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Assigning quantum labels and improving accuracy for the ro-vibrational eigenstates of H_3^+ calculated using *ScalIT*

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In a recent article [AIP Adv. 11, 045033 (2021)], we carried out exact quantum dynamical calculations and computed ro-vibrational energy levels and wave functions for the H_3^+ molecular ion up to the dissociation threshold (at $J = 46$) using a recently developed potential energy surface (PES) [Mol. Phys. 117, 1663 (2019)]—arguably, the most accurate to date —together with the ***ScalIT*** suite of parallel codes. In this work, we further improved the convergence accuracy and range of our ***ScalIT*** calculations for all J values up to $J = 20$ to a few 10^{-5} cm^{-1} (or better). In addition, we performed an *ab initio* assignment of the ro-vibrational energy levels, providing vibrational 'v_1, v_2, $|l|$' and rotational 'J, G, U, K' quantum labels for more than 2,200 ro-vibrational states, including every single $0 \le J \le 20$ state up to and above the barrier to linearity at 10,000 cm^{-1}. The main underlying motivation of our work is to provide a list of reliably labeled, spectroscopically accurate energy levels in a format that can be used in spectroscopic line lists, which are based on both experimental and theoretical levels. Such line lists are of huge importance in various astrochemical and astrophysical contexts.

KEYWORDS

ab initio, ro-vibrational energy levels, quantum label assignment, high accuracy, ScalIT code

1 Introduction

The H_3^+ molecular ion [1]—the smallest tri-atomic molecular system, with just three protons and two electrons—is a central molecule in molecular astrophysics and astrochemistry. It is the most common molecular ion in the Universe, serving as the main conduit of chemical reactions in outer space. H_3^+ can be found in the interstellar medium [2], supernova remnants [3], the atmospheres of gas giants, and exoplanets [4, 5], and also plays an important role in star formation [1]. Partially due to its simplicity, H_3^+ serves as a benchmark system for several different areas of science, in particular, high-resolution ro-vibrational spectroscopy experiments, accurate *ab initio* electronic structure calculations and potential energy surface (PES) development, high performance quantum dynamics calculations, and reaction dynamics. Despite its simplicity, the near-dissociation spectrum of H_3^+ [6, 7]—recorded 40 years ago!—still remains unassigned.

H_3^+ has been studied very extensively both experimentally and computationally in the last four decades, as was recently summarized in a very nice review [1].

On the experimental side, numerous spectroscopic studies have been conducted [6–14]. Of course, the primary challenge with respect to labeling is that experiments provide only spectroscopic *transitions*, not the ro-vibrational energy levels themselves. Although symmetry and selection rules help, extracting the latter from the former remains a challenge, and has traditionally been something of a "black art." Recently, more systematic approaches have been developed, based on graph theory and "spectroscopic networks" (SNs) [15, 16], in which the vertices represent rovibrational energy levels, and the lines represent experimentally observed spectroscopic transitions, to extract empirical energy levels directly from experimental data, with well-defined and realistic uncertainties. In particular, the MARVEL code (Measured Active Rotational–Vibrational Energy Levels) [17, 18], has been applied to ro-vibrational spectroscopic data of H_3^+ that were collected from 26 separate experimental sources [13]. The resultant energy levels and assignments replaced the earlier work of [8]. A MARVEL analysis was also carried out for two isotopologues, H_2D^+ and D_2H^+ [14], with the database last updated in 2019 [19]. Thus far, the number of validated, and therefore recommended, experimental quality ro-vibrational energy levels of H_3^+ are 652, [19] of which 259 belong to ortho-H_3^+ (I = 3/2) and 393 to para-H_3^+ (I = 1/2), with I being the quantum number of the total nuclear spin of the system.

On the theoretical side, due to its spectroscopic importance, a variety of H_3^+ PESs have been developed over the years [11, 12–26]—with the latest two [25, 26] published only very recently. A number of ro-vibrational state calculations have also been performed in the past for this system [12, 22–43], many employing empirical corrections of various kinds (e.g., empirically modified vibrational masses [44, 45]) in order to better match the available experimental data, and also to capture non-adiabatic effects [24, 25, 34, 37–39, and 41]. The empirical approach might be less effective at higher energies, [35]—e.g., in the context of reactive collisions, which have also been extensively studied for H_3^+ [46–48]. Additionally, empirical "corrections" can become a bit tricky, if there is any question as to how to match experimental and theoretical state labels.

For these reasons, we prefer a fully *ab initio* computational approach [43], both with regard to the ro-vibrational state calculation itself, as well as the determination of state labels. In particular, to the best of our knowledge, we are the first group to attempt a fully *ab initio* assignment of ro-vibrational state labels for H_3^+. Our first push in this direction was published in an article last year [43]; however, the set of J values considered in that work was restricted, and in addition, we did not use wave functions to help determine ro-vibrational state labels, but only D_{3h} symmetry labels. In addition, although the calculations were very well converged (10^{-4} cm^{-1}), better convergence would have allowed for a better determination of symmetry-induced vs. "accidental" degeneracies, which in turn leads to a less ambiguous state labeling, especially at higher vibrational and rotational excitation energies. All of these small deficiencies of the previous work have been rectified here, as discussed below.

As further motivation for adopting a purely *ab initio* approach, we point out that H_3^+ has always been targeted as an important benchmark system for achieving a direct spectroscopic agreement between theory and experiment. This has been a long-standing goal, which it can be argued, has only begun to be obtained fairly recently [12, 24]. Additionally, the highly accurate determination of the ro-vibrational spectrum of astrophysically relevant molecules such as H_3^+ is motivated by the "weed problem" [49, 50]. In the interstellar medium and planetary atmospheres, many different molecules or ions are present at the same time. As the spectra overlap, it is crucial to obtain highly accurate spectra in order to unambiguously differentiate the contributions from different species.

Therefore, creating highly accurate line lists can serve as an important tool, from both the experimental and computational points of view. The first such line list was created by [51] with 669 astronomically important lines. This was supplemented by [52], with about three million lines. The newest line list, MiZaTeP [53], contains more than 120 million lines by bringing together the experimental spectroscopic data using MARVEL [13], and theoretical levels computed with the DVR3D code [54–56]. This line list also contains 17 meta-stable states, which are quantum states with very long lifetimes.

In this work, in order to facilitate the expansion of already existing H_3^+ line lists, we focus our efforts on further improving the convergence accuracy of our *ab initio* ro-vibrational energy level calculations down to a few 10^{-5} cm^{-1}. This is far beyond the accuracy of the PES, and certainly much smaller than the discrepancies within the experiment. Nevertheless, such an extraordinarily high convergence accuracy is essential with respect to unambiguous state labeling, as discussed, especially at higher vibrational and rotational excitation energies. Additionally, we compute and analyze ro-vibrational wave functions to determine their "vibrational parent" states [57] as a further means of providing unambiguous labels. In the present work, we also consider *all* values of the rotational quantum number J, not just selected values—but only up to a maximum of J = 20. In the previous work [43], we considered higher J values, all the way up to rotational dissociation (J = 46). Here, we apply a restriction to comparatively low values, simply because the quantum label assignment (which is a primary focus of this work) becomes essentially impossible much beyond this point.

In all, we provide vibrational 'v_1, v_2, $|l|$' and rotational 'J, G, K, U' quantum labels for more than 2,200 ro-vibrational states, around 1,600 of which are new assignments complementing, and in certain cases arguably correcting, the ~650 assignments in the MARVEL database [19]. To the best of our knowledge, no previous work has attempted to provide purely *ab initio* quantum label assignments for computed ro-vibrational states—certainly not to the extent that we have done here, in any event.

2 Materials and methods

In a recent article [43], we carried out the exact ro-vibrational energy level and wave function calculations for the H_3^+ molecular ion for selected J values up to J = 46. As most of the computational details remain unchanged, here, we only provide a brief summary of the overall computational methodology, and focus primarily on the differences from the previous work.

2.1 *ScalIT*

The quantum dynamical calculations presented in this article were performed using the ***ScalIT*** [58–62] suite of parallel codes. ***ScalIT*** is a black-box molecular ro-vibrational spectroscopy code, which for tri- and tetratomic molecules employs an analytical kinetic energy operator expressed in (orthogonal) Jacobi coordinates. The use of direct product basis sets (DPBs) including discrete variable representations (DVRs) results in a Hamiltonian matrix with a sparse structure. For the radial coordinates, phase–space-optimized DVRs (PSO-DVRs) are used [63–68] while for the bend and rotation angles, standard associated Legendre polynomial or Wigner rotation function basis sets are utilized. The Hamiltonian is diagonalized iteratively using sparse Krylov subspace methods together with several different effective numerical optimization strategies, such as the preconditioned inexact spectral transform (PIST) method [69–71], optimal separable basis (OSB) preconditioning [72–75], and the standard iterative quasi-minimal residual (QMR) algorithm [59, 76]. All of these methods working together ensure the effective scaling across massively parallel supercomputing clusters (up to a few thousand cores) and the ability of ***ScalIT*** to accurately compute even extremely energetically high-lying quantum states. So far, ***ScalIT*** has been used for around a dozen challenging systems, such as Ne_4 and HCCH [43, 50, 68, and 77–86], and via extending the capabilities of the ***ScalIT*** code through the ***SwitchIT*** [87] algorithm to accommodate more complicated Hamiltonians, even CH_3CN [87].

The massively parallel capability of ***ScalIT*** is based on MPI parallelization, which makes the code uniquely qualified to compute many quantum states with high accuracy for small molecular systems. Other available ro-vibrational spectroscopy codes, e.g., ***DVR3D*** [54–56], ***TROVE*** [88–90], ***DOPI*** [33, 91, 92], ***DEWE*** [57, 93–95], ***GENIUSH*** [96, 97], and ***ElVibRot*** [98–100], in general traditionally only offer single node OPENMP parallelization (although ***ElVibRot*** has been made MPI parallel recently [101]). Also, it is worth mentioning that the use of GPUs is spreading slowly to the field of ro-vibrational molecular spectroscopy with a focus on computing ro-vibrational intensities [102].

2.2 Potential energy surface

In this work, we utilized the recently computed H_3^+ PES referred to as "PES75K+" [25] which is based on the Born–Oppenheimer *ab initio* points of the earlier "GLH3P″ PES [12, 24], the first "calibration quality" PES developed for H_3^+. In our previous work, we compared these two PESs and discussed the spurious asymptotic wells that appear in the GLH3P PES [43], which were causing significant numerical convergence problems for our ***ScalIT*** calculations. Although GLH3P has been used more frequently in previous computational ro-vibrational spectroscopy studies, PES75K+ has now been shown to provide more accurate energy levels higher up in the spectrum.

In any event, the H_3^+ PES shows this molecular ion to be quite stable. The first dissociation threshold (to $H_2 + H^+$) occurs at $D_0 = 35,076 \pm 2\ \mathrm{cm}^{-1}$ [25]. However, there is a much lower-lying (linear) isomerization barrier at around $10,000\ \mathrm{cm}^{-1}$.

2.3 Previous computational works

For the GLH3P PES [12, 24]—and other earlier PESs, including the PES developed by Cencek and colleagues [20, 21]—a wide range of ro-vibrational calculations have been performed [12, 22–24, 27–29, 31, 32, 34–40, 42, and 43]. Most of these are summarized in a fairly recent review article [40]. In the last couple of years, newer PESs have been also developed, among them, the PES75K+ PES [25] is used here, and also a multi-sheet fit PES including more than one electronic state [26]. By and large, the ro-vibrational studies have focused on increasing the accuracy of numerical convergence, as well as pushing the limits of vibrational/rotational excitation. Indeed, computing ro-vibrational energy levels of H_3^+ near dissociation has a long history [3, 27, 29]. To date, all energy levels were computed up to dissociation using atomic [30, 33], nuclear [35], and modified hydrogen masses [35] to investigate the properties of high-lying vibrational states. More restricted calculations—both in terms of energy and rotational excitation, but also accuracy—were also carried out, up to $J = 2$ and 15,300 cm^{-1} [32], and up to $J = 3$ and the then-experimental limit of ~17,000 cm^{-1} [24]. The dependence of Coriolis coupling on choice of "embedding" or body-fixed frame was also investigated [42].

2.4 Symmetry

Jacobi coordinates (denoted as r, R, and θ here) are usually the best choice for describing AB$_2$ triatomic molecules. In such cases, the full G_4 permutation–inversion (PI) symmetry of the molecules is fully described. Of course, H_3^+, with its three identical atomic nuclei, is an A$_3$ system, whose energy levels are labeled by the G$_{12}$ PI group irreducible representations (irreps) [103]. Note that G$_{12}$ is isomorphic with the D$_{3h}$ point group—which, in any event, describes the global minimum equilibrium structure of H_3^+, which is an equilateral triangle with a bond length of 1.65034a$_0$ = 0.873 322Å.

Nevertheless, since Jacobi coordinates, in contrast to hyperspherical coordinates [104], do not respect the cyclic permutation operations of the G$_{12}$ PI group, this poses certain challenges for the ***ScalIT*** calculation performed here, which essentially presumes an AB$_2$ structure. More specifically, it becomes necessary to correlate the symmetry labels from the G_4 symmetry-adapted ***ScalIT*** calculations to the G$_{12}$/D_{3h} labels, using the $\Gamma(D_{3h}) \downarrow G_4$ correlation table [43]. The "challenge" here actually only concerns the doubly-degenerate D_{3h} irrep pairs, which are computed in different ***ScalIT*** calculations corresponding to different G_4 irreps. In practice, one looks for identical eigenvalues across two G_4 irreps, and identifies those as comprising, in reality, a single doubly-degenerate G$_{12}$ irrep pair. Better convergence accuracy thus greatly improves the determination of numerically "identical" eigenvalues. Conversely, whatever pair splitting is observed numerically may be taken as an additional, independent measure of the overall numerical convergence accuracy.

The solutions of the AB$_2$ Jacobi Hamiltonian are computed in four separate "symmetry blocks", corresponding to the four (singly-degenerate) irreps of G_4. These irreps can be labeled by two good quantum numbers, $p = \pm 1$ (associated with the exchange of any two identical nuclei) and $\epsilon = \pm 1$ (the total parity). In addition, there are the two good rotational quantum numbers that can be used as completely reliable labels—i.e., the total angular momentum, J, and its projection along the space-fixed Z axis, M. The third rotational quantum number, K, associated with the projection of $\overrightarrow{\hat{J}}$ along the *body-fixed z* axis, is technically not a good quantum number—though for H_3^+, it may still often be used as a state label in practice, together with other approximate labels described in Section 3.2.

TABLE 1 **The total bend-rotation angular basis sizes of each G_4 symmetry block, $N_{jK}^{A^+}$, $N_{jK}^{B^+}$, $N_{jK}^{A^-}$, and $N_{jK}^{B^-}$, for all *ScalIT* calculations of H_3^+ performed here, from total angular momentum $J = 0$ to $J = 20$. The number of bend-angle basis functions in θ, i.e., $j_{\max}$, is always equal to 36. The radial basis sizes are $N_r = N_R = 300$, and the radial ranges (in atomic units) are $r_{\min} = 0.5$, $R_{\min} = 0.0$, and $r_{\max} = R_{\max} = 5.0$.**

	G_1	G_2 (S_2) blocks		G_4 blocks			
J	N_{jK}	N_{jK}^{A}	N_{jK}^{B}	$N_{jK}^{A^+}$	$N_{jK}^{B^+}$	$N_{jK}^{A^-}$	$N_{jK}^{B^-}$
0	37	37	0	19	18	0	0
1	109	36	73	18	18	37	36
2	179	108	71	55	53	36	35
3	247	105	142	53	52	72	70
4	313	175	138	89	86	70	68
5	377	170	207	86	84	105	102
6	439	238	201	121	117	102	99
7	499	231	268	117	114	136	132
8	557	297	260	151	146	132	128
9	613	288	325	146	142	165	160
10	667	352	315	179	173	160	155
11	719	341	378	173	168	192	186
12	769	403	366	205	198	186	180
13	817	390	427	198	192	217	210
14	863	450	413	229	221	210	203
15	907	435	472	221	214	240	232
16	949	493	456	251	242	232	224
17	989	476	513	242	234	261	252
18	1027	532	495	271	261	252	243
19	1063	513	550	261	252	280	270
20	1097	567	530	289	278	270	260

Lastly, given the fermionic nature of the H atom nuclei (i.e., protons), it is worth mentioning that the Pauli principle requires the total spin-plus-spatial nuclear wave function to have a totally anti-symmetric or A$_2$ character (in the S_3 permutation subgroup of the G$_{12}$ PI group). For three such particles, the eight-dimensional combined nuclear spin space representation reduces to an irrep direct sum as 4A$_1$⊕2E. The corresponding spatial wave functions (i.e., the ro-vibrational states actually computed) are thus restricted to belonging to either the A$_2$ or E irreps. Therefore, all A$_1$ ro-vibrational states (including what would otherwise be the ground vibrational state), are unphysical, and must be ignored.

3 Results

3.1 Computational details

ScalIT computations were carried out using nuclear masses, just as in our previous article [43]. The computational parameters of this work are summarized in Table 1. In DVR calculations such as those performed here, very often as one increases the basis size in order to improve numerical convergence, one crosses over from a regime where the basis set truncation error dominates, to a regime where the numerical quadrature error dominates. This is indicated by a fast, variational convergence (from above) being replaced by a slow, oscillatory convergence behavior. Usually, when this crossover has occurred, it becomes computationally unfeasible to push the calculation much further through a "brute force" increase in the basis size.

For extremely accurately converged ro-vibrational calculations, it is therefore necessary to ensure that the quadrature error is minimized. This requires two conditions. First, the PES must be very smooth and well-behaved—which, in the case of PES75K+ (but unlike GLH3P), has already been established. Second, the "primitive basis" calculations used to compute the PSO DVR basis representations must be performed as accurately as possible. To this end, a very large number of 1,001 primitive sinc-DVR grid points were used in the PSO DVR calculations for both of the Jacobi radial coordinates, r and R. The radial ranges used here were also wider than before [43]; here, we used $r_{\text{min}} = 0.5$ bohr, and $r_{\text{max}} = 5.0$ bohr for the r coordinate, and $R_{\text{min}} = 0.0$ bohr, and $R_{\text{max}} = 5.0$ bohr for the R coordinate.

Having put these measures into effect, our next task was to increase the basis sizes for the final calculation as far as possible, in hopes that an extremely high numerical convergence could be achieved prior to crossing over into the quadrature-error-dominated regime. We therefore used significantly larger radial basis sizes than in the previous calculation; i.e., $N_r = 300$ and $N_R = 300$. The angular dimensions were also increased compared to our previous work [43]; specifically, the number of bend-angle basis functions in the Jacobi coordinate θ was set to $j_{\text{max}} = 36$ for every J value considered. The resultant total bend-rotation angular basis sizes for each G_4 symmetry block calculation, i.e., $N_{jK}^{A^+}$, $N_{jK}^{B^+}$, $N_{jK}^{A^-}$, and $N_{jK}^{B^-}$, are listed in Table 1. Using these parameters, we were able to achieve better than 10^{-5} cm^{-1} numerical convergence for all ro-vibrational states with $J \leq 10$.

3.2 State Labeling

The ro-vibrational calculations of H_3^+ for each $J > 0$ were carried out in four blocks corresponding to the four G_4 irreps. Note that the inversion parity is linked to the value of K, with even $\epsilon = +1$ parity corresponding to the even K values, and odd $\epsilon = -1$ parity to the odd K values. Thus, for $J = 0$, we only have two even parity blocks. States with $|K| \bmod 3 = 0$ are ortho-states with a spin weighting $g_s = 4$, while those with K not exactly divisible by 3 are para-states with $g_s = 2$ [1]. As the convergence accuracy of our calculations is very high, the degenerate energy levels can be unambiguously identified, and therefore, it is easy to assign the D_{3h} (i.e., G_{12}) irrep labels even for highly vibrationally and rotationally excited states.

Next, we address the vibrational state labels. The H_3^+ molecular ion has two normal modes, the totally symmetric stretch mode ν_1 (belonging to the singly degenerate A_1 irrep), and the asymmetric stretch-bend mode, ν_2 (belonging to the doubly degenerate E irrep). Displacements of the latter distort the A_1 symmetry of the global minimum geometry, thereby producing a transition dipole moment. Also, being doubly degenerate, excitations of the ν_2 mode give rise to a new quantum number, the vibrational angular momentum l, adopting the values, $l = \{\nu_2, \nu_2 - 2, \ldots - \nu_2 + 2, - \nu_2\}$. Therefore, the vibrational part of the ro-vibrational states can be described by the labels, 'ν_1, ν_2, $|l|$'—although it must be borne in mind that these quantum numbers are not perfectly "good". Also note that the quantum number $|l|$ is linked to the D_{3h} irrep labels. In particular, the $l = 0$ vibrational states are always singly degenerate A_1' states. For $|l| > 0$, the degenerate pair can be labeled as E', unless $|l| \bmod 3 = 0$, for which the $\pm\, l$ pair splits into an A_1' and an A_2' state.

After first determining the D_{3h} irrep labels, we assigned vibrational state labels to the $J = 0$ pure-vibrational states, which were found to be in complete agreement with earlier studies [9, 10, 12, 13, 24, 32, and 43]. For $J > 0$, it is advantageous to first determine the vibrational labels, indicating which "vibrational parent" state the ro-vibrational state "belongs to". This is straightforward to do for low-vibrational and/or rotational excitations, where the energy level spacing is so high that the rotational progressions do not overlap. Higher up in energy, determining the "vibrational parents" becomes much more challenging. For $J = 1$, the different ro-vibrational progressions start to overlap at the 26th vibration at 10,000 cm^{-1}. Increasing J, this threshold energy value shifts down drastically. For $J = 11$, even the ro-vibrational states belonging to the zero-point vibration start to overlap with the ro-vibrational progression of the first vibration. Beyond a certain point in both (ν_1, ν_2, $|l|$) and J, it becomes impossible to assign vibrational parents based solely on energy values and D_{3h} symmetry labels.

In order to overcome this difficulty, the ***GENIUSH*** code [96, 97] was invoked, which is capable of semi-automatically assigning vibrational parent labels using the rigid rotor decomposition scheme (RRD) [57], based on computing wave function overlaps. To do this, the ***ScalIT*** calculations were repeated using ***GENIUSH***, but with greatly reduced accuracy (10^{-2}–10^{-3} cm^{-1})—which was nevertheless sufficient to match the energy levels with the ***ScalIT*** ones. The RRD overlap matrices were then computed using ***GENIUSH***. In this manner, we were able to assign vibrational parent labels to much more highly excited ro-vibrational states—and for many more such states—than was previously possible.

We next move on to rotational state labels. The H_3^+ molecular ion can be characterized as an oblate symmetric top, for which

TABLE 2 The lowest ro-vibrational energy levels of H_3^+, in cm^{-1}, up to $J = 20$ total angular momentum and their comparison with the literature. The past calculations employed different PESs and masses (VRM stands for Unequal Vibrational and Rotational Masses) [35].

	PES75K+		**GLH3P PES**			**Comparison**			
	nuclear mass				**VRM**				
J	**This work**	**Ref. 43**	**Ref. 43**	**Ref. 35**	**Ref. 35**	**Ref. 43**	**Ref. 43**	**Ref. 35**	**Ref. 35**
0	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
1	64.1277	64.1273	64.1283	64.1283	64.1233	0.0004	¯0.0006	¯0.0006	0.0044
2	169.3071	169.3075	169.3086	169.3086	169.2872	–0.0004	¯0.0015	¯0.0015	0.0199
3	315.3617	315.3621	315.3644	315.3644	315.3164	¯0.0004	¯0.0027	¯0.0027	0.0453
4	502.0545	502.0549	502.0588	502.0588	501.9737	¯0.0004	¯0.0043	¯0.0043	0.0808
5	729.0368	729.0372	729.0431	729.0431	728.9106	¯0.0004	¯0.0063	¯0.0063	0.1262
6	995.9055	995.9060	995.9140	995.9141	995.7241	¯0.0004	¯0.0085	¯0.0086	0.1814
7	1302.1793	1302.1798	1302.1903	1302.1904	1301.9329	¯0.0005	¯0.0110	¯0.0111	0.2464
8	1647.3068	1647.3072	1647.3208	1647.3208	1646.9864	¯0.0004	¯0.0139	¯0.0140	0.3204
9	2030.6710	2030.6714	2030.6881	2030.6881	2030.2674	¯0.0004	¯0.0171	¯0.0171	0.4036
10	2451.5921	2451.5925	2451.6127	2451.6127	2451.0967	¯0.0004	¯0.0206	¯0.0206	0.4954
11	2909.3322			2909.3565	2908.7365			¯0.0243	0.5957
12	3403.0987			3403.1270	3402.3957			¯0.0283	0.7030
13	3932.0489			3932.0815	3931.2291			¯0.0326	0.8198
14	4495.2944			4495.3314				¯0.0370	
15	5091.9050	5091.9053	5091.9466	5091.9467		¯0.0003	¯0.0416	¯0.0417	
16	5720.9135			5720.9601				¯0.0466	
17	6381.3199			6381.3715				¯0.0516	
18	7072.0957			7072.1524				¯0.0567	
19	7792.1880			7792.2501				¯0.0621	
20	8540.5241	8540.5246	8540.5914	8540.5916		¯0.0005	¯0.0673	¯0.0675	

rotational states can be described using the J and K rotational quantum labels as:

$$E_{JK} \sim BJ(J+1) + (C-B)K^2. \tag{1}$$

where E_{JK} is the relative energy of the ro-vibrational state corresponding to its vibrational parent. Although for H_3^+ J is always a good quantum number, due to the coupling of the rotational and the vibrational (l) angular momenta in this case, it has been argued [8, 105–107] that instead of using K, it is better to use $G = |K - l|$, which becomes a much better quantum number at low energies [8]. However, we will assign values to both.

For $l = 0$, $G = |K|$, and so the usual $(2J + 1)$-fold rotational progression arises. For $|l| > 0$, however, the$\pm l$ values double the number of the rotational excited states to $2\,(2J + 1)$. For $|l| > J$, there is only one rotational progression, where $G_{\min} = (|l| - J) \leq G \leq G_{\max} = (|l| + J)$. For $|l| \leq J$, the rotational excited states can be separated into two distinct rotational progressions [8, 107], with $0 \leq G \leq G_{\max} = (J + |l|)$, and $0 \leq G' \leq G'_{\max} = (J - |l|)$, and they have $(2G_{\max} + 1)$ and $(2G'_{\max} + 1)$ states, respectively. These two rotational progressions often have different rotational constants and a trend similar to Eq. 1

$$E_{JG} \sim BJ(J+1) + (C-B)G^2 \tag{2}$$

$$E'_{JG'} \sim B'J(J+1) + (C'-B')G'^2. \tag{3}$$

As it usually holds that $G_{\max} > J$, E_{JG} can become *negative*—as happens, e.g., for the A_2'' state, $(v_1, v_2, |l|, J, G)$=(0 2 2 1 3). This behavior is similar to the negative rotational energies observed for "quasi-structural" molecules [108] such as H_5^+ [109], CH_5^+ [110–112], $CH_4{\cdot}H_2O$ [113], $CH_4{\cdot}CH_4$, and $H_2O{\cdot}H_2O$ [114].

The presence of the two progressions requires that in addition to G, a new quantum number, U [8, 107], has to be introduced. U can take the values "u", "l", or "m" to distinguish between upper and lower energy levels with the same (v_1, v_2, $|l|$, J, G) assignment (note, that U = "l" always refers to levels within the G' progression). Therefore, the rotational part of the wave function can be unambiguously described by the (J, G, U) quantum labels. This, however, does not mean that we cannot assign K values to each ro-vibrational state, as from the definition of G, we can assign $|K| = |G - |l||$ for the unprimed progressions, and $|K| = G' + |l|$ for the primed progressions. Therefore, in the end, we characterize the rotational part using the (J, G, U, K) quantum label quartet.

For $J > 0$, D_{3h} irrep labels are also linked to the quantum numbers, but it is actually G which is most directly impacted (for $J = 0$, $|l| = G$). The D_{3h} irrep is A_1 or A_2 if $G = 0$ (if $l = 0$, we have A_1 for even and A_2 for odd J values), and for $G > 0$, similarly to $J = 0$, the degenerate pair can be labeled as E unless $|l| \bmod 3 = 0$, where the $\pm\, l$ pair splits into $A_1 \oplus A_2$. For large G values, especially for $G \geq 12$, the two singly degenerate levels can get closer than $10^{-5}\,\mathrm{cm}^{-1}$; therefore, in certain cases, G values have to be taken into account when assigning D_{3h} labels.

Finally, note that to further aid in the assignment of the rotational labels, the RRD overlaps of ***GENIUSH*** also provide insights into the value of K. This occurs through the vibrational parent being assigned (in particular, l) into the G quantum number, as the symmetric top rigid rotor functions are labeled by K. This feature of the approach helped us tremendously in carrying out the task of assigning labels—so long as the RRD overlap values were significantly large.

3.3 Ro-vibrational energy levels

The ro-vibrational energy levels reported in this article are presented in cm^{-1}, relative to the zero-point vibrational energy, 4362.1726 cm^{-1}. The levels were obtained for each J, ϵ, and p set of values in a separate ***ScalIT*** calculation with a single PIST spectral window, usually including 70 to 120 ro-vibrational states. The number of computed levels and the highest energy level computed is summarized in Table 3 for each J value. Note that these numbers include the unphysical states, and the doubly degenerate states are counted twice. In total, 105 vibrational energy levels were computed, up to 16,500 cm^{-1}, significantly over the isomerization barrier. For $J = 1$, the computed states (around 350 in all) covered the range up to 17,300 cm^{-1}. For $2 \leq J \leq 7$, around 420 to 480 levels were computed for each J up to the decreasing energy limit of 15,600 to 12,600 cm^{-1} with the increase of J. For higher J values, around 300 levels were computed for each J. For $8 \leq J \leq 20$, the energy range increased from 10,800 cm^{-1} for $J = 8$ to up to 16,700 cm^{-1} for $J = 20$. All of the computed levels are included in the Supplementary Material.

In Table 2, the lowest ro-vibrational energy levels of H_3^+ for each J up to $J = 20$ are compared with past [35, 43] calculations. The PES75K+ has been only used in our previous study [43] so far, using nuclear masses. The levels computed here are only slightly lower than those, by $3–5 \times 10^{-4}$ cm^{-1} for all levels. In our previous study, we also carried out computations [43] using the GLH3P PES, just as Ref [35], as well. Those two sets of numbers are identical and slightly higher than the numbers of this work, by up to 0.07 cm^{-1}. Ref [35] also repeated their calculations by unequal vibrational and rotational masses, which yielded eigenvalues lower than ours, by 0.8 cm^{-1} up to $J = 13$. We did not modify our masses because we prefer keeping our calculations "ab initio". In the future, we plan to do further investigations where we include non-adiabatic effects explicitly through non-adiabatic calculations with multiple PESs. [26].

TABLE 3 For each J value, the total number of states computed (comp.) and labeled (lab.). Note that the former number includes the unphysical states as well, and there the doubly degenerate states are counted twice. E_{comp} and E_{lab} are the threshold energies for computation and labeling, respectively. As not all the states were labeled up to E_{lab}, a separate threshold was also included, up to which all the states are labeled ($E_{\mathrm{lab}}' < E_{\mathrm{lab}}$).

J	Comp	Lab	E_{comp}	E_{lab}	E_{lab}'
0	105	29	16 460.5	14 056.4	14 056.4
1	354	107	17 327.3	14 193.8	14 193.8
2	429	111	15 662.9	14 850.8	14 319.1
3	442	127	14 409.2	13 641.7	12 680.0
4	450	117	13 514.7	11 892.5	11 624.5
5	467	117	13 131.6	10 116.4	10 116.4
6	421	122	12 236.7	10 166.2	10 166.2
7	477	117	12 634.2	10 023.6	9019.8
8	302	113	10 775.2	10 230.3	9842.5
9	295	117	10 951.7	10 467.7	9893.7
10	311	126	11 398.6	11 077.1	10 187.2
11	293	135	11 374.0	11 237.6	10 899.2
12	300	98	11 840.5	10 713.4	10 673.5
13	298	102	12 289.8	11 132.4	11 132.4
14	301	102	12 845.1	12 035.7	11 789.9
15	295	108	13 373.0	12 990.1	12 168.4
16	300	66	14 013.6	12 695.7	11 445.3
17	311	70	14 759.9	13 694.8	12 067.3
18	300	70	15 268.0	14 720.9	12 845.8
19	303	61	15 959.9	14 263.7	13 409.8
20	310	58	16 736.1	14 997.5	14 213.4

The main focus of this work is, however, to provide vibrational and rotational quantum labels for as many states as possible. In our previous study [43], although D_{3h} irrep labels were provided for selected J values ($J = 10, 20, 30, 40, 46$) up to $J = 46$, we only provided a limited number of vibrational and rotational quantum label assignments. Only low J values $0 \leq J \leq 5$ and $J = 10$ were considered, and even those were mostly restricted to up to 8,000–9,000 cm^{-1}, so overall, below the isomerization limit. Only for $J = 0$ and 1 did we go above 10,000 cm^{-1}. Here, we pushed our efforts further with the help of wave function overlaps and provided assignments for almost all states below 10,000 cm^{-1}. In Table 3, we summarize the number of states labeled in this work for each J value separately as well as include the labeling threshold, E_{lab}. As for most J values, not all of the levels were assigned up to the given threshold energy, we separately include the energy value up to which all states are labeled, E'_{lab}.

TABLE 4 Suggested vibrational (v_1, v_2, $|l|$) and rotational (J, G, U, K) reassignments of H_3^+ MARVEL energy levels.

MARVEL									***ScalIT***							
Level	**Sym**	v_1	v_2	l_2	J	G	U	K	**Level**	δE	v_1	v_2	l_2	G	U	K
7008.75	E'	0	1	1	11	7	u	6	7009.14	0.40	0	1	1	5	l	6
7676.65	E''	1	1	1	9	8	u	7	7677.00	0.34	1	1	1	8	l	9
8135.75	E''	0	2	2	9	5	l	7	8136.23	0.49	0	2	0	1	m	1
8176.10	E''	0	2	0	9	1	m	1	8176.60	0.49	0	2	2	5	l	7
8532.45	E'	1	2	2	4	2	l	4	8533.20	0.75	1	2	0	2	m	2
8872.11	E''	0	2	2	9	1	u	1	8872.72	0.61	1	1	1	2	l	3
8924.60	E''	1	1	1	9	2	l	3	8925.22	0.62	0	2	2	1	u	1
9158.44	E'	0	3	1	7	1	l	2	9159.14	0.70	0	3	3	7	m	4
9251.70	E''	0	2	2	11	7	u	5	9252.28	0.58	0	2	2	7	l	9
9313.04	E'	1	2	2	6	4	u	2	9313.88	0.84	2	1	1	7	m	6
9409.49	A_2''	0	3	3	6	0	m	3	9410.28	0.79	1	2	0	3	m	3
9428.61	E'	0	3	3	6	1	u	2	9429.39	0.78	1	2	0	2	m	2
9497.27	A_2''	0	2	2	12	9	u	7	9497.85	0.58	0	2	2	9	l	11
9643.34	E''	0	2	2	12	7	l	9	9643.78	0.44	0	2	0	7	m	7
9661.29	A_2'	1	2	0	7	6	m	6	9661.61	0.32	1	2	2	6	m	4
11 027.20	E'	0	5	3	2	5	m	2	11 028.01	0.82	0	5	1	1	l	2
11 108.27	E'	0	5	1	2	1	l	2	11 109.10	0.83	0	5	3	5	m	2
11 188.65	E''	2	2	2	3	1	u	1	11 189.51	0.87	0	5	1	2	l	3
11 207.16	E''	0	5	1	3	2	l	3	11 208.19	1.03	2	2	2	1	u	1
11 298.59	E'	0	5	3	3	5	m	2	11 299.41	0.82	0	5	1	1	l	2
11 369.04	A_2'	0	5	1	4	3	u	2	11 369.88	0.84	0	5	1	3	l	4
11 484.07	E'	0	5	1	3	1	l	2	11 484.92	0.86	0	5	3	5	m	2
11 771.38	E'	0	5	5	2	5	m	0	11 772.46	1.08	0	5	5	7	m	2
11 946.50	E'	1	4	0	2	2	m	2	11 947.55	1.05	0	5	5	5	m	0
11 984.97	E''	0	5	3	3	2	m	1	11 985.99	1.02	0	5	5	2	m	3
11 957.57	E''	0	5	3	2	2	m	1	11 958.60	1.03	0	5	5	4	m	1
12 058.87	E'	0	5	5	3	5	m	0	12 059.94	1.07	0	5	5	7	m	2
12 208.46	A_2''	0	5	3	3	0	m	3	12 209.51	1.05	0	5	5	6	m	1
12 267.00	E''	1	4	0	3	1	m	1	12 268.10	1.10	0	5	5	4	m	1
12 506.09	E''	1	4	4	1	5	m	1	12 507.17	1.08	0	6	0	1	m	1
12 687.29	E'	1	4	4	1	4	m	0	12 688.34	1.05	0	6	2	2	m	0
12 840.66	A_2'	1	4	4	3	6	m	2	12 841.77	1.11	2	3	1	2	m	2
13 135.71	E'	2	3	3	2	1	m	2	13 136.77	1.06	0	6	2	2	m	0

During this work, 2,210 ro-vibrational levels of H_3^+ have been assigned (v_1, v_2, $|l|$) vibrational and (J, G, U, K) rotational quantum labels. All of the labeled energy levels and their assignments are included in the Supplementary Material. For 1,571 of these levels, quantum labels have not been assigned before, while the remaining 639 levels are part of the 652 experimental ro-vibrational levels currently included in MARVEL. For 33 of these MARVEL levels, new vibrational (v_1, v_2, $|l|$) and/or rotational (J, G, U, K) assignments have been proposed (see Table 4).

In order to obtain all the quantum labels presented here, our approach has been adapted keeping in mind the difficulties we faced in Ref. [43]. Based on the energy formula of Eqs 2, 3, one would expect a somewhat regular behavior in the shifting of the rotationally excited energy levels belonging to the same vibrational parent. However, this seems to hold only for the $l = 0$ cases. In Figure 1, the change of B rotational constant is illustrated as J is increased. Each rotational progression belonging to a vibrational state can be characterized by a slightly different B rotational constant, which also shifts slightly by the increase of J. As the vibrational excitation increases, this shift becomes more significant (e.g. in case of 0, 2, 0 and 0, 4, 0). However, for the $l > 0$ vibrational parents, this shift can be more chaotic (see Figure 2)

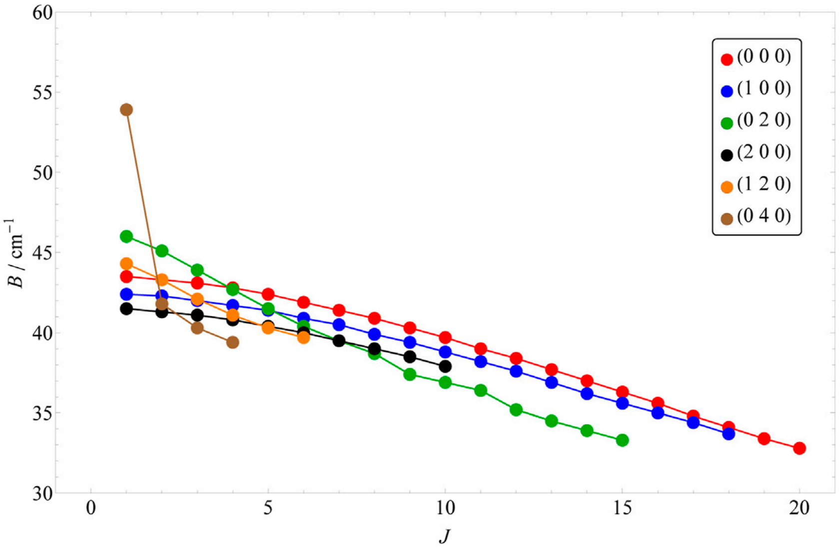

FIGURE 1
The shift of the *B* rotational constants with the increase of the *J* value for the first 6 *l* = 0 vibrational parents.

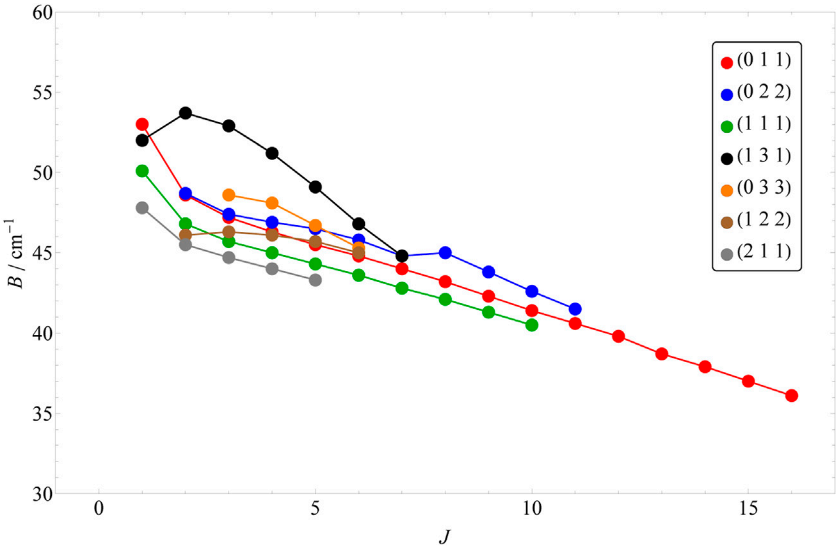

FIGURE 2
The shift of the *B* rotational constants with the increase of the *J* value for the first 7 *l* > 0 vibrational parents. The numbers included here correspond to the *G* progression.

and it is different for the two distinct rotational progressions, assigned to *G* and *G*′ (see Figures 2, 3). For the (1, 3, 1) vibrational parent, e.g., the shift seems to first be positive and then it turns negative as it is in all other cases for both progressions. The *G* = 0 energy levels of the first 13 vibrational states up to *J* = 20 are listed in Table 5, while *G*′ = 0 energy levels of the first 7 *l* > 0 vibrational states up to *J* = 16 are included in Table 6.

Using the RRD method [57] of ***GENIUSH*** to compute wave function overlaps and assign vibrational parents we can push the labeling a lot further than simply relying on the

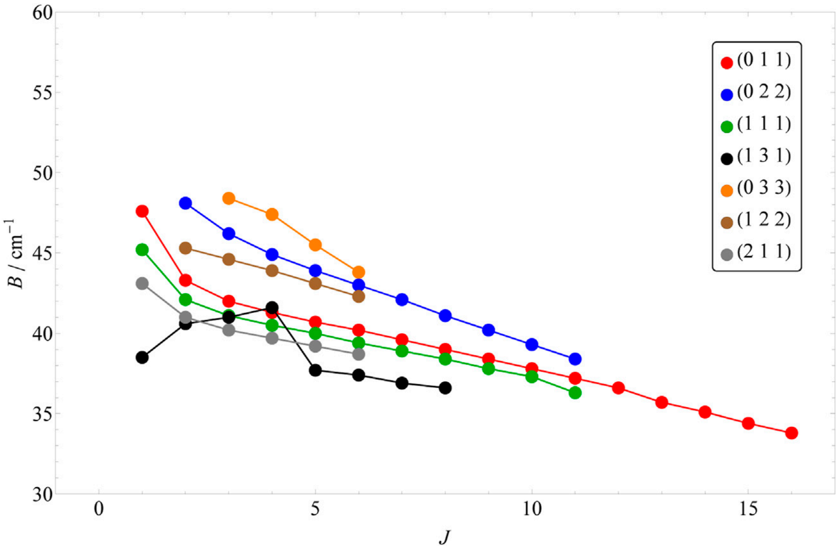

FIGURE 3
The shift of the *B* rotational constants with the increase of the *J* value for the first 7 $l > 0$ vibrational parents. The numbers included here correspond to the G' progression.

TABLE 5 The $G = 0$ energy levels of the first 13 vibrational states (v_1, v_2, $|l|$) of H_3^+ up to $J = 20$.

J	0,0,0	0,1,1	1,0,0	0,2,0	0,2,2	1,1,1	2,0,0	0,3,1	0,3,3	1,2,0	1,2,2	2,1,1	0,4,0
0	0.0		3178.7	4778.7			6262.8			7770.1			9002.4
1	87.0	2627.5	3263.5	4870.6		5655.0	6345.8	7110.7		7858.7		8584.5	9110.3
2	259.9	2813.0	3432.3	5049.3	5290.7	5835.9	6510.7	7328.7		8029.8	8147.6	8762.2	9253.3
3	516.9	3087.6	3683.2	5305.9	5567.8	6103.7	6755.8	7641.7	7869.3	8275.5	8426.2	9024.8	9486.6
4	855.2	3447.3	4013.4	5632.3	5937.1	6454.3	7078.3	8031.5	8248.4	8592.0	8793.6	9368.4	9790.8
5	1271.3	3887.0	4419.6	6023.5	6392.3	6883.0	7475.2	8478.8	8686.6	8978.6	9241.9	9788.4	
6	1761.2	4401.3	4898.0	6476.7	6922.0	7384.5	7942.6	8972.9	9189.5	9437.8	9761.4		
7	2320.5	4984.2	5444.4	6990.2	7505.5	7953.2	8476.4	9513.2					
8	2944.3	5629.4	6054.2	7566.0	8235.5	8583.5	9072.4						
9	3627.7	6330.4	6722.9	8146.3	8940.7	9269.7	9726.1						
10	4365.7	7080.8	7445.8	8836.7	9689.7	10 006.5	10 433.1						
11	5153.4	7883.3	8218.5	9586.4									
12	5985.6	8735.0	9036.9										
13	6857.9	9574.1	9897.1										
14	7765.7	10 471.3											
15	8704.9												
16	9671.9												
17	10 663.6												
18	11 677.3												
19	12 710.4												
20	13 760.6												

TABLE 6 The $G' = 0$ energy levels of the first 7 $l > 0$ vibrational states (v_1, v_2, $|l|$) of H_3^+ up to $J = 16$.

J	0,1,1	0,2,2	1,1,1	0,3,1	0,3,3	1,2,2	2,1,1
1	2616.9		5645.3	7083.6			8575.2
2	2781.5	5287.3	5807.4	7250.0		8142.8	8734.8
3	3026.1	5552.3	6048.1	7498.6	7867.0	8406.6	8971.5
4	3347.9	5897.3	6364.6	7839.5	8235.1	8748.9	9282.6
5	3743.4	6316.6	6753.7	8138.1	8651.9	9164.2	9664.7
6	4208.7	6804.2	7211.5	8577.3	9125.6	9647.0	10 114.1
7	4739.5	7354.0	7734.2	9075.2			
8	5331.3	7960.0	8317.8	9639.2			
9	5979.5	8616.7	8959.3				
10	6679.6	9318.7	9660.7				
11	7427.8	10 063.2	10 351.3				
12	8224.1						
13	9020.0						
14	9891.7						
15	10 788.5						
16	11 714.8						

energy progressions. However, after a certain point in the vibrational and/or the rotational energy excitation, the mixing of the wave functions becomes simply too much for the vibrational parents to be unambiguously identified. For low J values, up to $J = 6$, we were able to get past the isomerization barrier, and in most cases, we could continue on even further. As the rotational excitation increases, the highest vibrational parent we can possibly assign is also decreasing. From $J = 7$ to 10, we are barely reaching the barrier to linearity, while as J increases further, the rotational energy contribution is also getting bigger, therefore we are again getting past the isomerization barrier (see Table 3). Different vibrational parents also behave differently, e.g. the overlaps of the (1,2,0) state breaks down a lot sooner than those of the next few higher-lying vibrational states. The more spread out progressions are also more difficult to assign fully including all the states within the progression. Although the progression belonging to (1,0,0) can be fully identified up to $J = 18$, in the progression of (0,1,1) we already start missing levels at $J = 16$. The ground vibrational state is the only vibrational parent for which all the states were found within the progressions for each J up to $J = 20$. This, however, might not be possible for $J > 20$ values.

In certain cases, it can be observed that the $G = 0$ (or $G' = 0$) level is not the lowest level of the progression, which seemingly results in negative rotational excitations [108]. This happens for both higher vibrational excitations [e.g., for (0,5,1) at $J = 1$], higher rotational excitation (e.g., for (0,1,1) at $J = 11$), or for both [e.g., for (0,3,3) at $J = 3$ and for (0,3,1) at $J = 6$]. In certain cases, this reversing of the energy levels occurs sooner for the G' progression [e.g., for (0,3,1) at $J = 5$].

4 Discussion

In this article, we computed ro-vibrational energy levels and wave functions for the H_3^+ molecular ion using a recently developed PES [25] and the ***ScalIT*** suite of parallel codes. The calculations included every single J value up to $J = 20$, and for each J, all of the levels were computed up to the barrier of linearity or higher. The convergence accuracy of our calculations is further improved, now reaching up to a few 10^{-5} cm^{-1} (or better). Our work has also been compared to previous works using different potential energy surfaces and different masses. Among the nuclear mass computations, the numbers of the present work were the lowest, signaling that we are still operating in the "basis set truncation error-dominated regime" where the numerical convergence is variational from above.

In addition, we carried out vibrational (v_1, v_2, $|l|$) and rotational (J, G, U, K) quantum label assignments of ro-vibrational energy levels for more than 2,200 states. To enable this, ***GENIUSH*** calculations were also carried out with lower accuracy to obtain ro-vibrational wave functions, which were then used to compute wave function overlaps within the framework of the rigid rotor decomposition method. These RRD overlaps helped greatly to identify the vibrational parents. As part of our efforts, we suggested new vibrational (v_1, v_2, $|l|$) and rotational (J, G, U, K) reassignments for certain energy levels within the MARVEL database. We are hoping that the results of this work can be used to further improve previous efforts toward creating spectroscopic line lists (based on both theoretical and experimental data), through the list of all labeled energy levels as provided in the Supplementary Material of this article.

Data availability statement

The original contributions presented in the study are included in the article/Supplementary Material; further inquiries can be directed to the corresponding author.

Author contributions

JS and BP designed the research, JS carried out the calculations and analyzed the data, JS and BP discussed the results, JS and BP wrote the manuscript, and BP provided funding.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Publisher's note

Supplementary material

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fphy.2022.996001/full#supplementary-material

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