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Research paper

The *J*-dependent rotational Hamiltonian method for analyzing rovibrational spectra: Application to HO_2, H_2O, and O_3

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HIGHLIGHTS

- To assign and verify (J, K_a, K_c) and v quantum numbers to rovibrational energy levels.
- To fit flexible rotor rotational constants to experimental and theoretical rovibrational energy level data.
- To interpolate and extrapolate missing energy level data.
- To assess the quality and consistency of the rovibrational data.

ABSTRACT

A *J*-dependent rotational Hamiltonian method is presented for analyzing rovibrational spectra. The method is designed to: assign/verify (J, K_a, K_c) and v quantum numbers to rovibrational energy levels; fit flexible rotor rotational constants to experimental/theoretical rovibrational energy level data; interpolate/extrapolate missing energy level data; assess the quality/consistency of the rovibrational data. The method resembles the standard "effective Hamiltonian" approach (Watson, 1967, 1968) except that the rotational constants themselves depend on J, which provides a number of advantages. The method is applied here to three molecules: HO_2, O_3, and H_2O.

1. Introduction

Comprehensive and highly accurate vibrational and rovibrational energy level data for poly-atomic molecules is of vital importance for many cross-disciplinary applications—e.g., molecular astrophysics, remote sensing, and chemical reaction dynamics, to name a few. To obtain such high-resolution data numerically is extremely difficult—especially when the total angular momentum quantum number, J, is large [1–3]. For large J or system dimensionality d, there are a great many such states to compute, especially as one approaches the dissociation limit where the high density of states introduces additional computational challenges. To simplify such calculations, approximation methods that in some sense separate rotational and vibrational motions are used, such as helicity conserving (HC) and J-shifting (JS) methods [3–12]. The HC method, which ignores Coriolis coupling is considered a mild adiabatic approximation, for which the vibrational quantum states depend parametrically on the rotational quantum numbers [4–6].

In contrast, the JS method presumes a purely additive form for the rovibrational energy levels, in which a symmetric rigid rotor form is used for the rotational energy contribution [3,7–12], i.e.

$$\hat{H}_{\mathrm{R}}^{\mathrm{sym}} \propto B_{xy}\hat{J}_x^2 + B_{xy}\hat{J}_y^2 + B_z\hat{J}_z^2 = B_{xy}\hat{J}^2 + (B_z - B_{xy})\hat{J}_z^2. \tag{1}$$

Thus,

$$E_{vJK}^{\mathrm{JS}} = E_v + E_{JK}^{\mathrm{rot}}, \text{ where}$$
$$E_{JK}^{\mathrm{rot}} = B_{xy}J(J+1) + (B_z - B_{xy})K^2. \tag{2}$$

In Eq. (2) above, E_{vJK}^{JS} is the approximate JS rovibrational energy, E_v is the vibrational energy of the vibrational parent state v, and E_{JK}^{rot} is the rotational energy—i.e., an eigenvalue of Eq. (1). Since both $\hat{J}^2$ and $\hat{J}_z$ commute with $\hat{H}_{\mathrm{R}}^{\mathrm{sym}}$, the E_{JK}^{rot} can be labeled by the corresponding "good" quantum numbers, J and K. The two rotational constants, B_{xy} and B_z, do not depend on J and K—although in some more flexible treatments, they are allowed to depend on v. Also, either rotational constant may be larger than the other, thereby accommodating both prolate and oblate rotor situations.

In a recent paper, Petty and Poirier [10] examined the performance of various JS methods, which vary mostly with respect to how the rotational constants B_{xy} and B_z are chosen. In particular, they considered the (theory-based) Simple and Simple (R) methods, a vibrational-state-dependent (VSD) method [12–15], and various rotational-state-dependent (RSD) methods: EP, modEP, geoEP, geoEP (R). These all were

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applied to the HO_2 triatomic molecule—considered to be highly challenging, especially at high J, where substantial Coriolis coupling renders the standard JS approximation highly inaccurate. The authors found that the modEP method performs well across all v, J, and K values, compared to other JS-type methods. For example, root-mean square deviations (RMSDs) obtained for ($v = 0$, $J = 10$) and ($v = 3$, $J = 100$) HO_2 rovibrational levels [10,16] are 2.69 and 153 cm^{-1}, respectively.

These RMSDs represent the best performance that can reasonably be obtained for this system using any JS-type approximation. On the other hand, they are still quite high, if the goal is something like spectroscopic accuracy—*i.e.*, sub-wavenumber or better. To some extent, this reflects the fact that JS was born in the chemical physics community—specifically, in the context of computing thermal rate constants for chemical reactions, where high accuracy is not required (though JS has also been applied to rovibrational spectra [8–16]).

To do better, one should examine other methods, as developed in the spectroscopic community. Here, the standard approach is the "effective Hamiltonian" (eH) method, developed by Watson and others [17–20]. To begin with, the eH method does *not* assume a symmetric form for the rotational kinetic energy, but rather, an asymmetric form. Thus, the quantum number K is replaced with new labels, (K_a, K_c). Likewise, there are now three rotor constants, A, B, C, instead of two (see Section 2 for further details). In general, the increased flexibility leads to much better fits with the data, although there are theoretical reasons why a symmetric rotor form may be natural for triatomic systems in Jacobi coordinates [21]. Additionally however, the eH approach adopts a flexible rotor form, for which higher-order (than quadratic) terms in $\hat{J}_x$, $\hat{J}_y$, $\hat{J}_z$ are also included.

With such a generalization of $E_{JK}^{\rm rot}$ (or really $\widehat{H}_{JK}^{\rm rot}$) in Eq. (2), true spectroscopic accuracy is generally possible with as few as 6th order, or at most 8th order, terms in the effective rotational Hamiltonian—especially if the various rotational constants are taken to be v-dependent. On the other hand, there are theoretical complexities, e.g. introduced by the constraint $\hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2 = \hbar^2 J(J+1)\hat{I}$. Furthermore, for some simple molecules such as H_2O above ~10,000 cm^{-1}, the fits are still notoriously poor—motivating such complicated developments as the use of Pade approximants [22,23], but still with limited improvement in performance.

There thus remains a great demand for accurate and reliable methods that can better estimate rovibrational energy levels of polyatomic molecules, or can otherwise be used to verify or assign labels to both experimental and theoretical spectroscopic data. To this end, in this paper, we generalize eH still further, by introducing a dependence on the quantum number J into all flexible rotor parameters. The new "J-dependent rotational Hamiltonian method" (J-drH) gives much better estimates of rovibrational energy of poly-atomic molecules than HC and JS, and also improves upon eH in various ways that will be discussed in Section 2. More generally, it can also be directly applied as presented here, to molecules of arbitrary size.

2. Theory and computational details

While formally the rovibrational molecular Hamiltonian cannot be decoupled into separable vibration and rotation contributions, there are certainly many strategies for doing so approximately [3,5,6,10,11,17–20,24–29]. One common approach uses the asymmetric rigid rotor Hamiltonian,

$$\hat{H}_{\rm R} \propto A\hat{J}_a^2 + B\hat{J}_b^2 + C\hat{J}_c^2, \tag{3}$$

as an effective rotational Hamiltonian. As is standard practice, the individual vector components, (a, b, c), are reordered from the original (x, y, z) in order to ensure $A > B > C$ for both prolate and oblate situations. The z component (denoting the rotational constant that is "most different" from the others) is then associated with either a or c, depending on whether the rotor is more prolate or oblate.

Note that $\hat{H}_{\rm R}$ no longer commutes with *any* of the angular momentum vector components. As a consequence, K is no longer a good quantum number, for any vector component (although J remains a good quantum number). Nevertheless, K_a and K_c can still be used as labels for the asymmetric-top rotational energy levels, $E_{K_aK_c}^J$. This is done in the standard fashion, according to energetic ordering of the $(2J+1)$ levels for a given J [27]. The $E_{K_aK_c}^J$ are then added to the pure vibrational eigenenergies, E_v, to obtain approximate rovibrational energies, $E_{vK_aK_c}^J \approx E_v + E_{K_aK_c}^J$.

In Eq. (3), the rotational constants, (A, B, C), may be fixed, or—for improved accuracy—they may be chosen to depend on the vibrational parent state, v. Even better approximations may be obtained with a *flexible* rotor Hamiltonian, for which higher-order centrifugal distortion terms are added—typically only quartic, but sometimes sextic and higher [17,20,26,27]. Note that beyond second order, not all monomial terms are independent, even when a consistent operator-ordering convention is used. In the eH approach, it is thus necessary to specify a convention for "reducing" the flexible rotor Hamiltonian down to some subset of non-redundant terms [18–20]. This reduction procedure can get rather complicated, especially at higher orders, and is certainly not unique. Moreover, the optimally fit rotational Hamiltonian parameters that one subsequently obtains—for both the rigid rotor and higher-order contributions—turn out to depend (slightly) on the reduction convention used.

J-drH provides a substantial simplification in that the J blocks are treated independently—which is legitimate, because both the flexible and rigid rotor Hamiltonians are block-diagonal with respect to the rigorous quantum number J. At the level of individual J blocks, then, we have the following useful relation,

$$\tilde{J}_x^2 + \tilde{J}_y^2 + \tilde{J}_z^2 = \hbar^2 J(J+1)\tilde{I}, \tag{4}$$

where $\tilde{I}$ is the identity matrix, and (x, y, z) an appropriate permutation of (a, b, c), as discussed.

From Eq. (4), together with other arguments [17,20], it can be shown that any flexible rotor Hamiltonian may be *uniquely* expanded in the form

$$\tilde{H}_{\rm R}^J = 2\pi\hbar c\left\{C_{(0,0)}^J J\left(J+1\right)\tilde{I} + \sum_{m,n} C_{(m,n)}^J \left[\frac{\tilde{J}_\Delta^m \tilde{J}_z^n + \tilde{J}_z^n \tilde{J}_\Delta^m}{2\hbar^{m+n}}\right]\right\}, \tag{5}$$

where $\tilde{J}_\Delta^2 = (\tilde{J}_y^2 - \tilde{J}_x^2)/2$, m and n are both even nonnegative integers, and in the final summation, $m + n > 0$. Note that all of the $C_{(m,n)}^J$ have cm^{-1} units. For a prolate rotor [i.e. (x, y, z) = (c, b, a)], expansion of Eq. (5) to second order and comparison with Eq. (3) reveals the following associations with the conventional rotational constants: $C = [C_{(0,0)}^J - C_{(2,0)}^J/2]$; $B = [C_{(0,0)}^J + C_{(2,0)}^J/2]$; $A = [C_{(0,0)}^J + C_{(0,2)}^J]$.

Eq. (5) has the advantage that any term can be easily included or excluded from the summation at any order—which is not true for eH. In any event, for an almost prolate rotor such as HO_2, with $z = a$, it is generally more effective to expand further in n than in m. In comparison with an eH expansion, there are significantly fewer terms (*i.e.*, fitting parameters) up to a given order ($m + n$). Nevertheless, RMSDs (for optimal fits of the $E_{vK_aK_c}^J$ to a reference energy level dataset) are significantly *reduced* in the J-drH case, specifically *because* the parameters $C_{(m,n)}^J$ are now J-dependent.

In practice, the optimal $C_{(m,n)}^J$ values themselves do not change much with J, except for the smallest J or largest ($m + n$) values [see, *e.g.*, Table 2]. Furthermore, the slowly-varying J dependence of the $C_{(m,n)}^J$ is usually smooth and monotonic, and can itself be easily and accurately fit to simple functional forms. Likewise, the J dependence of the RMSDs is also smooth and monotonic. This presents two natural uses for the J-drH methodology. The first is to *predict* rovibrational energy levels, for missing J values from within (interpolation) or without (extrapolation) the J range of the dataset. Preliminary results suggest that such predictions may routinely be able to achieve

spectroscopic accuracy, although the prediction avenue is not pursued in the present paper.

The second application—which *is* considered here—is to determine spectroscopic labels for the individual rovibrational levels of the dataset. Specifically, we seek a reliable means of providing v and $(K_a,\ K_c)$ labels, based solely on the energy levels themselves—*i.e.*, without having to resort to a cumbersome wavefunction analysis [30]. The procedure is as follows:

1. For each subset of the dataset corresponding to specific values for J and other rigorous symmetry quantities (such as parity), assign tentative v and $(K_a,\ K_c)$ labels (with the latter based on energetic ordering, as discussed).
2. Based on these assignments, for each separate $(v,\ J)$ pair, perform an optimal fit of a given flexible rotor form [Eq. (5)] with a sufficient number of terms to reduce RMSD and individual level discrepancies to well below the level spacing for the given J.
3. If any labels are misassigned, this will immediately become clear, because the RMSD for the corresponding $(v,\ J)$ will be much larger than for other nearby J values. Likewise, the optimal $C^J_{(m,n)}$ values will not fit the pattern for nearby J values.
4. Having thus narrowed things down to the problematic $(v,\ J)$, identify problematic v and $(K_a,\ K_c)$ assignments by examining the individual $(2J + 1)$ (or fewer, depending on symmetry) energy level deviations.
5. If necessary, reassign, and repeat.

As a pedagogical example, in Fig. 1, we present data for the

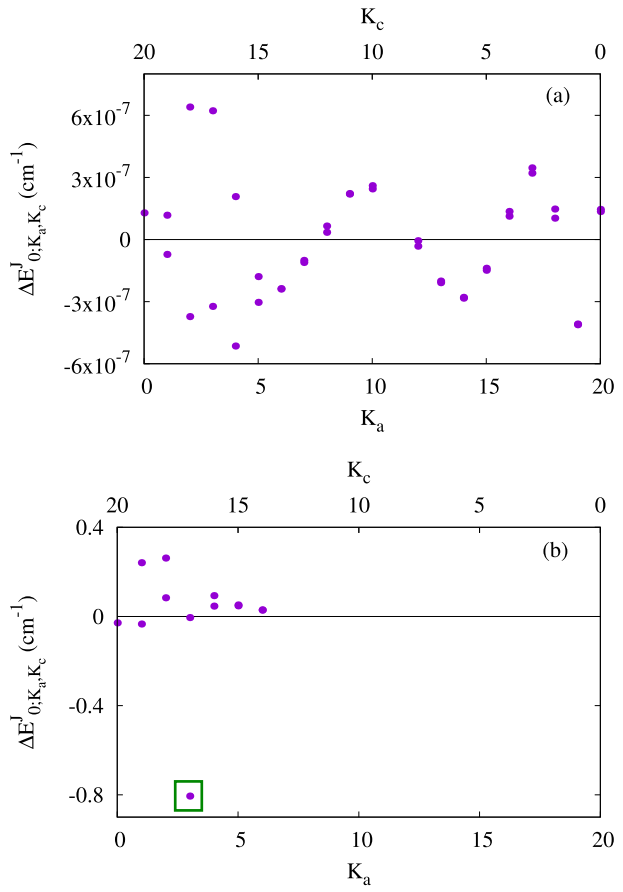

Fig. 1. Deviations between "exact" computed rovibrational energy levels of $(v = 0,\ J = 20)$ SO_2 vs. eight-parameter J-drH fits: (a) all levels are correctly assigned; (b) one level (marked by the green box) is misassigned.

$(v = 0,\ J = 20)$ rovibrational states of SO_2—obtained using an eight-parameter J-drH model, fit to theoretical results computed previously [8]. In panel (a), deviations for the individual $(2J + 1) = 41$ levels are roughly uniformly distributed across a very small range of $\approx \pm 1 \times 10^{-6}$ cm^{-1}. These levels are correctly assigned. In contrast, panel (b) shows the case where one of the 41 levels has been misassigned. Not only does that level immediately stand out from the others, but in addition, all deviations are orders of magnitude larger than in panel (a).

3. Results and discussion

The J-drH method is applied here to three molecular systems, HO_2, H_2O, and O_3 for representative total angular momentum quantum number values in the range $J = 2$–100. The HO_2 [10,16,31], and O_3 [32] rovibrational energy levels were computed using the *ScalIT* suite of parallel codes [16]; for H_2O, the MARVEL (Measured Active Rotational-Vibrational Energy Levels) procedure [33–37] was applied to experimental spectroscopic transition data [38].

3.1. Energy levels and rotational constants for HO_2

Table 1 reports J-drH HO_2 rovibrational energy level RMSDs in cm^{-1}, for $J = 10$, 50, and 100, and for $v = 0$–3. Both a four-parameter J-drH model $[(m, n) = (0, 0), (2,0), (0,2), (0,4)]$ and an eight-parameter model [4-param + (2,2), (2,4), (0,6), (0,8)] were considered. Note that performance improves significantly from the latter to the former, in the sense that RMSDs generally decrease by up to an order of magnitude or so—except for the very largest J and v values. In general, RMSDs increase with J.

J-drH performance for this system is extremely good, as evidenced by the comparison with other methods also presented in Table 1. For purposes of a fair comparison, we distinguish the "*ab initio*" JS methods [Simple and Simple (R)] from the "semiempirical" JS methods [RSD and VSD]. As the names imply, the former predict rotor constant values without any knowledge of the actual experimental or theoretical spectra, whereas the latter methods do exploit such information [10]. In what follows, we describe only comparisons with the four-parameter J-drH model.

The four-parameter J-drH model is found to be up to 2.5 orders of magnitude more accurate than even the best JS-type approximations. For $(v = 0, J = 10)$, J-drH achieves a remarkable RMSD of 0.04 cm^{-1}, which is 69× better than modEP, and much better than all other JS-type methods (Table 1). For $J = 10$, the largest J-drH RMSD is 0.36 cm^{-1}, for $v = 2$. The corresponding modEP RMSD is 8.87 cm^{-1}.

For $(v = 0, J = 50)$, J-drH achieves an RMSD of 0.069 cm^{-1}, which is 340× smaller than modEP (RMSD = 23.4 cm^{-1}), and much better than all other JS-type methods (Table 1). For $J = 50$, the largest J-drH RMSD is 0.135 cm^{-1}, for $v = 2$. The corresponding modEP RMSD is 90.876 cm^{-1}, for $v = 3$.

For $(v = 0, J = 100)$, J-drH achieves an RMSD of 2.25 cm^{-1}, which is 60× smaller than modEP (RMSD = 136.87 cm^{-1}), and much better than all other JS-type methods (Table 1). For $J = 100$, the largest J-drH RMSD is 4.05 cm^{-1}, for $v = 3$. The corresponding modEP RMSD is 153.418 cm^{-1}. Note that for the largest J values, all JS methods perform about equally poorly, with RMSD no better than about 100 cm^{-1}. J-drH thus represents an especially important improvement at large J.

We also consider HO_2 rovibrational label assignments, and compare with those from Petty et al. [10,16]. For $J = 10$, the new J-drH HO_2 state labels match the Petty et al. labels (Table 3 of Ref. [16]) in every instance except for three—these being one even parity $(v = 1, K = 7, n = 26)$ and two odd parity $(v = 0, K = 8, n = 11$ and $v = 1, K = 8, n = 28)$ states (where n labels are from Petty et al.) For $J = 50$ with odd permutation symmetry, labels agree with Petty et al. (Table 3 of Ref. [10]) except four even parity states $[(v = 0, K = 8, n = 12), (v = 1, K = 5, n = 19), (v = 2, K = 6, n = 25), (v = 1, K = 7, n = 26)]$ and three odd parity states $[(v = 1, K = 3, n = 13), (v = 1, K = 4, n = 16), (v = 2, K = 5, n = 23)]$.

Table 1
RMSDs for HO_2, in cm^{-1}, obtained by fitting four- and eight-parameter *J*-drH models to (v, J) *ScalIT* rovibrational levels, for vibrational parent state $v = (0, i, 0)$, i = 0–3, and for J = 10, 50, 100. A comparison with various JS-type methods is also provided. States are restricted as follows. For the JS methods, the number of states considered (n) is {11, 8, 7, 4}, respectively, for v = {0, 1, 2, 3}. For the *J*-drH models, n is listed in Column 5.

J	v	*J*-drH			*ab initio* JS		RSD JS				VSD JS
		Four-	Eight-	n	Simple	Simple (R)	modEP	EP	geoEP	geoEP (R)	
10	(0,0,0)	0.039	0.008	21	66.18	88.15	2.69	36.97	84.99	109.9	9.79
	(0,1,0)	0.004	0.002	15	35.81	46.76	7.50	18.26	39.89	52.71	26.40
	(0,2,0)	0.012	0.006	13	35.52	43.65	8.87	21.24	37.08	46.79	28.97
	(0,3,0)	0.006	0.001	7	4.67	6.00	7.57	4.91	4.62	6.23	N/A
50	(0,0,0)	0.069	0.007	21	74.72	95.73	23.41	67.10	94.77	118.0	25.40
	(0,1,0)	0.090	0.061	15	38.44	42.78	45.68	37.41	40.59	46.79	637.7
	(0,2,0)	0.135	0.024	13	58.97	64.64	45.54	54.73	60.27	67.06	693.3
	(0,3,0)	0.120	0.034	7	85.51	84.08	90.88	86.90	85.44	83.79	N/A
100	(0,0,0)	2.251	0.262	19	156.1	168.1	136.9	220.0	193.9	208.0	135.4
	(0,1,0)	1.524	0.131	13	95.17	96.91	96.25	109.6	101.0	105.0	2424
	(0,2,0)	0.936	0.803	7	76.85	77.08	80.05	82.81	77.98	79.97	2815
	(0,3,0)	4.055	3.196	7	149.0	147.4	153.4	142.9	145.9	144.5	N/A

Table 2
J-drH parameters, traditional rotational constants, and RMSDs for HO_2, in cm^{-1}, obtained by fitting four-parameter *J*-drH model to (v, J) *ScalIT* rovibrational levels, for vibrational parent state $v = (0, 0, 0)$, and for J = 2, 3, 5, 6, and 10. Experimental rotational constants A_{exp}, B_{exp}, C_{exp} are also given [39,40].

J	v	$C^J_{(0,0)}$	$C^J_{(2,0)}$	$C^J_{(0,2)}$	$C^J_{(0,4)}$	A	B	C	RMSD
2	(0,0,0)	1.09022	0.0645242	19.3699	−0.00467128	20.4601	1.1225	1.0580	5.10E−5
3	(0,0,0)	1.09041	0.0618367	19.3649	−0.00356997	20.4553	1.1213	1.0595	1.12E−3
5	(0,0,0)	1.09063	0.0623757	19.3650	−0.00361835	20.4556	1.1218	1.0594	6.33E−4
6	(0,0,0)	1.09027	0.0622214	19.3609	−0.00358974	20.4512	1.1214	1.0592	2.41E−3
10	(0,0,0)	1.09086	0.0621077	19.3471	−0.00342336	20.4380	1.1219	1.0598	3.88E−2

A_{exp} = 20.3560, B_{exp} = 1.1846, C_{exp} = 1.0565.

For higher J values, for which individual quantum states exhibit significant probability across a broad range of K values, one can expect very different state labels compared to those of Refs. [10,16]. On the whole, for J = 10 and 50, analysis of the label assignments using *J*-drH compared to modEP reveals similar trends and general conclusions.

All of the above fits were restricted to a *reduced* set of states (i.e., fewer than $2J + 1$). This was done in order to effect a fairer comparison with the prior work [10]—although in reality, the present *J*-drH fits were always *less* restricted than for the other methods, as indicated in Table 1. In order to better address trends, a separate, *unrestricted* set of *J*-drH fits was also conducted, for $v = 0$ and $J \leq 10$. RMSDs for the four-parameter *J*-drH model, as well as fit coefficient values [i.e., $C^J_{(0,0)}$, $C^J_{(2,0)}$, $C^J_{(0,2)}$, and $C^J_{(0,4)}$] are shown in Table 2. Conventional rotational constants, A, B, C, are also indicated. Experimental rotational constants [39,40] are also indicated, and found to be quite close to the fit values. In any event, $C^J_{(m,n)}$ values vary smoothly—and very little—from one J to the next, which is the first major observed trend. The second major trend is that RMSDs increase rapidly with J, also as expected.

3.2. Energy levels and rotational constants for H_2O

In this section, *J*-drH is applied to analyze rovibrational energy levels and rotational constant terms of H_2O via a comparison with the experimental rovibrational energy levels obtained using the MARVEL procedure [38]. The computed RMSDs and rotational constant terms for J = 2–5, 10, and 15, and for $v = 0$, obtained using four- and eight-parameter models, are given in Tables 3 and 4, respectively. For ($v = 0$, $J = 2$) using the four-parameter model, *J*-drH achieves an RMSD of 6.82E-04 cm^{-1}, which gradually increases with J, reaching 4.43 cm^{-1} for ($v = 0$, $J = 15$). The corresponding eight-parameter model ($v = 0$, $J = 15$) RMSD is 0.18 cm^{-1}, representing a 25× improvement.

Though not reported in the tables, the $J = 15$ RMSD can be substantially reduced still further, down to 0.023 cm^{-1}, by using a ten-parameter model. This represents true spectroscopic accuracy, and is therefore quite a significant achievement—given that other methods such as eH fail in this context. More specifically, Polyanski and coworkers found that standard Taylor-series eH expansions *fail to converge* for ($v = 0$, J) H_2O beyond $J = J_{max} = 5$ [22]! Their solution was to introduce Padé approximants, but even this required a *sixty*-parameter eH expansion in order to achieve spectroscopic accuracy.

All in all, the results for H_2O behave exactly as desired, with fit coefficient values $C^J_{(m,n)}$ changing little with J and even less with the number of model parameters, except for the highest $m + n$ values. More importantly, RMSDs diminish very rapidly with increasing model order, even up to $J = 15$.

3.3. Energy levels and rotational constants for O_3

We also applied *J*-drH to analyze rovibrational energy levels and rotational constant terms of the $^{16}O^{16}O^{16}O$ (666) isotopologue of O_3, as computed using a global potential energy surface [43] and the *ScalIT* suite of parallel codes [32]. More specifically, we computed RMSDs and rotational constant terms for J = 2–5, and 10, and for v = 0–2, using four- and six-parameter *J*-drH models, as listed in Tables 5 and 6.

From Table 5, we see that even with as few as four parameters—and

Table 3
J-drH parameters traditional and RMSDs for H_2O, in cm^{-1}, obtained by fitting four-parameter model to (v, J) MARVEL rovibrational levels, for vibrational parent state v = (0, 0, 0), and for J = 2–5, 10, 15. Experimental rotational constants A_{exp}, B_{exp}, C_{exp} are also given [41,42].

J	v	$C^J_{(0,0)}$	$C^J_{(2,0)}$	$C^J_{(0,2)}$	$C^J_{(0,4)}$	A	B	C	RMSD
2	(0,0,0)	11.8931	5.2270	16.0106	−0.0315	27.9037	14.5066	9.2796	6.82E−04
3	(0,0,0)	11.8863	5.2147	16.0382	−0.0307	27.9245	14.4937	9.2790	0.003
4	(0,0,0)	11.8777	5.1995	16.0671	−0.0295	27.9448	14.4775	9.2780	0.012
5	(0,0,0)	11.8676	5.1815	16.0942	−0.0282	27.9618	14.4583	9.2768	0.033
10	(0,0,0)	11.7984	5.0550	16.1150	−0.0211	27.9134	14.3259	9.2709	0.844
15	(0,0,0)	11.7010	4.8746	15.8687	−0.0153	27.5697	14.1383	9.2637	4.429

A_{exp} = 27.8761, B_{exp} = 14.5074, C_{exp} = 9.2877.

even for J as large as J = 10—*J*-drH RMSDs are only around .01 cm^{-1}. Spectroscopic accuracy is thus achieved much more readily, even, than for HO_2 and H_2O—reflecting the heavy and quite rigid structure of the ozone molecule. On the other hand—and also quite unlike the other molecules considered here—ozone RMSDs do *not* diminish appreciably, neither as J is reduced, nor as the model order is increased. Remarkably, an RMSD value of around .01 cm^{-1} is always observed, across *all* v and J values considered, and for both the four- and six-parameter models (Table 6). Additionally, in the six-parameter fit, optimal values for even the intermediate $C^J_{(0,4)}$ coefficient vary quite a bit with (v, J). This situation indicates that *the theoretical data has ~.01 cm^{-1} of "noise"*. Indeed, convergence tests for the underlying rovibrational spectroscopy calculations reveal a comparable level of numerical accuracy [32]; nevertheless, *J*-drH provides a quite valuable independent means of verification, based solely on the dataset itself.

4. Summary and conclusions

We have developed a new *J*-drH rovibrational state prediction and labeling method, and applied it to rovibrational energy levels for three separate triatomic systems: HO_2, H_2O, and O_3. One of these (i.e. H_2O) is experimental, and the other two are theoretical. Total angular momentum values are considered within the range J = 2–100; likewise, several low-lying vibrational excitations are also considered. A range of increasingly accurate *J*-drH models is used, with four, six, and eight adjustable $C^J_{(m,n)}$ effective rotational Hamiltonian parameters. Although only triatomic molecules are considered explicitly here, it should be stressed that the method can be applied without modification to molecules of arbitrary size.

Model performance is measured using RMSDs of the fit rovibrational energy levels. Generally speaking, RMSDs decrease as the number of $C^J_{(m,n)}$ parameters in the *J*-drH model (i.e., the model order) increases. Likewise, RMSDs tend to increase substantially with increasing J and v values. Also, the pattern of RMSDs and fit $C^J_{(m,n)}$ parameter values usually varies little with (v, J), and even less with model order, except for the lowest J and highest $m + n$ values. When the above patterns are *not* observed, it can indicate either: (1) label misassignments; (2) the limits of data quality. In particular, (1) is signalled locally, by individual (v, J) values (and even individual levels) that "stand out" prominently from their neighbors, making them easy to identify. This feature was used to correct some earlier "misassignments" in HO_2 (although these assignments were generally already understand to be tentative). In contrast, (2) is signalled globally, by "flat" RMSDs. These can occur either across the full range of (v, J) and model orders considered (as is the case here for O_3), or may manifest only beyond a certain minimum order and/or below a certain maximum J value (as observed in separate calculations not reported here).

Generally speaking, *J*-drH achieves spectroscopically small RMSDs with remarkably few model parameters, even for challenging anharmonic systems such as HO_2. The performance is orders of magnitude better than for all JS methods, including modEP, which was recently found to be the best of the JS class for this molecule [10]. *J*-drH also presents a number of advantages over the traditional spectroscopic eH approach, including: *unique* expansion coefficients; complete *flexibility* in the fit parameters; *fewer* parameters needed to achieve spectroscopic accuracy. As an additional advantage over eH: once the $2J + 1$ levels for a given (v, J) are obtained, there is never a need to refit at a later date when more data (e.g. at higher J) becomes available. *J*-drH could therefore also be of service, e.g., in efforts to standardize data in spectroscopic information systems.

Table 5
J-drH parameters and RMSDs for $^{16}O^{16}O^{16}O$, in cm^{-1}, obtained by fitting four-parameter model to (v, J) *ScalIT* rovibrational levels, for vibrational parent state v = (0, i, 0), i = 0–2, and for J = 2–5, 10.

J	v	$C^J_{(0,0)}$	$C^J_{(2,0)}$	$C^J_{(0,2)}$	$C^J_{(0,4)}$	RMSD
2	(0,0,0)	0.4204	−0.0401	3.1306	3.3770E−03	9.67E−03
3	(0,0,0)	0.4193	0.0556	3.1513	−5.5700E−04	9.66E−03
4	(0,0,0)	0.4197	0.0473	3.1478	−1.4200E−04	9.19E−03
5	(0,0,0)	0.4197	0.0524	3.1493	−2.4600E−04	0.011
10	(0,0,0)	0.4199	0.0499	3.1487	−2.1200E−04	0.013
2	(0,1,0)	0.4217	−0.0355	3.1771	5.1850E−03	0.015
3	(0,1,0)	0.4182	0.0595	3.2042	−2.2700E−04	0.013
4	(0,1,0)	0.4182	0.0466	3.2047	−2.4800E−04	0.011
5	(0,1,0)	0.4183	0.0546	3.2054	−2.7600E−04	0.017
10	(0,1,0)	0.4182	0.0507	3.2045	−2.3400E−04	0.018
2	(0,2,0)	0.4191	−0.0378	3.2349	5.1900E−03	0.014
3	(0,2,0)	0.4162	0.0599	3.2631	−3.9100E−04	0.012
4	(0,2,0)	0.4163	0.0481	3.2620	−2.4100E−04	0.011
5	(0,2,0)	0.4164	0.0554	3.2631	−3.0100E−04	0.016

Table 4
J-drH parameters and RMSDs for H_2O, in cm^{-1}, obtained by fitting eight-parameter model to (v, J) MARVEL rovibrational levels, for vibrational parent state v = (0, 0, 0), and for J = 4, 5, 10, 15.

J	v	$C^J_{(0,0)}$	$C^J_{(2,0)}$	$C^J_{(0,2)}$	$C^J_{(0,4)}$	$C^J_{(2,2)}$	$C^J_{(2,4)}$	$C^J_{(0,6)}$	$C^J_{(0,8)}$	RMSD
4	(0,0,0)	11.8754	5.2041	16.0940	−0.0323	−5.2115E−03	9.9623E−05	1.2835E−04	−5.8142E−07	
5	(0,0,0)	11.8631	5.1843	16.1509	−0.0330	−5.2334E−03	9.9164E−05	1.2485E−04	−4.8005E−07	1.26E−05
10	(0,0,0)	11.7687	5.0332	16.5793	−0.0327	−5.3961E−03	9.6972E−05	8.6124E−05	−1.2854E−07	7.99E−03
15	(0,0,0)	11.6283	4.8076	17.0440	−0.0287	−5.1762E−03	5.7252E−05	4.4638E−05	−2.9477E−08	0.178

Table 6
J-drH parameters and RMSDs for $^{16}O^{16}O^{16}O$, in cm^{-1}, obtained by fitting six-parameter model to (v, J) *ScalIT* rovibrational levels, for vibrational parent state $v = (0, i, 0)$, $i = 0–2$, and for $J = 3–5$, 10.

J	v	$C^J_{(0,0)}$	$C^J_{(2,0)}$	$C^J_{(0,2)}$	$C^J_{(0,4)}$	$C^J_{(0,6)}$	$C^J_{(0,8)}$	RMSD
3	(0,0,0)	0.4200	0.0556	3.1307	4.6725E−04	−2.8054E−04	−1.8190E−05	8.39E−03
4	(0,0,0)	0.4200	0.0473	3.1307	4.0170E−04	−1.0412E−03	3.7342E−05	7.40E−03
5	(0,0,0)	0.4197	0.0524	3.1532	−4.7833E−05	9.5532E−05	−2.1690E−06	0.011
10	(0,0,0)	0.4197	0.0499	3.1489	−1.9091E−06	−2.2139E−07	1.7641E−09	0.012
3	(0,1,0)	0.4183	0.0595	3.2023	3.8535E−04	−3.4031E−05	−1.2094E−06	0.013
4	(0,1,0)	0.4182	0.0466	3.2045	7.2444E−05	−5.2354E−05	2.0772E−06	0.011
5	(0,1,0)	0.4182	0.0546	3.2117	−1.8745E−03	1.1829E−04	−2.5723E−06	0.016
10	(0,1,0)	0.4182	0.0506	3.2054	−2.6193E−04	2.3423E−07	−3.7988E−10	0.018
3	(0,2,0)	0.4165	0.0599	3.2524	2.8327E−03	−1.4935E−04	−9.2583E−06	0.012
4	(0,2,0)	0.4164	0.0481	3.2542	3.5321E−03	−4.8730E−04	1.7595E−05	0.011
5	(0,2,0)	0.4163	0.0554	3.2693	−1.9496E−03	1.2494E−04	−2.7525E−06	0.015

Declaration of Competing Interest

The authors declare no competing financial interest.

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