

# An Active Database Approach to Complete Rotational–Vibrational Spectra of Small Molecules

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## 1. INTRODUCTION

Spectroscopy has traditionally been considered as the branch of sciences offering the perhaps most precise measurement results. As a consequence, molecular spectroscopic results are usually extremely hard to match even by the most sophisticated nonadiabatic computational approaches based on quantum electrodynamics (QED). Nevertheless, experimental molecular spectroscopy, when the aim is the determination of complete spectra, has several important limitations,

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as follows: (1) while line positions can be measured with outstanding accuracy that is almost impossible to match by computations, line intensities and shapes usually have much larger relative uncertainties; (2) experiments measure transitions but in many application of spectroscopic results, e.g., for the determination of temperature-dependent partition functions through direct summation [1], one needs accurate energy levels; (3) since even for small systems the number of allowed transitions is huge, it is in the billions for each isotopologue of a triatomic species, the complete line-by-line experimental determination of a spectrum is clearly impossible; (4) many important species and many important spectroscopic regions are hardly amenable to experimental scrutiny or require expensive instrumentation, for example, even the stretching fundamentals of the triplet ground electronic state of the  $\text{CH}_2$  radical have not been measured [2]; and (5) measurement of transitions without detailed assignment is hardly useful for most practical purposes and as the energy grows the level density increases drastically while the clear description of energy levels using traditional simple schemes starts to fail.

As suggested herein, the best quantum mechanical computations are able to solve or at least remedy all of the above problems. While highly specialized techniques exist for few-electron systems [3], the canonical process of obtaining accurate computational predictions for rotational–vibrational spectra of many-electron systems is normally divided into two steps. First, one or more potential energy surfaces (PESs) [4,5], and possibly property surfaces (like the dipole moment surface, DMS) are obtained, based on solving the electronic part of the Schrödinger equation on a grid including a large number of nuclear configurations. PESs are defined as the total energy of the quantum system as a function of its geometric variables. Property surfaces are defined similarly to PESs. Second, the PESs, usually after proper fitting, are used to solve the nuclear motion problem resulting in a large number of eigenpairs, while the appropriate property surfaces are then used to obtain the full spectrum.

Many approaches have been developed in electronic-structure theory for determining accurate energy and property hypersurfaces [4,5]. Ideally, one would do complete basis set (CBS) full configuration interaction (FCI) computations at a very large number of structures employing an appropriately chosen relativistic Hamiltonian. Of course, this is not practical and introduction of several approximations is mandated. This is a field of electronic-structure theory where sufficiently large experience has been acquired to allow meaningful choices to be made. If the aim is the accurate determination of complete rotational–vibrational spectra, even non-relativistic CBS FCI computations are not sufficient, effects usually considered to be small must also be taken into account, most importantly effects resulting from the theory of special relativity [6,7], even for molecules containing only light atoms, and the (partial) breakdown of the Born–Oppenheimer (BO) [8,9] approximation, especially for H-containing species. Furthermore, at least close to dissociation limit(s) or intersections, interactions between PESs might need to be considered, leading to additional difficulties.

For decades high-resolution rotational–vibrational spectroscopy treated nuclear motion in terms of near-rigid rotations and small-amplitude vibrations, relying heavily on perturbation theory (PT) [10–16]. While the formulas [11,14,15]

resulting from PT, even at second order, are often rather complex, they are easy to program, running them is almost cost free, and they reproduce many experimental data though only at low to medium excitation. These low-order PT approaches are unable to yield complete molecular spectra. From the very beginning there have been attempts to compute rovibronic spectra of polyatomic molecules by computationally more intensive variational techniques. Variational nuclear motion computations can be made, at least in principle and within the BO approximation, arbitrarily accurate and in principle allow the determination of complete spectra. Nevertheless, for the first-principles approach to complete rotational–vibrational spectra to be really successful one has to utilize sophisticated procedures. This means that one needs not only highly accurate electronic-structure techniques to compute energy and property surfaces but also involved protocols to represent them, and numerically efficient ways for the (nearly) variational nuclear motion treatments. Recent developments suggest that, in favorable cases, the rovibrational eigenvalues obtained can approach what quantum chemists call spectroscopic accuracy, which is  $1\text{ cm}^{-1}$  on average [17].

Neither experiments nor first-principles computations can determine the complete rotational–vibrational spectra of even small molecules with the required accuracy. It seems to us that the most practical approach to overcome most of the difficulties is through an active database approach. This requires building two databases linked together through a unique assignment scheme, one containing energy levels and the other the related transitions. This way one can take advantage of the strengths of the two main sources of spectroscopic information. Variational computations can yield all the possible energy levels, with various assignment possibilities, and thus all the possible labeled transitions, though with limited accuracy deteriorating as the level of excitation increases [17]. Experimental transitions, and the energy levels obtained through an appropriate inversion procedure, have a much higher accuracy but are limited in number even in the spectroscopically most easily accessible regions. We do not see any other possible route to the determination of complete molecular spectra and thus strongly advocate the active database approach what we call MARVEL, standing for Measured Active Rotational–Vibrational Energy Levels [18,19]. MARVEL requires not only complex tools for handling information in the databases but also experimental efforts to obtain and analyze high-resolution spectra of important small species and theoretical developments that allow efficient and accurate computation of complete spectra.

The fields of electronic-structure theory and variational nuclear motion computations are diverse and involve a huge number of papers. Consequently, it is impossible to review the advances in these fields. Only efforts in our group related to the computation of complete rotational–vibrational spectra of small molecules is overviewed and references from other groups are given only when directly relevant to our own efforts.

## 2. NONADIABATIC COMPUTATIONS—WHERE THEORY DELIVERS

For the smallest quantum systems, comprising perhaps up to five particles, one can afford not introducing the separation of the electronic and nuclear degrees of freedom, i.e., not introducing the BO approximation. For historical reasons such computations of energy levels are usually referred to as nonadiabatic though strictly speaking they should be called diabatic.

For three- and four-particle systems, like  $\text{H}_2^+$  and  $\text{H}_2$ , sophisticated nonadiabatic computations have been performed with specialized techniques [3,20–27]. These computations can yield rovibronic energy levels whose accuracy is limited only by the Hamiltonian used for their evaluation. Unlike a BO treatment, nonadiabatic computations can distinguish between certain spectroscopic characteristics of the different isotopologues. Nevertheless, while nonadiabatic computations yield energy levels in a quantitative way, the qualitative characterization of them is somewhat difficult.

In a recent paper [23] we made an attempt to retain the notion of a PES in a nonadiabatic treatment. This was achieved by fixing the internuclear separation in  $\text{H}_2^+$ -like systems, a straightforward procedure in Jacobi coordinates. The resulting energy correction to the BO energies was termed adiabatic Jacobi correction (AJC). The AJC numerical values are considerably smaller than the well-established diagonal Born–Oppenheimer corrections (DBOC) [28–33], suggesting that the DBOC might correct for more than simply the translational motion. More work needs to be done to understand better the deviations between the AJC and DBOC corrections and to see which one stands closer to the fully nonadiabatic limit.

The fully nonadiabatic treatment of few-body systems have yielded very accurate energy levels and transition energies. At the limit of these calculations, when even QED effects are considered, the energies have not only internal consistency but are in almost full accord with the relevant results of measurements.

As to many-electron systems, corrections to the BO approximation can be obtained by means of a second-order contact transformation method [28]. This introduces two terms: (a) the simple DBOC, which gives rise to a mass-dependent correction to the PES; and (b) the considerably more difficult second-order (also called non-adiabatic) correction, which introduces coupling between electronic states and primarily results in corrections to the kinetic energy operator. In the most sophisticated first-principles treatments [17,34,35] allowance is made for non-adiabatic effects though further work is required to explore the best possible strategies for computation and utilization of this information.

## 3. MARVEL—AN ACTIVE DATABASE APPROACH

There are several areas in the sciences where experimentally measured quantities, with well defined uncertainties, and quantities preferred on some theoretical ground, again with appropriate uncertainties, are decidedly distinct but relations can be worked out between the two sets of data. Such areas include thermochemistry [36,37], reaction kinetics [38,39], and, of course, spectroscopy.

In spectroscopy the relation between transitions and energy levels is linear and exceedingly simple. To the best of our knowledge Flaud and co-workers [40] were the first to suggest a useful procedure for inverting the information contained in measured transitions to energy levels. Their method has been extended [18,19] to treat all measured rotational–vibrational transitions available and obtain the related energy levels in one grand inversion and refinement process. The active database protocol and program developed is called MARVEL [18]. The energy levels so obtained are considered measured as they are obtained from experiment. The set of measured energy levels is called active in the sense of the Active Thermochemical Tables approach of Ruscic [36], and implies that if new experimental transitions become available the refinement process must be repeated resulting in a new set of improved rotational–vibrational energy levels.

Determination of a set of energy levels and an improved set of transitions by MARVEL is based on the following steps:

- (1) Collect, critically evaluate, and compile all transitions, including their assignments and uncertainties, into a database.
- (2) Determine those energy levels which belong to a particular spectroscopic network (SN).
- (3) Within a given SN, set up a vector containing all the transitions, another one comprising the requested measured levels, and a sparse inversion matrix describing the relation between transitions and levels.
- (4) During solution of the resulting set of linear equations uncertainties in the measured transitions can be incorporated which result in uncertainties for the energy levels. The absolute energy levels of a given SN can only be obtained if the value of the lowest energy level within the SN, with zero uncertainty, is set up correctly.

The MARVEL procedure and code developed has been tested for H<sub>2</sub><sup>17</sup>O (Table 9.1). H<sub>2</sub><sup>17</sup>O was chosen as it contains a relatively small number of accurately measured transitions (on the order of 7000) [41–46], including a large number of transitions on the ground vibrational state, and water is probably the single most important polyatomic molecule whose spectroscopy on the ground electronic state is especially relevant in a number of applications, including understanding of the greenhouse effect on Earth. In the case of H<sub>2</sub><sup>17</sup>O, and indeed for all other symmetrically substituted isotopologues of water, the transitions can be divided unequivocally into two main SNs, para and ortho [47].

A good model must be available prior to using MARVEL in order to give unique labels for the upper and lower states participating in the transitions. Approximate Hamiltonians, variational computations based on PESs, and even perturbation-resonance approaches [48] are able to provide these labels. In the MARVEL program the normal mode labeling is used for the states, e.g., ( $n_1n_2n_3JK_aK_c$ ) in the case of water, where  $n_1$ ,  $n_2$ , and  $n_3$  stand for the symmetric stretching, angle bending, and antisymmetric stretching quantum numbers, respectively, and the standard asymmetric top notation,  $JK_aK_c$ , applies for the rotational states.

The uncertainties of the MARVEL vibrational levels of  $\text{H}_2^{17}\text{O}$  are on the order of  $10^{-6} \text{ cm}^{-1}$  (Table 9.1). Since the complete list of vibrational states is available from computations, it is clear that even in the experimentally most accessible low-energy region several vibrational levels are not available from experiment.

MARVEL supplies important information both for spectroscopists and quantum chemists. Running MARVEL for a transitions dataset collected from several publications will determine whether there are any outliers in the transition set assembled and whether the experimental uncertainties are realistic. This contributes to the validation of the experimental results. The resulting energy levels can be used for the empirical improvement of PESs and for checking existing assignments or suggesting new ones. Execution of MARVEL for the most important isotopologue of water,  $\text{H}_2^{16}\text{O}$ , is in progress.

## 4. ELECTRONIC STRUCTURE COMPUTATIONS

It is useful if the energy-level database within MARVEL contains a (complete) set of accurate rotation–vibration levels. This information also helps the assignment of measured transitions. For many-electron systems the levels can only be determined using PESs obtained from sophisticated, though approximate first-principles techniques, like the focal-point approach (FPA) [49,50].

### 4.1 The focal-point approach (FPA)

A fundamental characteristic of the FPA is the dual extrapolation to the one- and  $n$ -particle electronic-structure limits. The process leading to these limits can be described as follows: (a) use families of basis sets, such as the correlation-consistent (aug-)cc-p(wC)V $n$ Z sets [51,52], which systematically approach completeness through an increase in the cardinal number  $n$ ; (b) apply lower levels of theory with extended [53] basis sets (typically direct Hartree–Fock (HF) [54] and second-order Møller–Plesset (MP2) [55] computations); (c) use higher-order valence correlation treatments [CCSD(T), CCSDTQ(P), even FCI] [5,56] with the largest possible basis sets; and (d) lay out a two-dimensional extrapolation grid based on the assumed additivity of correlation *increments* followed by suitable extrapolations. FPA assumes that the higher-order correlation increments show diminishing basis set dependence. Focal-point [2,49,50,57–62] and numerous other theoretical studies have shown that even in systems without particularly heavy elements, account must also be taken for core correlation and relativistic phenomena, as well as for (partial) breakdown of the BO approximation, i.e., inclusion of the DBOC correction [28–33].

Note that the FPA can be used for more than spectroscopic applications. In fact it has helped to redefine first-principles thermochemistry, see the HEAT (High-accuracy Extrapolated *Ab initio* Thermochemistry) [63,64] and  $W_n$  (Weizmann- $n$ ) [65] protocols and Refs. [37,66,67], for example.

**TABLE 9.1** *Ab initio* (CVRQD), empirical (FIS3), and experimental (MARVEL) vibrational energy levels (in  $\text{cm}^{-1}$ ) of  $\text{H}_2^{17}\text{O}$  up to  $14300 \text{ cm}^{-1}$ 

$n_1n_2n_3$	CVRQD	FIS3	MARVEL <sup>a,b</sup>	Levels <sup>c</sup>
000	4630.367	4630.168	0.000000	279
010	1591.644	1591.346	1591.325655(43)	184
020	3145.535	3144.925	3144.980456(44)	93
100	3653.138	3653.157	3653.142275(96)	113
001	3748.115	3748.200	3748.318070(93)	150
030	4657.888	4657.007		
110	5228.214	5227.816	5227.705615(386)	150
011	5320.482	5320.211	5320.250932(66)	122
040	6122.609	6121.559		
120	6765.588	6764.799	6764.725615(966)	28
021	6857.887	6857.267	6857.272719(105)	78
200	7192.896	7193.186	7193.246625(193)	76
101	7238.116	7238.557	7238.713600(185)	100
002	7430.918	7431.136	7431.076115(1450)	26
050	7528.957	7527.914		1
130	8261.877	8260.780		3
031	8357.439	8356.514		7
210	8750.235	8750.000		34
111	8792.566	8792.525	8792.544310(926)	106
060	8855.488	8854.751		1
012	8983.119	8982.897	8982.869215(966)	51
140	9709.883	9708.660		
041	9814.524	9813.391		
070	10070.793	10070.693		
220	10270.377	10269.703		12
121	10311.631	10311.179	10311.202510(926)	73
022	10502.067	10501.444		
300	10584.956	10585.923		65
201	10597.244	10598.352	10598.475610(926)	100
102	10853.042	10853.561	10853.505315(966)	53
003	11011.416	11011.933		45
150	11082.442	11081.789		
051	11221.331	11220.134		
080	11235.025	11234.647		
230	11750.948	11749.946		
131	11793.487	11792.703	11792.827010(6019)	31
032	11985.407	11984.450		
310	12121.917	12122.290		26
211	12132.557	12133.072	12132.992610(926)	87
160	12360.562	12360.454		
112	12389.311	12389.173		17

**TABLE 9.1** (Continued)

$n_1n_2n_3$	CVRQD	FIS3	MARVEL <sup>a,b</sup>	Levels <sup>c</sup>
090	12511.995	12510.737		
013	12541.086	12541.118	12541.225510(926)	13
061	12562.935	12561.916		
240	13186.424	13185.271		
141	13234.029	13233.034		1
042	13428.499	13427.338		1
320	13620.792	13620.773		3
221	13631.364	13631.483	13631.499810(1019)	48
170	13640.751	13640.414		
071	13807.707	13809.693	13808.273310(926)	1
400	13809.863	13810.343		25
301	13811.086	13812.195	13812.158110(926)	68
0100	13829.143	13827.954		
122	13890.137	13889.483		
023	14039.711	14039.317		
202	14202.553	14203.479		11
103	14295.039	14296.298	14296.279510(370)	26
			Total:	2308

*a* Values in parentheses correspond to  $2\sigma$  uncertainties, in units of  $10^{-6} \text{ cm}^{-1}$ . The lowest level was set exactly to zero with zero uncertainty.

*b* The ranges ( $\text{cm}^{-1}$ ) of measured transitions: 0–177 [41], 177–600 [42], 500–8000 [43], 8000–9400 [44], 9711–11335 [45], and 11365–14377 [46].

*c* Number of rotational energy levels corresponding to the given vibrational energy level.

## 4.2 Ab initio force fields

One old difficulty of nuclear motion computations for larger systems, namely the representation of PESs, plagues applications of even the most sophisticated procedures. While low-order force fields [68,69] may not provide a good representation of the PES for systems undergoing large-amplitude motions, for many systems of practical interest an anharmonic force field representation of the PES should provide at least the first important stepping stone to understand the complex internal dynamics of the system at low energies.

Internal coordinate quartic force fields have been computed for relatively large systems, e.g., for the 17-atom amino acid L-proline [70]. Nevertheless, despite the fact that electronic-structure programs to compute analytic geometric first and second derivatives of the energy have become available at almost any level [71–74], to the best of our knowledge [68], complete sextic force fields in internal coordinates are available only for a handful of triatomic systems,  $\text{N}_2\text{O}$  [75–78],  $\text{CO}_2$  [79–82], and  $\text{H}_2\text{O}$  [48,59]. This is due to several factors. First, it is exceedingly difficult to determine accurate higher-order force constants strictly from experimental information. Second, force fields computed from most electronic-structure



codes are given in rectilinear Cartesian or normal coordinates and their nonlinear transformation to more meaningful representations involving curvilinear internal coordinates is nontrivial [83]. Third, polynomial expansions are subject to rather limited ranges of applicability. Fourth, quartic normal coordinate force fields give excellent frequencies when used with VPT2 formulas, a precision of  $1\text{--}2\text{ cm}^{-1}$  is not uncommon [84], but when used in variational procedures the computed frequencies show much larger deviations from experiment. This was discouraging as variational procedures render the use of somewhat complex and tedious procedures [48,85] treating resonances present in PT treatments unnecessary. Nevertheless, as shown in section 5.2, one can use internal coordinate force fields in an exact and completely general way not only within internal coordinate Hamiltonians but also within Hamiltonians [86,87] expressed in normal coordinates. This should result in a renewed interest in force fields for lower-energy (ro)vibrational studies of systems having more than three atoms.

### 4.3 *Ab initio* (semi)global PESs

Since one cannot compute truly high quality PESs and DMSs in a single step, one needs to build them piecewise. It is advantageous to utilize the focal-point approach [49,50] detailed in subsection 4.1 for this purpose. In fact, it has been employed successfully to obtain highly accurate semiglobal PESs for a number of triatomic systems, including  $\text{H}_2\text{O}$  [17,59],  $[\text{H,C,N}]$  [88], and  $\text{H}_2\text{S}$  [60]. The so far most elaborate and most successful application of FPA yielded the adiabatic CVRQD PESs of the water isotopologues. CVRQD means that the final *ab initio* ground electronic state surface includes corrections due to core (C) and valence (V) correlation, as well as relativistic (R) and QED (Q) contributions, and it is an adiabatic surface utilizing the DBOC correction (D) [28–30]. For purposes of illustration, it is insightful to repeat the steps resulting in the presently most accurate *ab initio* semiglobal surfaces of the water isotopologues, which can reproduce all the measured transitions of all isotopologues with an average accuracy better than  $1\text{ cm}^{-1}$  [17].

The CVRQD PESs of the water isotopologues are based upon valence-only aug-cc-pV $n$ Z [51,52],  $n = 4, 5, 6$ , internally contracted multi-reference configuration interaction (ICMRCI) [89] calculations including the size-extensive Davidson correction [90], which were extrapolated to the CBS limit. The largest correction to the valence-only surface comes from core correlation, which should be determined using a size-extensive technique. Nevertheless, the core correction surface of the CVRQD PESs was determined at the averaged coupled pair functional (ACPF) [91] level lacking strict size-extensivity. The relativistic surfaces were obtained by first-order perturbation theory as applied to the one-electron mass-velocity (MV) and one- and two-electron Darwin terms (MVD2) [92,93], supplemented by a correction obtained from the inclusion of the higher-order Breit term in the electronic Hamiltonian [93]. A correction surface due to the one-electron Lamb shift has also been determined. Consideration of the Lamb shift was shown to have contributions as much as  $1\text{ cm}^{-1}$  for some levels beyond  $20000\text{ cm}^{-1}$  [94]. Finally, a DBOC correction surface was obtained, at the cc-pVTZ MRCI level [17]. The un-

**TABLE 9.2** Approximate per quanta contributions (in  $\text{cm}^{-1}$ ) of so called small corrections to the low-lying VBOs of  $\text{H}_2^{16}\text{O}^a$ 

Correction surface	STRE	BEND
MVD1	$-2.8(n_1 + n_3)$	$+1.4n_2$
D2	$-0.04(n_1 + n_3)$	$+0.12n_2$
Breit	$-0.6(n_1 + n_3)$	$-0.02n_2$
Lamb-shift	$+0.18(n_1 + n_3)$	$-0.11n_2$
Core correction	$+7.3(n_1 + n_3)$	$-0.5n_2^2$
DBOC	$+0.4(n_1 + n_3)$	$-0.45n_2$

*a* MVD1 = one-electron mass-velocity plus Darwin; D2 = two-electron Darwin; DBOC = diagonal Born–Oppenheimer correction. Please see text for details.  $n_1$  and  $n_3$  are the stretching,  $n_2$  is the bending quantum number.

precedented precision of the CVRQD PESs in determining the vibrational levels of water can be judged from the relevant entries in Table 9.1. The importance of the correction surfaces can be judged from entries in Table 9.2, showing the approximate per quanta changes in the vibrational band origins (VBOs) of  $\text{H}_2^{16}\text{O}$ .

To use the *ab initio* energies computed over a grid most efficiently in nuclear motion computations we need to fit them to analytical surfaces. Fitting the surfaces involves several delicate choices if the high quality of the underlying electronic-structure calculations is not to be lost. Notwithstanding the importance of this step the fitting process is not discussed here; for important details please consult, for example, Refs. [59,95,96].

#### 4.4 Empirical PESs

Whatever complicated procedures are employed for their determination, *ab initio* PESs can hardly produce transitions matching the accuracy of experimentally determined transitions. A partial remedy to this problem is offered by the empirical adjustment of the surface to best match the available experimental data in a least-squares sense.

*Ab initio* PESs, like CVRQD for water, provide an excellent starting point for the refinement of empirical PESs. The rule of thumb seems to be that the higher the quality of the initial surface the better the resulting empirical PES. In fact the best empirical PES for water, termed FIS3 [96], as it is a joint fitted surface for three isotopologues,  $\text{H}_2^{16}\text{O}$ ,  $\text{H}_2^{17}\text{O}$ , and  $\text{H}_2^{18}\text{O}$ , utilized the CVRQD PESs as a starting point. To assemble a reliable set of experimental rotational–vibrational energy levels for the refinement process is far from trivial. As detailed in section 3, it is possible to invert the directly measured transitions to energy levels and obtain a partial set of high-accuracy levels. As to the functional form of the fit, several choices are possible and these mainly depend on the accuracy of the starting PES. The methods that can be used to fit PESs are basically the same as the nuclear motion methods described in section 5, thus they need no further discussion here.

The energy levels determined with the help of empirical PESs cannot match the extreme accuracy of the MARVEL levels but they also provide a complete set.

Empirical PESs interpolate very well but their extrapolation potential is inferior to those of the *ab initio* PESs. Therefore, even if a highly accurate empirical PES is available, the *ab initio* surface must be retained as it might prove to be a better choice for finding new transitions in a new region of the spectrum and a better starting point for further refinement of the surface if more detailed experimental information became available.

#### 4.5 Dipole moment surfaces (DMSs)

Determination of first-principles transition intensities of rotational–vibrational levels relies on knowledge of the DMS and the nuclear motion wavefunctions of the states involved in the transition. The former can be obtained from electronic-structure computations while the latter can be determined from a variational solution of the nuclear motion problem. The DMS is a two- or three-component vector function. While a lot of work has been devoted to obtaining high-accuracy PESs and the corresponding rotation-vibration energy levels and wavefunctions for small molecules, there is only limited experience accumulated about the determination of high-accuracy DMSs. Furthermore, while empirical adjustment of PESs is common practice, empirical adjustment of DMSs does not seem to be viable, partly due to the inferior quality of the available experimental data. Accurate measurement of the intensities of rotational–vibrational transitions in the laboratory is a technically demanding task even at room and especially at elevated temperatures. The range of intensities and their observational uncertainties are much larger for transition intensities than those for line positions. New, high-precision experiments have started to appear but this changes the present-day scenario rather slowly [97,98].

*Ab initio* studies of the PESs of triatomic molecules [17,59,60,88] have shown the importance of appending so-called small corrections to standard non-relativistic valence-only *ab initio* predictions. So far these have not been considered for the DMSs of polyatomic molecules. It is up to future high-accuracy computation of DMSs and the utilization of new measurements to decide whether such corrections have a significant effect on computed rotational–vibrational intensities making their computation worth pursuing.

Obtaining a high-quality analytical fit to *ab initio* dipole data is a challenging problem [99]. This is connected to the fact that the resulting DMS must be able to reproduce transition intensities which vary by many orders of magnitude. Fits using procedures proven adequate for PESs may suffer from small unphysical oscillations. Construction of a new DMS, including relativistic effects, is underway for water [100].

### 5. VARIATIONAL NUCLEAR MOTION COMPUTATIONS

Breaking away from the traditional treatment of molecular spectra using perturbative approaches, variational computation of rovibronic energy levels was intro-

duced in the early 70s [101,102], following the prior derivation of simplified and exact normal coordinate Hamiltonians for nonlinear [86] and linear [87] molecules. Two routes can be followed in variational-type nuclear motion computations. One employs Hamiltonians in curvilinear, preferably orthogonal internal coordinates [103–106] offering the advantage that such Hamiltonians, with appropriately chosen basis sets, matrix element computations, diagonalization techniques, and PESs, can yield the complete eigenspectrum. Due to obvious dimensionality problems, this technique could only be pursued for small species, most notably for triatomics. Recognizing the difficulties associated with the development and use of tailor-made internal coordinate Hamiltonians, the other direction prefers to have a unique Hamiltonian which would be the same for almost all molecular systems. This is offered by the Hamiltonians derived by Watson [86,87] applying an Eckart frame. Perhaps the so far most elaborate use of the Eckart–Watson Hamiltonians has been allowed by the MULTIMODE set of programs [107].

For tri- and tetratomic systems solution of the rovibrational problem was made particularly tractable by the introduction of the discrete variable representation (DVR) [108–115] of the Hamiltonian. Initially, the DVR was developed with standard orthogonal polynomial bases and the associated Gaussian quadratures, employing the same number of basis functions and quadrature points. DVRs based on such basis sets, quadrature points, and weights possess remarkable properties. The most relevant is the diagonality of the potential energy matrix  $\mathbf{V}$  making DVR a nearly ideal technique for nuclear motion computations even though the simplifications introduced in the computation of  $\mathbf{V}$  make the eigenvalues not strictly variational. Nowadays solution strategies have started to appear to not only the four- [116–125] but also the five- [126–128] and six-atomic [129] problems.

## 5.1 Computations in internal coordinates

As Refs. [116–134] testify, there are several strategies to set up matrix representations of multidimensional rotational–vibrational Hamiltonians. One of the simplest ones is the following. The rotational–vibrational Hamiltonian is expanded in orthogonal (O) coordinates [103,135] so that there are no cross-derivative terms in the kinetic energy operator, its matrix is represented by the discrete variable representation (D) [108–112] coupled with a direct product (P) basis for the vibrational modes multiplied by a rotation function formed by combining the normalized Wigner rotation functions, and advantage is taken of the sparsity of the resulting Hamiltonian matrix whose selected eigenvalues can thus be determined extremely efficiently by variants of the iterative (I) Lanczos technique [136]. The resulting procedure has been termed DOPI [2,137].

A particularly important feature of internal coordinate rovibrational Hamiltonians is that singularities will always be present in them when expressed in the moving body-fixed frame [138]. Protocols that do not treat the singularities in these rovibrational Hamiltonians may result in sizeable errors for some of the rovibrational wave functions which depend on coordinates characterizing the singularity, thereby preventing their use for the computation of the complete rovibrational eigenspectrum.

Apart from approaches which avoid the introduction of certain singularities during construction of the Hamiltonian [139–141], it seems that there are only a few *a posteriori* strategies to cope with singular terms in rovibrational Hamiltonians when solving the related time-independent Schrödinger equation by means of (nearly) variational techniques. Building partially on previous efforts [142–146], Czakó and co-workers [147–149] developed a generalized finite basis representation (GFBR) strategy based on the use of the Bessel-DVR functions of Littlejohn and Cargo [150], and several resulting implementations for coping with the radial singularities present, for example, in the Sutcliffe–Tennyson triatomic rovibrational Hamiltonian expressed in orthogonal internal coordinates. In this strategy a non-polynomial nondirect-product basis is employed. An efficient GFBR has been developed with nondirect-product basis functions having structure similar to that of spherical harmonics [148]. It was shown there that the use of an FBR which couples different grid points to each basis function can be useful even if it results in a non-symmetric representation of the Hamiltonian.

## 5.2 Computations in normal coordinates

The Eckart–Watson Hamiltonians [86,87] expressed in normal coordinates are universal and thus make the introduction and programming of tailor-made Hamiltonians for each new system exhibiting unique bonding arrangements unnecessary. While the use of these Hamiltonians for systems having more than three atoms has a long and successful history [151–154], their application is not without difficulties. In particular, due to the numerical integration schemes employed for the potential, in general it has proved to be impossible to use PESs expressed in arbitrary coordinates with this Hamiltonian without resorting to some kind of an expansion of the PES in normal coordinates, thus separating, to a certain extent, otherwise non-separable functions. One of the best approximate techniques developed so far for computing the matrix representation of the potential is due to Gerber [152] and Carter et al. [154] and is called the *n*-mode representation.

This shortcoming has so far excluded the possibility of the exact inclusion of general high-quality PESs in vibrational computations for systems having more than three atoms even if they were available. Nevertheless, as shown here and in Ref. [155] in more detail, this problem can be eliminated. To achieve this, one needs to (a) represent the Hamiltonian using the DVR technique; and (b) apply a formalism allowing the exact expression of arbitrary internal coordinates in terms of normal coordinates.

To express curvilinear internal coordinates in terms of normal coordinates, bond vectors in terms of normal coordinates are needed. A bond vector pointing from nucleus *p* to *i* (*i*, *p* = 1, 2, . . . , *N* and *i* ≠ *p*) in a molecule with *N* nuclei is given as

$$\mathbf{r}_{pi} = \mathbf{C} \left[ \mathbf{a}_i - \mathbf{a}_p + \sum_{k=1}^{3N-F} \left( \frac{1}{\sqrt{m_i}} \mathbf{I}_{ik} - \frac{1}{\sqrt{m_p}} \mathbf{I}_{pk} \right) Q_k \right],$$

where the orthogonal matrix **C** describes spatial orientation, **a<sub>i</sub>** (*i* = 1, 2, . . . , *N*) are the Cartesian coordinates of the chosen reference structure, and elements of **I<sub>ik</sub>**

**TABLE 9.3** Variational vibrational band origins (VBOs, in  $\text{cm}^{-1}$ ) with  $l = 0$  up to the highest fundamental of  $^{12}\text{C } ^{16}\text{O}_2$  obtained with Chédin's [80] sextic empirical force field<sup>a</sup>

$(n_1, n_2^{ l }, n_3)^b$	Internal <sup>c</sup>	Normal <sup>d</sup>	Expt. <sup>e</sup>
$(0, 0^0, 0)$	2535.4	2535.4	–
$(1, 0^0, 0)$	1285.0	1285.0	1285.4
$(0, 2^0, 0)$	1387.5	1387.5	1388.2
$(0, 0^0, 1)$	2347.3	2347.3	2349.2

*a* A potential energy cutoff of  $20000 \text{ cm}^{-1}$  was applied, as described in detail in Ref. [137].

*b* Standard normal coordinate notation of the VBOs for a triatomic linear molecule.

*c* The variational results based on a triatomic internal coordinate Hamiltonian were obtained with the DOPI algorithm [137], the results are the same as in Table 9.3 of Ref. [137].

*d* Variational results obtained with the DEWE algorithm [155].

*e* Experimental vibrational frequencies taken from Ref. [80].

( $i = 1, 2, \dots, N$ ,  $k = 1, 2, \dots, 3N - F$ , where  $F = 5/6$  if the molecule is linear/nonlinear) are the transformation coefficients between normal coordinates and the instantaneous displacement coordinates in the Eckart frame. Bond vectors are thus expressed in terms of  $Q_k$  ( $k = 1, 2, \dots, 3N - F$ ) and the Euler angles (through **C**). Curvilinear internal coordinates, expressed as scalar and triple products of bond vectors, are functions of only the normal coordinates [156]. Due to this transformation, arbitrary potentials given in curvilinear internal coordinates can be called in a program working in the  $Q_k$  ( $k = 1, 2, \dots, 3N - F$ ) normal coordinates.

Along these lines an efficient protocol, called DEWE has been developed [155] which is based on the DVR of the Eckart–Watson Hamiltonians involving an exact inclusion of potentials expressed in an arbitrary set of coordinates. The DEWE procedure has been tested both for nonlinear ( $\text{H}_2\text{O}$ ,  $\text{H}_3^+$ , and  $\text{CH}_4$ ) and linear ( $\text{CO}_2$ ,  $\text{HCN}$ , and  $\text{HNC}$ ) molecules.

For  $\text{H}_2^{16}\text{O}$ , employing the high-accuracy CVRQD PES [17,59], the lower vibrational energy levels obtained with DEWE were the same, within numerical precision, as those determined with the DOPI procedure. However, unlike in the case of DOPI, the higher bending levels, with the bending quantum number  $n_2 \geq 4$ , could not be converged tightly. This convergence problem corresponds to the singularity present in the Eckart–Watson Hamiltonian.

VBOs applying Chédin's sextic empirical force field [80] are presented in Table 9.3 for  $^{12}\text{C } ^{16}\text{O}_2$  using exactly the same potential with the internal and normal coordinate Hamiltonians. When comparison can be made, the two approaches result in the same eigenenergies. It is also worth mentioning that for  $\text{CO}_2$  no convergence (singularity) problems appeared, in clear contrast to the case of the nonlinear  $\text{H}_2\text{O}$  molecule.

## 6. OUTLOOK

Understanding the complete rotational–vibrational spectra of small molecules is an almost formidable task. This is partly due to the fact that complete spectra contain information about billions of lines even for a triatomic species. Understanding these spectra requires sophisticated instrumentation and experiments, involving measurement and assignment of high-resolution molecular spectra, high-accuracy first-principles computations, involving electronic-structure and nuclear-motion determinations, empirical adjustments of *ab initio* PESs, and allowance for nonadiabatic effects. Only by interplay of all these experimental and computational elements can one expect that for polyatomic species the intricacies of complete molecular spectra will be unraveled some day. It seems most advantageous to us to combine results from experiment and theory by centering on a database approach sketched in this report. Work along these lines is underway for the isotopologues of water, arguably the most important polyatomic molecule.

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