD) method; because H$_2$ and H$_3^+$ are two-electron systems CISD for these systems is equivalent to full CI (FCI); this means that electron correlation is accounted for exactly and the error in nonrelativistic energies is

entirely due to basis-set incompleteness. In all calculations we used the augmented correlation-consistent polarized valence *n* zeta (aug-cc-pV*n*Z) correlation-consistent family of basis sets introduced by Dunning [35], with *n* = D, T, Q, 5, and 6; these will be referred to by the shorthand notation a*nz*. Two-term basis-set extrapolated values used the extrapolation formula $E_n = E_\infty + A/n^4$ and are denoted a[*n,m*]z; as discussed below, this extrapolation form was used because it gives the best agreement with very accurate reference results for H$_2$. For comparison, we also include results obtained using explicitly correlated methods of the F12 family [36–39]; in particular, we used the CISD-F12 code available in MOLPRO [40].

We did not include H$_2^+$ in this comparison because it is a one-electron system and it is well known [38] that basis-set-incompleteness error is dominated by the electron-correlation part, so that basis-set convergence results for H$_2^+$ are not representative of many-electron systems.

A. Nonrelativistic surfaces

Our MOLPRO-based results were compared with much more accurate calculations performed using explicitly correlated exponentials (H$_2$) [41] and explicitly correlated Gaussians (ECG; H$_3^+$) [17]; these reference values should provide clamped-nuclei Born-Oppenheimer energies with an accuracy of at least 10^{-4} cm^{-1} for H$_2$ and 10^{-3} cm^{-1} for H$_3^+$ and will be referred to as "exact" below.

Results for H$_2$ are collected in Table I and are represented in Fig. 1. An analysis of the convergence pattern reveals that FCI errors decrease with the basis-set cardinal number *n*, with an n^{-4} dependence; for this reason the basis-set extrapolation formula $E_n = E_\infty + A/n^4$ works best for this system and

TABLE I. Errors in H$_2$ vibrational ($J = 0$) energy levels computed from FCI nonrelativistic energy curves and various basis sets (see text for details). All values are in cm^{-1}.

		Exact − calculated					
v	Exact[a]	a4z	a5z	a6z	a[5,6]z[b]	a4z/F12	a5z/F12
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1	4163.40	4.43	1.33	0.65	0.02	0.92	0.06
2	8091.16	8.68	2.64	1.36	0.17	1.82	0.08
3	11788.14	12.79	3.97	2.07	0.30	2.57	0.06
4	15257.39	16.82	5.41	2.83	0.43	3.15	0.02
5	18499.88	20.89	6.99	3.65	0.54	3.61	−0.03
6	21514.30	25.16	8.77	4.57	0.65	3.97	−0.11
7	24296.64	29.80	10.78	5.60	0.77	4.24	−0.25
8	26839.64	35.01	13.07	6.79	0.94	4.46	−0.42
9	29131.99	41.01	15.71	8.18	1.18	4.69	−0.60
10	31157.32	48.08	18.78	9.82	1.48	5.02	−0.76
11	32892.55	56.51	22.40	11.78	1.89	5.57	−0.87
12	34305.64	66.62	26.76	14.17	2.44	6.39	−0.89
13	35352.20	78.85	32.19	17.14	3.13	7.63	−0.72
14	35970.80	94.16	39.21	20.97	4.00	9.81	−0.12
rms[c]		45.04	18.00	9.53	1.66	4.90	0.47

[a]Using the very accurate BO potential energy points by Pachucki [42].
[b]Using the extrapolation formula $E_n = E_\infty + A/n^4$.
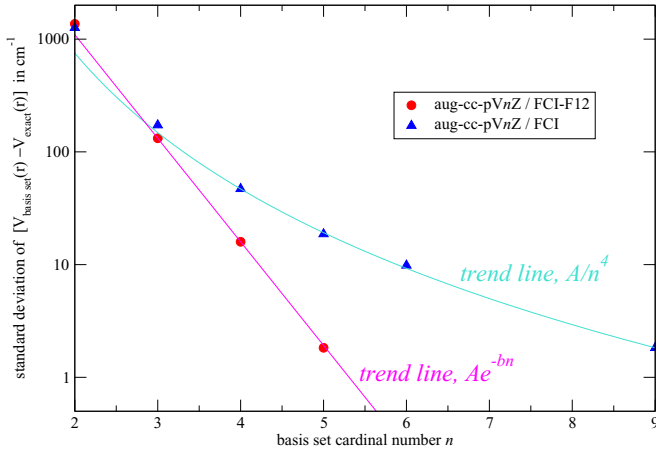[c]Root-mean-square deviation.

FIG. 1. (Color online) Convergence speed of H_2 relative energies with various basis sets. The quantity plotted is the standard deviation of the difference between a potential curve obtained with a given basis set and the virtually exact one from Ref. [42] in the range $r = 0.75a_0$ to $r = 12a_0$. The trend lines are fits to the last three points of each series.

was used throughout. This observation is in line with several recent studies [43,44] which show very good performance for the similar formula $E_n = E_\infty + A/(n + 1/2)^4$ with respect to other basis-set extrapolation schemes. As a result of this regular convergence behavior, extrapolated a[5,6]z energy levels improve very significantly over the raw a6z values and have an accuracy comparable with the expected one for the a9z basis set. In particular, the error of a[5,6]z vibrational energy levels is very nearly linear up to $v = 9$ and has an approximate magnitude of $0.12v$ cm^{-1}. As discussed in detail below, similar basis-set errors are found for H_3^+.

Explicitly correlated methods of the F12 type do exceptionally well for H_2 and show exponential convergence in terms of n (see Table I and Fig. 1); as a result a5z/F12 energy levels are of overall higher quality than extrapolated a[56]z ones, especially for energies above $20\,000$ cm^{-1}. We also considered the basis sets of the cc-pVnZ-F12 family ($n = $ D, T, and Q) [45,46] especially designed for F12 calculations; these basis sets too show exponential convergence and moreover reduce errors with respect to the corresponding anz basis set by a factor 7 for a2z and by a factor 3 for a3z and a4z.

The first FCI calculations for H_3^+ were performed in a classic work by Meyer, Botschwina, and Burton (MBB) [47]; subsequent studies gradually increased the accuracy of the PES and extended its range. Most of this work was performed *ab initio* [17,48–53], but in a few cases the PES was improved by fitting to spectroscopic data [17,54–56]. These theoretical studies proved indispensable for the assignment of new observed lines of H_3^+ (see, for example, Refs. [57–60]).

We performed FCI calculations at the 69 geometries originally used by MBB [47] for H_3^+ using the same methodology described above for H_2; energies were fitted in a standard way, following the procedure described previously [28]. These calculations are compared to the high-accuracy values computed by Cencek *et al.* [49] instead of the more recent and accurate one by Pavanello *et al.* [17,27] used elsewhere in this work because the latter were computed on

TABLE II. Errors in H_3^+ vibrational band origin ($J = 0$) energy levels computed from FCI nonrelativistic energy curves and various basis sets (see text for details). All values are in cm^{-1}.

		Exact − calculated			
(v_1,v_2^ℓ)	Exact[a]	a5z	a6z	a5z/F12	a[5,6]z[b]
$(0,1^1)$	2521.51	0.74	0.47	0.17	0.11
$(1,0^0)$	3179.59	0.44	0.35	0.07	0.16
$(0,2^0)$	4778.34	1.58	0.94	0.32	0.12
$(0,2^2)$	4998.31	1.52	0.92	0.32	0.14
$(1,1^1)$	5555.42	1.17	0.80	0.23	0.26
$(2,0^0)$	6264.44	0.90	0.66	0.13	0.30
$(0,3^1)$	7006.10	2.42	1.40	0.46	0.42
$(0,3^3)$	7285.50	2.52	1.43	0.44	0.44
$(1,2^0)$	7770.20	2.87	1.18	0.33	−0.09
$(1,2^2)$	7870.84	2.04	1.26	0.35	−0.00
$(2,1^1)$	8489.38	1.70	1.11	0.25	−0.03
$(0,4^0)$	9001.04	3.32	1.87	0.58	0.62
$(0,4^2)$	9112.17	3.44	1.90	0.56	0.74
$(3,0^0)$	9254.77	1.43	0.97	0.16	0.17
$(1,3^1)$	9653.33	3.00	1.75	0.45	−0.51
$(1,3^3)$	9966.80	2.91	1.68	0.16	−0.96
$(0,4^4)$	9997.51	2.54	1.58	0.36	−0.96
$(2,2^0)$	10592.76	2.15	1.37	0.11	−2.22
$(2,2^2)$	10643.45	2.31	1.46	0.02	−2.41
$(0,5^1)$	10855.91	3.83	1.90	−0.08	−0.18
rms[c]		2.33	1.33	0.32	0.85

[a]Using the very accurate BO potential energy surface by Cencek *et al.* [49].
[b]Using extrapolation formula $E_n = E_\infty + A/n^4$.
[c]Root-mean-square deviation in cm^{-1}.

a different grid. The results of Cencek *et al.* are sufficiently accurate for this purpose and will be labeled as exact below. The results of the vibrational $J = 0$ energy levels are reported in Table II. Explicitly correlated F12 methods show improved convergence speed but are not quite as fast as for H_2; as a result extrapolated a[56]z and a5z-F12 energy levels have comparable accuracies (see Table II).

Our FCI-based energy levels for H_2 have a rms deviation with respect to the exact reference values of 1.66 cm^{-1} (extrapolated a[56]z energies) or 0.47 cm^{-1} (a5z-F12 energies); the rms errors for H_3^+ in the energy range to $10\,000$ cm^{-1} are 0.85 cm^{-1} (a[56]z) and 0.32 cm^{-1} (a5z-F12). We conclude that F12 methods at the a5z level are capable of providing energy levels accurate to better than 0.5 cm^{-1} and a[56]z generally to better than 1.5 cm^{-1}. Such calculations are therefore a viable, good-quality alternative when explicitly correlated Gaussian methods are too expensive.

B. Relativistic surfaces

The most accurate relativistic corrections for H_3^+ are those by Bachorz *et al.* [51] and were computed as the expectation value (using a very accurate wave function based on explicitly correlated Gaussians) of the complete Breit-Pauli relativistic Hamiltonian [61], i.e., including mass-velocity, one- and two-electron Darwin contributions, Breit retardation, and a spin-spin Fermi contact term. The relativistic correction for H_3^+ is

overall very small, spanning the range -4.3 to -1.8 cm^{-1} over all the geometries considered. As discussed below, such a small contribution is due to almost complete cancellation between the main contributions to the overall relativistic correction.

We used MOLPRO [34] to compute relativistic corrections as the expectation value of the mass-velocity (MV) and one-electron Darwin (D1) operator using FCI wave functions. The MOLPRO-based aug-cc-pV6Z MVD1 energies are converged with respect to basis set to about 0.05 cm^{-1}; they typically agree with the more complete relativistic corrections by Bachorz to 0.15 cm^{-1}, which can only be considered a moderate agreement considering the overall smallness of the relativistic correction. This should indicate that the contribution to relative energies of terms neglected in the MOLPRO-based calculation (Breit, two-electron Darwin, and Fermi contact) is non-negligible for very accurate work. On the other hand this also indicates that the two-electron QED correction (based on the two-electron Darwin contribution) should be negligible, as it is expected to be about 6 times smaller than the one-electron part.

It is worth performing a more detailed analysis of the MVD1 correction. The MV term has an absolute magnitude of about -23 cm^{-1}, while the D1 term has an absolute magnitude of about $+20$ cm^{-1}; both contributions show a variation with geometry spanning about 6 cm^{-1}. However, the variation with geometry of MV and D1 are almost perfectly anticorrelated, resulting in mutual cancellation when summed. As a result of this cancellation the MVD1 contribution turns out to be only slightly larger than the QED one (see Sec. III).

The situation is somewhat similar for water (analysis performed for energies up to 40 000 cm^{-1}) [62]. The MV term is in absolute terms (average value) $-57\,000$ cm^{-1}, with a variation of 500 cm^{-1}, and D1 is $+45\,000$ cm^{-1}, with a variation of 400 cm^{-1}. The MVD1 term has a magnitude of $-11\,500$ cm^{-1}, with a variation of 140 cm^{-1}. The QED correction for water is 1000 cm^{-1}, with a variation of 2 cm^{-1}. So in the case of water there still is considerable cancellation but not as much as in H$_3^+$.

III. QUANTUM ELECTRODYNAMICS CORRECTIONS FOR H$_2$ AND H$_3^+$

Pyykkö *et al.* [1,63] proposed making use of approximate proportionality formulas between the leading QED corrections to order α^3 (namely, the electron self-energy) and the one- and two-electron Darwin corrections. We neglect the two-electron contribution and compute the one-electron Darwin term with MOLPRO and FCI wave functions; as discussed in Sec. II B the two-electron contribution is expected to be about a factor of 6 smaller than the one-electron one. Pyykkö *et al.*'s method requires a scaling factor, for which we use 0.04669, as reported in Table II of Pyykkö *et al.* for all systems studied.

QED corrections are known accurately both for H$_2^+$ [29] and H$_2$ [14–16]; we compare our scheme with these reference calculations in Tables III and IV.

The QED values differ, on average, from exact ones by less than 0.001 cm^{-1} for H$_2^+$ and less than 0.02 cm^{-1} for H$_2$ (see Tables III and IV). Columns 3 and 4 of Table IV give the relativistic and QED shifts in the energy levels of H$_2$ from the

TABLE III. QED corrections for $J = 0$ vibrational levels of H$_2^+$. All energies are in cm^{-1}.

| | | | QED corrections | | | | | |
| | | | This work | | | Exact − this work | | |
v	BO[a]	Exact[b]	a4z	a5z	a6z	a4z	a5z	a6z
0	0.00	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1	2192.04	−0.009	−0.009	−0.009	−0.009	−0.001	0.000	0.000
2	4256.71	−0.018	−0.016	−0.017	−0.018	−0.001	−0.001	0.000
3	6198.28	−0.026	−0.024	−0.025	−0.025	−0.002	−0.001	0.000
4	8020.34	−0.033	−0.030	−0.032	−0.033	−0.003	−0.001	0.000
5	9725.84	−0.040	−0.036	−0.038	−0.039	−0.003	−0.001	0.000
6	11317.03	−0.046	−0.042	−0.044	−0.045	−0.003	−0.001	0.000
7	12795.56	−0.051	−0.047	−0.050	−0.051	−0.004	−0.001	0.000
8	14162.40	−0.056	−0.052	−0.055	−0.056	−0.004	−0.001	0.000
9	15417.90	−0.061	−0.056	−0.059	−0.061	−0.004	−0.001	0.000
10	16561.70	−0.065	−0.060	−0.063	−0.065	−0.005	−0.001	0.000
11	17592.67	−0.068	−0.063	−0.067	−0.068	−0.005	−0.001	0.000
12	18508.81	−0.072	−0.066	−0.070	−0.072	−0.005	−0.001	0.000
13	19307.16	−0.074	−0.069	−0.073	−0.074	−0.005	−0.001	0.000
14	19983.67	−0.076	−0.071	−0.075	−0.077	−0.005	−0.001	0.000
15	20533.04	−0.078	−0.073	−0.077	−0.078	−0.005	−0.001	0.000
16	20948.70	−0.079	−0.074	−0.078	−0.080	−0.005	−0.001	0.000
17	21223.28	−0.080	−0.075	−0.079	−0.081	−0.005	−0.001	0.001
18	21352.91	−0.080	−0.075	−0.079	−0.081	−0.005	−0.001	0.001
19	21375.30	−0.080	−0.075	−0.079	−0.081	−0.005	−0.001	0.001

[a]Indicative nonrelativististic Born-Oppenheimer values obtained with basis-set-extrapolated a[5,6]z energies; the extrapolation formula is $E_n = E_\infty + A e^{-\alpha\sqrt{n}}$. Reported values have an estimated error of less than $0.10v$ cm^{-1}.
[b]Taken from Ref. [29].

TABLE IV. QED corrections for H$_2$ for $J = 0$ vibrational levels. All energies are in cm^{-1}.

		Exact[b]			This work			Error
v	BO[a]	α^2	α^3	Total	α^2	α^3	Total	total[c]
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-0.00
1	4163.40	0.02	-0.02	0.00	0.03	-0.02	0.01	-0.01
2	8091.16	0.04	-0.04	0.00	0.06	-0.04	0.01	-0.01
3	11788.14	0.05	-0.06	-0.01	0.07	-0.06	0.01	-0.02
4	15257.39	0.06	-0.08	-0.02	0.08	-0.08	0.00	-0.02
5	18499.88	0.06	-0.09	-0.03	0.09	-0.10	-0.02	-0.02
6	21514.30	0.05	-0.11	-0.05	0.08	-0.12	-0.04	-0.02
7	24296.64	0.04	-0.12	-0.08	0.07	-0.13	-0.07	-0.02
8	26839.64	0.02	-0.13	-0.12	0.04	-0.15	-0.10	-0.02
9	29131.99	-0.02	-0.15	-0.16	0.01	-0.16	-0.15	-0.01
10	31157.32	-0.06	-0.16	-0.22	-0.04	-0.17	-0.21	-0.01
11	32892.55	-0.12	-0.17	-0.29	-0.10	-0.19	-0.29	-0.00
12	34305.64	-0.20	-0.18	-0.37	-0.18	-0.20	-0.38	0.01
13	35352.20	-0.29	-0.18	-0.48	-0.29	-0.21	-0.50	0.02
14	35970.80	-0.42	-0.19	-0.61	-0.43	-0.22	-0.65	0.04

[a]Using the very accurate BO potential energy points by Pachucki [42].

[b]From Komasa *et al.* [14]; corrections to order α^4 were also estimated in Ref. [14] but contribute by less than 0.002 cm^{-1} for all energy levels.

[c]Exact minus this work.

exact calculations [14]. Column 6 gives the relativistic FCI a[5,6]z calculation of MVD1 using MOLPRO, and column 7 gives the value of column 6 scaled by 0.04669, which gives our approximate QED value. One can see that the exact shifts differ from our approximate calculations by 0.02 cm^{-1} or less for all except the highest, $v = 14$, vibrational level. We expect that the QED calculations for H$_3^+$, given below, will deviate from any future exact calculation by not much more than this value.

Let us now consider our analogous QED calculations for H$_3^+$. The MVD1 calculations were also performed using MOLPRO and the a6z basis set. However, our comparison of these calculations with one performed using an aQz basis set showed rapid convergence of the relativistic calculations with the basis set, so in practice our aQz results could also have been used. Table V gives values for the calculated QED corrections at all 69 MBB geometries. It can be seen that the magnitude of the QED correction is small, less than 1 cm^{-1} everywhere, but that it varies significantly with geometry and even changes sign. We fitted the 69 QED points computed at the a6z level to the functional form used in Ref. [17] to fit the relativistic energies. The function contained nine fitting parameters, polynomials up to degree 4, and reproduced the *ab initio* values with a rms deviation of 3.3×10^{-3} cm^{-1}.

IV. ROVIBRATIONAL CALCULATIONS FOR H$_3^+$ WITH THE QED SURFACE

We used the DVR3D program suite [64] to compute rovibrational energy levels using the same parameters employed in previous studies [17,27]; energy levels are converged with respect to the nuclear motion problem to 0.001 cm^{-1}.

TABLE V. QED corrections ΔV_{QED} (in cm^{-1}), computed at the 69 MBB geometries [47] using a MOLPRO and an a5z FCI wave function. The indices n_a, n_x, and n_y specify the grid geometries as described in Ref. [47].

n_a	n_x	n_y	ΔV_{QED}	n_a	n_x	n_y	ΔV_{QED}
-4	0	0	0.5588	1	-1	0	-0.0890
-3	0	0	0.3879	1	-2	0	-0.0611
-2	0	0	0.2403	1	-3	0	-0.0126
-1	0	0	0.1121	1	-4	0	0.0594
0	0	0	0.0000	2	-1	0	-0.1749
1	0	0	-0.0981	2	-2	0	-0.1482
2	0	0	-0.1838	2	-3	0	-0.1022
3	0	0	-0.2580	2	-4	0	-0.0345
4	0	0	-0.3217	3	-1	0	-0.2494
5	0	0	-0.3750	3	-2	0	-0.2236
0	-1	0	0.0095	3	-3	0	-0.1797
0	-2	0	0.0391	3	-4	0	-0.1152
0	-3	0	0.0910	4	-1	0	-0.3133
0	-4	0	0.1677	4	-2	0	-0.2883
-1	-1	0	0.1223	4	-3	0	-0.2461
-1	-2	0	0.1542	5	-1	0	-0.3668
-1	-3	0	0.2101	1	1	0	-0.0891
-2	-1	0	0.2515	1	2	0	-0.0624
-2	-2	0	0.2863	1	3	0	-0.0178
-2	-3	0	0.3466	2	1	0	-0.1750
-3	-1	0	0.4002	2	2	0	-0.1485
-3	-2	0	0.4380	2	3	0	-0.1032
-4	-1	0	0.5719	3	1	0	-0.2493
0	1	0	0.0093	3	2	0	-0.2225
0	2	0	0.0366	4	1	0	-0.3129
0	3	0	0.0820	4	2	0	-0.2847
-1	1	0	0.1218	5	1	0	-0.3658
-1	2	0	0.1504	0	0	2	0.0378
-1	3	0	0.1977	-2	0	2	0.2839
-2	1	0	0.2508	-2	0	3	0.3393
-2	2	0	0.2815	0	0	3	0.0864
-2	3	0	0.3319	0	0	4	0.1568
-3	1	0	0.3995	2	0	2	-0.1483
-3	2	0	0.4328	2	0	3	-0.1032
-4	1	0	0.5713				

Nuclear motion calculations used the new, accurate, global GLH3P PES of Pavanello *et al.* [27]. This is the most accurate PES available for H$_3^+$ and includes a nonrelativistic BO component computed using explicitly correlated Gaussian functions [17,27,65], an adiabatic Born-Oppenheimer diagonal correction (BODC) surface [17], and a relativistic surface [17,27]. The BO, adiabatic, and relativistic surfaces are supposed to be accurate to about 10^{-2} cm^{-1} [17,27]. Here we combine our QED surface with the other surfaces used previously [17]. Calculations were performed without and with allowance for nonadiabatic effects; results are collected in Table VI.

Without inclusion of QED effects, the rms deviation obtained for the vibrational band origins below 16 000 cm^{-1} is 0.99 cm^{-1} using nuclear masses and no allowance for non-adiabatic effects; inclusion of QED effects results in a reduction of the rms deviation to 0.84 cm^{-1}. The effect of QED is therefore much larger than the desired accuracy of

TABLE VI. Vibrational band origins ($J = 0$ energy levels) for H_3^+ calculated with various models of nonadiabatic effects and with or without QED corrections. All energies are in cm^{-1}.

		Nonadiabatic[a]					
		nuc	nuc	PT	PT	Din	Din
(v_1, v_2^ℓ)	obs.[b]	no QED[c]	with QED	no QED	with QED	no QED	with QED
$(0,1^1)$	2521.41	-0.18	-0.14	0.11	0.16	0.01	0.05
$(0,2^2)$	4998.04	-0.42	-0.33	0.14	0.23	-0.03	0.05
$(1,1^1)$	5554.06	-0.78	-0.71	-0.14	-0.07	-0.35	-0.28
$(0,3^3)$	7492.91	-0.74	-0.61	0.13	0.26	-0.15	-0.03
$(0,4^2)$	9113.08	-0.88	-0.73	0.04	0.19	-0.26	-0.11
$(2,2^2)$	10645.38	-1.05	-0.95	0.06	0.20	-0.30	-0.16
$(0,5^1)$	10862.91	-0.85	-0.66	0.16	0.34	-0.18	0.00
$(3,1^1)$	11323.10	-1.27	-1.14	-0.02	0.11	-0.41	-0.29
$(0,5^5)$	11658.40	-1.08	-0.90	0.09	0.27	-0.28	-0.10
$(2,3^1)$	12303.37	-1.15	-0.95	0.03	0.22	-0.35	-0.16
$(0,6^2)$	12477.38	-1.18	-0.98	-0.02	0.18	-0.39	-0.19
$(0,7^1)$	13702.38	-1.33	-1.12	-0.21	0.00	-0.62	-0.41
$(0,8^2)$	15122.81	-1.28	-1.06	0.16	0.38	-0.39	-0.18
rms[d]		0.99	0.84	0.12	0.22	0.33	0.19

[a]Treatment used for nonadiabatic effects. Here, "nuc" indicates nuclear masses were used (i.e., no allowance made for nonadiabatic effects). "PT" indicates the Polyansky-Tennyson model [28] with constant effective rotational and vibrational masses. "Din" is the model by Diniz *et al.* [30]. Values show observed minus calculated residues.
[b]Experimentally derived energy levels, from Furtenbacher *et al.* [26].
[c]Indicates whether the QED correction surface was included ("with QED") or not ("no QED").
[d]Root-mean-square deviation.

10^{-2} cm^{-1} for H_3^+. The resulting observed minus calculated residues can be ascribed almost completely to nonadiabatic effects.

To further increase the accuracy nonadiabatic effects have to be taken into account; at the moment this can be done only in an approximate way, for example, using effective rotational and vibrational masses (PT model [28]) or using the more refined model by Diniz *et al.* [30].

To extend the Diniz *et al.* model to higher vibrational states we first calculated $J = 0$ energies and wave functions Ψ_n using nuclear masses. We used these wave functions and the mass surface $m(\underline{R})$, given by Diniz *et al.* to obtain an improved effective mass m_n, for each vibrational state n computed as $m_n = \langle \Psi_n | m(\underline{R}) | \Psi_n \rangle$. Energies for $J = 0$ were then recalculated for each vibrational state in turn using the improved (constant) state-dependent mass.

Calculations with a vibrational mass of 1.0007537 u using the PT model result in a rms deviation of 0.12 cm^{-1}(see Table VI). Inclusion of QED degrades the rms deviation to 0.22 cm^{-1} in this model. On the other hand, in the more refined model of Diniz *et al.* [30] for nonadiabatic effects, inclusion of QED effects leads to a reduction of the rms deviation from 0.33 cm^{-1} without QED effects to 0.19 cm^{-1} when QED is included.

Table VI therefore demonstrates that further work is needed to improve nonadiabatic models and that QED corrections are indispensable to any calculations which include nonadiabatic corrections in order to approach observed values.

V. CONCLUSIONS

We calculated a QED energy correction surface for H_3^+ using the approximate method of Pyykkö *et al.* [63]. This method is benchmarked against accurate QED calculations for H_2^+ and H_2; the comparisons suggest that our QED surface for H_3^+ should provide QED corrections to rotational-vibration energy levels with an accuracy better than 0.02 cm^{-1}. The effect of QED on low-lying energy levels is of the order of 0.2 cm^{-1} and hence is much larger than the accuracy of 10^{-2} cm^{-1}, which has already been achieved for all components of *ab initio* calculations on H_3^+ with the notable exception of nonadiabatic effects.

Inclusion of QED effects leads to H_3^+ energy levels being reproduced with a rms deviation which is reduced from 0.99 to 0.84 cm^{-1} when no allowance is made for nonadiabatic effects (nuclear masses used for energy-level calculation). These calculations, which include highly accurate BO, adiabatic, relativistic, and QED effects but no provision for nonadiabatic effects, therefore represent an accurate characterization of the value of nonadiabatic effects for each H_3^+ level. Allowance for nonadiabatic effects using the simple model of PT [28] results in a further reduction of this deviation to 0.22 cm^{-1}. Use of the nonadiabatic model of Diniz *et al.* shows that in this model the use of QED corrections reduces the errors in the results by almost a factor of 2 from 0.33 to 0.19 cm^{-1}. This demonstrates the necessity of including QED corrections in accurate *ab initio* treatments of H_3^+ rotation-vibration energy levels; it opens the way for the development of an accurate nonadiabatic model which could potentially reach the 10^{-2} cm^{-1} accuracy necessary for the assignment of the Carrington-Kennedy [18] near-dissociation spectrum of H_3^+ and its isotopologs.

[1] P. Pyykkö, Chem. Rev. **112**, 371 (2012).

[2] W. Liu, Phys. Rep., doi:10.1016/j.physrep.2013.11.006.

[3] J. Autschbach, J. Chem. Phys. **136**, 150902 (2012).

[4] W. Liu, Phys. Chem. Chem. Phys. **14**, 35 (2012).

[5] W. Kutzelnigg, Chem. Phys. **395**, 16 (2012).

[6] M. Iliaš, V. Kellö, and M. Urban, Acta Phys. Slovaca **60**, 259 (2010).

[7] G. Tarczay, A. G. Császár, W. Klopper, and H. M. Quiney, Mol. Phys. **99**, 1768 (2001).

[8] M. Reiher and A. Wolf, *Relativistic Quantum Chemistry* (Wiley, Hoboken, NJ, 2009).

[9] K. G. Dyall and K. Faegri, *Introduction to Relativistic Quantum Chemistry* (Oxford University Press, Oxford, 2007).

[10] R. E. Moss, J. Phys. B **32**, L89 (1999).

[11] V. I. Korobov, Phys. Rev. A **74**, 052506 (2006).

[12] V. I. Korobov, Phys. Rev. A **77**, 022509 (2008).

[13] Z.-X. Zhong, P.-P. Zhang, Z.-C. Yan, and T.-Y. Shi, Phys. Rev. A **86**, 064502 (2012).

[14] J. Komasa, K. Piszczatowski, G. Łach, M. Przybytek, B. Jeziorski, and K. Pachucki, J. Chem. Theory Comput. **7**, 3105 (2011).

[15] E. J. Salumbides, G. D. Dickenson, T. I. Ivanov, and W. Ubachs, Phys. Rev. Lett. **107**, 043005 (2011).

[16] G. D. Dickenson, M. L. Niu, E. J. Salumbides, J. Komasa, K. S. E. Eikema, K. Pachucki, and W. Ubachs, Phys. Rev. Lett **110**, 193601 (2013).

[17] M. Pavanello, L. Adamowicz, A. Alijah, N. F. Zobov, I. I. Mizus, O. L. Polyansky, J. Tennyson, T. Szidarovszky, A. G. Császár, M. Berg *et al.*, Phys. Rev. Lett. **108**, 023002 (2012).

[18] A. Carrington, J. Buttenshaw, and R. A. Kennedy, Mol. Phys. **45**, 753 (1982).

[19] A. Carrington and R. A. Kennedy, J. Chem. Phys. **81**, 91 (1984).

[20] A. Carrington and I. R. McNab, Acc. Chem. Res. **22**, 218 (1989).

[21] J. Tennyson, Rep. Prog. Phys. **58**, 421 (1995).

[22] K.-Y. Wu, Y.-H. Lien, C.-C. Liao, Y.-R. Lin, and J.-T. Shy, Phys. Rev. A **88**, 032507 (2013).

[23] J. N. Hodges, A. J. Perry, P. A. Jenkins, B. M. Siller, and B. J. McCall, J. Chem. Phys. **139**, 164201 (2013).

[24] T. Furtenbacher, A. G. Császár, and J. Tennyson, J. Mol. Spectrosc. **245**, 115 (2007).

[25] T. Furtenbacher, T. Szidarovszky, C. Fábri, and A. G. Császár, Phys. Chem. Chem. Phys. **15**, 10181 (2013).

[26] T. Furtenbacher, T. Szidarovszky, E. Mátyus, C. Fábri, and A. G. Császár, J. Chem. Theory Comput. **9**, 5471 (2013).

[27] M. Pavanello, L. Adamowicz, A. Alijah, N. F. Zobov, I. I. Mizus, O. L. Polyansky, J. Tennyson, T. Szidarovszky, and A. G. Császár, J. Chem. Phys. **136**, 184303 (2012).

[28] O. L. Polyansky and J. Tennyson, J. Chem. Phys. **110**, 5056 (1999).

[29] R. E. Moss, Mol. Phys. **80**, 1541 (1993).

[30] L. G. Diniz, J. R. Mohallem, A. Alijah, M. Pavanello, L. Adamowicz, O. L. Polyansky, and J. Tennyson, Phys. Rev. A **88**, 032506 (2013).

[31] O. L. Polyansky, A. G. Császár, S. V. Shirin, N. F. Zobov, P. Barletta, J. Tennyson, D. W. Schwenke, and P. J. Knowles, Science **299**, 539 (2003).

[32] O. L. Polyansky, R. I. Ovsyannikov, A. A. Kyuberis, L. Lodi, J. Tennyson, and N. F. Zobov, J. Phys. Chem. A **117**, 9633 (2013).

[33] O. V. Boyarkin, M. A. Koshelev, O. Aseev, P. Maksyutenko, T. R. Rizzo, N. F. Zobov, L. Lodi, J. Tennyson, and O. L. Polyansky, Chem. Phys. Lett. **568-569**, 14 (2013).

[34] H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz *et al.*, MOLPRO, version 2012.1, University College Cardiff Consultants Limited, Cardiff, UK, 2012, http://www.molpro.net.

[35] T. H. Dunning, Jr., J. Chem. Phys. **90**, 1007 (1989).

[36] T. Shiozaki and H.-J. Werner, Mol. Phys. **111**, 607 (2013).

[37] C. Hättig, W. Klopper, A. Köhn, and D. P. Tew, Chem. Rev. **112**, 4 (2012).

[38] L. Kong, F. A. Bischoff, and E. F. Valeev, Chem. Rev. **112**, 75 (2012).

[39] S. Ten-No and J. Noga, WIREs Comput. Mol. Sci. **2**, 114 (2012).

[40] T. Shiozaki, G. Knizia, and H.-J. Werner, J. Chem. Phys. **134**, 034113 (2011).

[41] K. Pachucki, Phys. Rev. A **85**, 042511 (2012).

[42] K. Pachucki, Phys. Rev. A **82**, 032509 (2010).

[43] K. A. Peterson, D. Feller, and D. A. Dixon, Theor. Chem. Acc. **131**, 1079 (2012).

[44] D. Feller, K. A. Peterson, and J. G. Hill, J. Chem. Phys. **135**, 044102 (2011).

[45] K. A. Peterson, T. B. Adler, and H.-J. Werner, J. Chem. Phys. **128**, 084102 (2008).

[46] K. E. Yousaf and K. A. Peterson, J. Chem. Phys. **129**, 184108 (2008).

[47] W. Meyer, P. Botschwina, and P. R. Burton, J. Chem. Phys. **84**, 891 (1986).

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

[49] W. Cencek, J. Rychlewski, R. Jaquet, and W. Kutzelnigg, J. Chem. Phys. **108**, 2831 (1998).

[50] O. L. Polyansky, R. Prosmiti, W. Klopper, and J. Tennyson, Mol. Phys. **98**, 261 (2000).

[51] R. A. Bachorz, W. Cencek, R. Jaquet, and J. Komasa, J. Chem. Phys. **131**, 024105 (2009).

[52] L. P. Viegas, A. Alijah, and A. J. C. Varandas, J. Chem. Phys. **126**, 074309 (2007).

[53] L. Velilla, B. Lepetit, A. Aguado, J. A. Beswick, and M. Paniagua, J. Chem. Phys. **129**, 084307 (2008).

[54] B. M. Dinelli, S. Miller, and J. Tennyson, J. Mol. Spectrosc. **163**, 71 (1994).

[55] J. Tennyson, B. M. Dinelli, and O. L. Polyansky, J. Molec. Struct. THEOCHEM **341**, 133 (1995).

[56] R. Prosmiti, O. L. Polyansky, and J. Tennyson, Chem. Phys. Lett. **273**, 107 (1997).

[57] W. A. Majewski, P. A. Feldman, J. K. G. Watson, S. Miller, and J. Tennyson, Astrophys. J. **347**, L51 (1989).

[58] S. S. Lee, B. F. Ventrudo, D. T. Cassidy, T. Oka, S. Miller, and J. Tennyson, J. Mol. Spectrosc. **145**, 222 (1991).

[59] B. M. Dinelli, L. Neale, O. L. Polyansky, and J. Tennyson, J. Mol. Spectrosc. **181**, 142 (1997).

[60] O. Asvany, E. Hugo, S. Schlemmer, F. Muller, F. Kuhnemann, S. Schiller, and J. Tennyson, J. Chem. Phys. **127**, 154317 (2007).

[61] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Systems*, reprint (Dover, Mineola, NY, 2008). First published 1957 by Academic Press.

[62] L. Lodi and J. Tennyson, J. Phys. B **43**, 133001 (2010).

[63] P. Pyykkö, K. G. Dyall, A. G. Császár, G. Tarczay, O. L. Polyansky, and J. Tennyson, Phys. Rev. A **63**, 024502 (2001).

[64] J. Tennyson, M. A. Kostin, P. Barletta, G. J. Harris, O. L. Polyansky, J. Ramanlal, and N. F. Zobov, Comput. Phys. Commun. **163**, 85 (2004).

[65] M. Pavanello, W.-C. Tung, F. Leonarski, and L. Adamowicz, J. Chem. Phys. **130**, 074105 (2009).