Advanced Review

Accurate variational calculations for line lists to model the vibration–rotation spectra of hot astrophysical atmospheres

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The first principles calculation of the spectra of small molecules is making a significant impact on high-resolution spectroscopy as well as astrophysics and atmospheric physics. Variational nuclear motion calculations, combined with high-accuracy *ab initio* electronic structure computations, are being used to make spectral predictions of increasing accuracy with very few *a priori* assumptions. This work is important for spectral analysis and particularly for dipole transition intensities, which are often very difficult to measure reliably but are essential inputs for many applications such as modeling of radiative transport and remote sensing. Demands for very extended line lists covering many, many millions of transitions which are required to simulate spectra of hot sources are best met using high-quality theoretical models. This aspect of the use of variational nuclear motion calculations is discussed with reference to both the benchmark water molecule and future data needs, in particular, for models of the atmospheres of extrasolar planets. © 2011 John Wiley & Sons Ltd.

How to cite this article:
WIREs Comput Mol Sci 2011. doi: 10.1002/wcms.94

INTRODUCTION

High-resolution vibration–rotation spectroscopy of molecules is of great practical and scientific importance. It is the technique by which nearly all high-precision observational information on the structure of molecules and the shape of their potential energy surfaces is obtained. It provides data for models of radiative transport for many systems including our own atmosphere and is a powerful tool for remote sensing, in the context of astrophysics, very remote sensing. Indeed, it is only through the use of such spectroscopy that it is possible to investigate the rich and varied chemistry in the Universe about us.

Laboratory high-resolution vibration–rotation spectroscopy has produced a wealth of data on small and not so small molecules. Transitions frequencies, which yield a unique fingerprint for the species under investigation, are often recorded to an accuracy of 8 or 9 figures. This precision is largely unachievable using entirely *ab initio* quantum mechanical procedures and usually can only be matched theoretically by direct fits to the observations. Nonetheless, the first principles calculation of vibration–rotation spectra of small molecules has become a major activity.

Accurate calculations require treating both the electronic and nuclear motion problems with a precision not required for many other problems, such as, for example, reaction dynamics. This in turn means that both the assumed separation between these two motions via the Born–Oppenheimer approximation, and other 'minor' effects which are often neglected can lead to significant contributions to calculated transition frequencies. Such effects include the contribution of core electrons, relativistic corrections, and, as alluded to already, relaxation of the Born–Oppenheimer approximation through both the adiabatic and nonadiabatic corrections. In extreme examples, even the effects which can only be modeled using quantum electrodynamics have been shown to significantly influence both vibrational and rotational spectra.[1–3] These corrections can be systematically

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DOI: 10.1002/wcms.94

TABLE 1 | Hot Astronomical Objects in which Molecules Are Important: Note the Lists Are Far from Exhaustive and that All These Objects Contain Hydrogen Molecules

Object	Approximate Temperature (K)	Chemistry and Key Molecules
G-stars, e.g., the Sun	5200 – 6000	Diatomics, e.g., CH, CO, OH
K-stars	3700 – 5200	Diatomics, e.g., TiO, CO, etc.
M-dwarfs	2000 – 3700	Oxygen rich: H_2O, CO, TiO
Sunspots	3200	H_2O, CO, SiO, TiO, FeH
C-stars	2000 – 3700	Carbon rich: CH_4, HCN, C_2, C_3, HCCH, CO, etc.
Brown dwarfs	500 – 2000	CH_4, H_2O, NH_3, TiO, VO, FeH, etc.
"Hot Jupiter" exoplanets	500 – 2000	So far detected[19]: CH_4, H_2O, CO_2, CO

combined using the focal-point approach of Allen and coworkers.[4,5]

The pioneering work of Kolos and Wolniewicz[6,7] showed that, at least for the hydrogen molecule, first principles quantum mechanics could produce results competitive with experiment, and indeed occasionally correct it. For the case of H_2, at least, Komasa and coworkers[1,8] have shown that theoretical improvements have kept pace with experiment. However, achieving the outstanding accuracy of these calculations required considering many aspects of the problem and even including the effects of quantum electrodynamics up to third order. However, the addition of only a single extra proton, to give H_3^+, leads to problem where high-accuracy *ab initio* treatments are still not competitive in accuracy with experimental measurements.[9]

For few-atom molecules it is possible to obtain more accurate solutions to the nuclear motion problem than it is to the many-electron electronic structure problem.[10] It is thus common to adjust the *ab initio* potential energy surface upon which the nuclear motion calculations are based so that the results better reproduce observations. The resulting spectroscopically determined potentials are widely used for practical calculations.[11–14]

Applications of spectroscopy generally require knowledge of the intensity of individual transitions. Intensities calculated using high-quality *ab initio* procedures are competitive with and, in favorable cases, more accurate than intensities determined experimentally.[15] Computationally, determining accurate dipole moments as a function of molecular geometry, upon which the transition intensities depend, is more straightforward than computing the corresponding potential energy surface. However, finding a suitable analytic continuation ("fit") to the dipole moment as a function of geometry can prove to be far from straightforward.[16]

Finally, besides a position and an intensity, every transition also has a shape. There are three major contributors to the line profile: the natural width, the Doppler width, and the collisional width. Except in cases involving quasi-bound states of finite lifetime,[17] determining the natural width of a line due to the Uncertainty Principle is straightforward; furthermore, the natural width generally gives a contribution much smaller than the other two and only needs to be considered in very special circumstances. The Doppler width, caused by the thermal motions of the molecules, can be significant, particularly at elevated temperatures. This, however, is also straightforward to model using a Gaussian profile. The real challenge is to correctly predict the effects of collisional (or pressure) broadening, and indeed any shift in the line position due to these collisions.[18]

In this review, I pay particular attention to the application of variational calculations to the production of the extensive line lists necessary to model spectra of hot bodies. For this purpose, calculations on water vapor (steam) are used as an example.

Although molecules are abundant in the vast, cold regions of the interstellar medium, they are also important in many hot astronomical environments. Table 1 lists some of the hot ($T > 500$ K) astronomical objects were molecules have been seen. There are many more examples: for instance, spectra of hot molecules have been observed in the remnants following stellar explosions of both the totally destructive supernova[20] and more repetitive nova.[21] Brown dwarfs are substellar objects in that they do not burn hydrogen and therefore never join the main sequence. There are a number of subclassifications of brown dwarfs with different chemistry,[22] the coolest of which, so-called Y-dwarfs, have yet to be positively identified. The generation of extended line lists of transitions is important for modeling the atmospheres and spectra of the objects listed in Table 1; this is one of several applications of accurate variatonal calculations considered in the following section.

WHY CALCULATE VIBRATION–ROTATION SPECTRA?

There are several reasons for computing vibration–rotation spectra.[23] In practice, of course, a single calculation, particularly the comprehensive ones needed at elevated temperatures, may be performed for a variety of different reasons.

The concept of the potential energy surfaces, which in turn is based on the Born–Oppenheimer approximation, underpins nearly all of gas phase chemical physics. The original motivation for calculating spectra was to test potential energy surfaces. Such tests give pointers about not only the accuracy of the potential energy surface but also information on how it needs improving.[24] This procedure has now been turned round and spectra are routinely used to construct, or more commonly refine,[25] potential energy surfaces.

Of course, accurate calculations can be used predictively, and the more accurate the calculations, the better the predictions. Predicted spectra can be used to model future observations, either in the laboratory or elsewhere. Experience shows that except in cases of interpolation between and rather minor extrapolations from observed spectra, high-quality *ab initio* methods provide the most useful predictions (e.g., see Ref 26).

The fact that spectra can be recorded to high accuracy does not necessarily mean that they are easy to interpret. For many molecules assigning spectra, which is associating individual transitions with fully specified upper and lower states, is far from straightforward. Calculated vibration–rotation spectra can play an important role in making line assignments. These assignments are important not only because they give physical insight into the molecule concerned but they are also necessary if the observed data is to be used to model spectra at, for example, different temperatures.

Calculations can be used to estimate whether very weak spectra displaying novel effects can be observed. Examples of this include extreme behavior predicted on the basis of classical mechanics such as clustering of energy levels[27] and quantum monodromy, which was first found by analyzing the results of *ab initio* calculations[28] and subsequently observed in hot emission spectra.[29] Similarly, predictions have been made about very weak spectra sensitive to generally unobserved effects such as nuclear spin coupling[30] or possible parity violating transitions in chiral molecules.[31]

A major application of rotation–vibration calculations exploits the computer's ability to generate and handle huge spectroscopic datasets which can then extend studies to temperatures well above those covered by traditional, line-by-line high-resolution spectroscopy experiments. These are important for the analysis of spectra or, indeed, radiation transport models at high temperatures. The rotation–vibration spectra of even rather small molecules become very complicated at higher temperatures. A comprehensive understanding requires the knowledge of many millions, perhaps even billions, of individual transitions.[32] It is not practical to measure this much data in the laboratory and therefore a more realistic approach is the development of an accurate theoretical model, benchmarked against experiment. Examples of this application for astronomical purposes are discussed below.

The incompleteness of most experimental datasets means that calculations are useful for computing other properties that can be associated with spectra. Notable among these are partition functions and the variety of thermodynamic properties, such as the specific heat of the species in question, which depend directly on the partition function.[33] Again, calculations are particularly useful for estimating these quantities at high temperature.[34,35]

THEORETICAL TECHNIQUES

Separating Electronic, Vibrational, Rotational and Translational Motion

It is straightforward to write down the Schrödinger equation governing the motion of a molecule containing N atoms and n electrons and the associated nonrelativistic Hamiltonian which defines the wavefunction and energy levels of a vibrating–rotating molecule. This Hamiltonian has $3(N + n)$ degrees of freedom and is essentially insoluble in this form. In practice, there are a number of approximations that are routinely made before one can even begin to search for tractable solutions to the related Schrödinger equations. These steps can be characterized as separating the nuclear and electronic motions, removing the translational motion of the whole system by considering only the nuclear coordinates and, less crucially, distinguishing between the vibrational and rotational nuclear motion. While there are different methods available for studying molecules which skip each of these steps,[36,37] none of them are in wide use for the study of the rotation–vibration states of chemically bound, and particularly hot, molecules.

The Born–Oppenheimer Approximation

Although attempts are being made to compute spectroscopic properties of simple molecules without treating the nuclear and electronic coordinates separately,[38,39] such calculations are extremely challenging and have yet to make a significant impact on practical vibration–rotation spectroscopy. This means that spectroscopic calculations follow what is the standard first step in the analysis of practically any problem in chemical physics and separate between the motions of the electrons and the nuclei. This step generally is based upon what is known as the Born–Oppenheimer approximation.

The Born–Oppenheimer approximation starts by writing the total wavefunction of the system as a product of electronic and nuclear wavefunctions:

$$\Psi = \psi^{\mathrm{elec}}(\mathbf{r}_i; \mathbf{R}_I)\psi^{\mathrm{nuc}}(\mathbf{R}_I). \tag{1}$$

As the notation shows, the nuclear motion wavefunction, ψ^{nuc}, is a function only of the nuclear coordinates, denoted as $\mathbf{R}_I$, and the electronic motion wavefunction, ψ^{elec}, depends explicitly on the electronic coordinates, denoted as $\mathbf{r}_i$ in Eq. (1) and parametrically on the nuclear coordinates. That is, there is a different electronic wavefunction for each nuclear configuration although, in practice, the electronic wavefunction only depends on the internal or vibrational coordinates, which I will call $\mathbf{Q}$ and which are defined below.

Within the Born–Oppenheimer approximation the electronic wavefunction is obtained as the solution of the Schrödinger equation given by the electronic kinetic energy operator and Coulomb interactions of the electrons with each other and the nuclei. The resulting electronic energy, E^{elec}, depends parametrically on the relative nuclear coordinates, $\mathbf{Q}$, which carry the vibrational motion and are discussed in the next section. Adding the Coulomb repulsion between the nuclei, which also depends on $\mathbf{Q}$, gives the nuclear coordinate-dependent potential used in the nuclear motion Schrödinger equation. This potential is independent of the mass of the nuclei and therefore is the same for all isotopologues of a particular molecule. This is an important result of the Born–Oppenheimer approximation and can be used to quantify its reliability by comparisons of spectra calculated for different isotopologues of the same molecule.[40]

The Born–Oppenheimer approximation actually involves two approximations: the separation of the electronic and nuclear wavefunctions, Eq. (1), and neglect of the term where the nuclear kinetic energy operator acts on the electronic wavefunction. It is reasonably straightforward to improve on the Born–Oppenheimer approximation by allowing for the case where the nuclear kinetic energy operator acts on the ground state electronic wavefunction.[41] This correction is variously known as the Born–Oppenheimer diagonal correction (BODC), the diagonal Born–Oppenheimer correction and the adiabatic correction. Adding this correction to the potential defined above gives the adiabatic approximation. It is important to note that the BODC is mass dependent and therefore the effective potential energy surface given by the adiabatic approximation is mass dependent and there is a new effective potential for each isotopologue.

If one writes the nuclear kinetic operator in Cartesian coordinates, the BODC simply depends on the second derivative of electronic wavefunction with respect to the coordinates of the nuclei.[42] Integrals involving such terms are available in a number of electronic structure programs where they are used to compute harmonic vibrational frequencies.[42] The use of $3N$ Cartesian coordinates actually involves a slight approximation since it does not allow for the separation of the translational motion, an issue which is discussed in the next section. This method of calculation leads to the electronic contribution to the translation motion of the whole molecule being neglected. Early treatments of the BODC used rigorous, generally complicated, formulation of the Hamiltonian.[43] The more recent consensus is that this is not really necessary[41] as the error introduced by using the simpler Cartesian form[42] is so small that this form is sufficient for all practical purposes. It should be noted that in cases where there are identical atoms, particularly hydrogen atoms, there are symmetries between the adiabatic correction for different isotopologues which can be exploited when both identifying the need for beyond Born–Oppenheimer corrections and in constructing the adiabatic correction.[40] As a result of this, calculation of the contributions to the BODC separately for each nucleus allows the BODC to be calculated for every isotopologue in a single calculation (e.g., see Ref 44); alternatively including the BODC as part of the whole electronic structure calculation requires the whole surface to be recalculated for each isotopologue.[13]

Correcting for the remainder of the Born–Oppenheimer approximation by introducing so-called nonadiabatic corrections is altogether a more difficult proposition. Within the spirit of the wavefunction separation of Eq. (1), one can write the exact wavefunction as

$$\Psi = \sum_{n=0}^{\infty} \psi_n^{\mathrm{elec}}(\mathbf{r}_i;\mathbf{R}_I)\psi_n^{\mathrm{nuc}}(\mathbf{R}_I), \qquad (2)$$

where ψ_0^{elec} is the ground state electronic wavefunction that has been considered up until now. The sum in Eq. (2) runs over all electronic states of the molecule including those lying in the electronic continuum. Formally, the nonadiabatic correction can be calculated using a sum in this form. However, an infinite sum over electronic states is undesirable and full treatments of the nonadiabatic corrections are rare. In practice, the sum is often truncated after two or three terms in the important case of electronic states which lie near to each other. Schwenke[45] developed a method whereby a full sum over all states is obtained by considering only single excitations from a restricted Hartree–Fock (HF) treatment of the electronic wavefunction, which, of course, neglects effects due to electron correlation.

More pragmatic treatments of the nonadiabatic problem are usually employed (e.g., see Refs 46 and 47). The starting point for these is the observation that the nonadiabatic corrections are usually best modeled by corrections to the nuclear kinetic energy operator rather than the potential. Furthermore, these corrections take a rather different form for the vibrational and the rotational motions.[48,49] For diatomic molecules, nonadiabatic effects have been explicitly taken into account when modeling the vibration–rotation spectrum for a variety of even quite heavy diatomic species. In this case, geometry-dependent, distinct effective masses are used for both vibrational and rotational motion.[50,51]

On physical grounds, the effective “atomic” masses must lie between an upper limit of the actual atomic mass (i.e., nucleus plus electrons) and a lower limit of the mass of the bare nucleus. Physically, this distinction depends on the degree to which the electrons travel with the nuclei. For many electron systems, it is therefore likely that inner shell electrons will contribute to the effective nuclear mass but less likely that the outer electrons will. In practice, there are a number of ways of choosing optimal masses, for example, to give the correct behavior upon dissociation or to allow for the distribution of electrons within the system.[52] It can also be argued on theoretical grounds that use of atomic masses in some part compensates for errors introduced by the Born–Oppenheimer approximation,[53] a procedure deployed in many actual calculations seeking a pragmatic rather ultra-high-accuracy solution to the problem.

NUCLEAR COORDINATES

The nuclear kinetic energy operator in $3N$ nuclear coordinates mixes both continuous and discrete states of the nuclei. In order to resolve discrete spectra, it is therefore necessary to remove, or at least separately identify, the portion due to translational motion. It is common to classify the motions of the nuclei in a molecule according to three categories:

(1) Translation of the whole molecule through space;
(2) Rotation of the whole molecule;
(3) Vibration or internal motion of the molecule.

The translational motion of the whole system gives a continuous spectrum which is not interesting if one is dealing with spectroscopy. It is therefore necessary to separate off the three coordinate which carry the translational motion of the whole molecule. The resulting nuclear kinetic energy operator is straightforward to derive for diatomic molecules but for polyatomic molecules there is no unique way of defining either the internal kinetic energy operator or, indeed, the reduced mass which depends on the precise choice of coordinates. This is in distinct contrast to the electronic structure problem where the Hamiltonian that has to be solved is easily written down and unique.

The $3N - 3$ coordinates which remain after the separation of the center-of-mass motion are usually known as space-fixed coordinates and mix vibrational motion and overall rotation of the molecule. They are useful for representing collision complexes such as van der Waals molecules where a knowledge of the various angular momenta of component molecules in the cluster is more important than separating between vibrational and rotational motions of the system as a whole.[36] Space-fixed coordinates are also useful for solving problems in an external field, as in this case the isotropic nature of space is lost and the orientation of the molecule in the laboratory frame becomes important.

However, for most applications one usually separates the coordinates representing vibrations from those representing rotations to give body-fixed coordinates. The distinction between vibrational and rotational coordinates is useful for a number of reasons and essential for the two-step treatment of rotational motion which is an important part of keeping calculations on highly excited molecule tractable.

However, only for diatomic systems is there a unique and trouble-free way of achieving the separation. For polyatomic molecules, there are a number of issues that need considered when making a choice of coordinates.

To define body-fixed coordinates one has to select a set of internal coordinates to represent the vibrational motions and a Cartesian axis system defined in the frame of the molecule. The coordinates for the rotational motions are the Euler angles which link the space-fixed and body-fixed axis system; thus different choices of body-fixed axes lead to different rotational coordinates. Usually, the transformation from space-fixed to body-fixed axis systems requires three angles to be defined, although two can be used.[54]

Within the body-fixed frame there are $3N - 6$ internal or vibrational coordinates or $3N - 5$ if the system is linear. The optimal separation of vibrational and rotational motion uses the so-called Eckart conditions.[55] However, these are difficult to work with when using geometrically defined internal coordinates.[56] I have discussed, with illustrations, the use of different internal coordinates and axis embeddings elsewhere.[57] One issue that has to considered when choosing internal coordinates is that body-fixing the coordinates always introduces singular points into the Hamiltonian and that the range of the coordinates must be carefully considered to keep the problem within its true domain. Whether either of these issues is a problem for a given calculation has to be considered for each class of molecules and choice of internal coordinates and axis embedding.

Several programs are available for solving the rotation–vibration problem for three atom[58–61] and four atom[59,62–65] systems. For single surface problems, these programs can work to essentially arbitrary accuracy. Increasingly similar programs are becoming available which work for larger molecules[66,67] or ones of arbitrary size.[68] A particularly interesting development, which has aided the development of general programs for treating larger molecules, is the use of numerically defined kinetic energy operators[69] which avoids the need to derive and the program new kinetic energy operators on a case-by-case basis, although I note that rather general, analytically defined kinetic energy operators are possible for certain classes of coordinates.[70]

Vibrational Motion

The traditional method of treating vibrational motion is to use perturbation theory, often based on the use of harmonic oscillators as the zeroth-order basis functions. Programs like Multimode[71] or DEWE[72] build on this idea to give quasi-variational treatments of the nuclear motions states of semirigid molecules. These approaches take advantage of the fact that the harmonic approach and Eckart conditions give a general Hamiltonian, originally derived in its most compact and elegant form by Watson,[73] which readily accommodates different numbers of atoms in the molecule. Use of harmonic basis functions makes this Hamiltonian fairly easy to apply. This is particularly true if the potential energy surface is expressed in terms of force constants since the integrals can be evaluated analytically; these force constants can now be calculated as a routine part of many *ab initio* quantum chemistry packages. However, programs based on the Watson Hamiltonian and general potential energy surfaces are available[71] and the methodology has been used for relatively large systems. However, accurate results can only be obtained with this procedure for states of semirigid molecules which tends to mean lower-lying states since no molecule remains semirigid as it is excited to near its dissociation limit.

Direct Integration

For diatomics, the nuclear motion Schrödinger equation can be solved accurately by direct numerical integration for the vibrational motion. There are several programs available for this, in particular, the program named LEVEL due to LeRoy[74] which has been developed with particular attention to accuracy. LEVEL works for both bound and quasi-bound states and gives results whose accuracy are essentially determined by the underlying potential energy curve.

Variational Methods

The variational principle as it applies to ground state energies is well known and widely quoted. Spectroscopy probes the energy difference between many states and it is therefore the generalization of the variational principle due to Macdonald[75] which is important. Macdonald showed that if the problem is formulated using a basis set which leads to a matrix of dimension p, then the eigenvalues of the matrix give upper bound estimates for the lowest p eigenenergies of the physical system being modeled:

$$E_i^{(\infty)} \leq E_i^{(p)}, \quad \text{for all } i = 1, \ldots, p, \tag{3}$$

where $E_i^{(\infty)}$ is the exact value of the ith eigenenergy and $E_i^{(p)}$ is the approximate solution obtained using p basis functions in what is sometimes called the finite basis representation (FBR). This method has flourished with the advent of modern-day computers which can diagonalize large rotation–vibration Hamiltonian matrices.

The basic idea of what are classed variational methods for the nuclear motion problem is the use of a finite set of basis functions (an FBR) to represent the vibrational motions of a molecule. These are then used to obtain approximate wavefunctions and energies for the vibrational motion problem and, when augmented by the appropriate Wigner rotation matrices to represent the rotational motion,[57] for both the rotation–vibration wavefunction and the associated energy level. Most commonly, the vibrational motions are represented using products of one-dimensional basis functions. A variety of basis functions can be used in the expansion. The most common are based on orthogonal polynomials (which are often solutions of model problems) such as Hermite polynomials (Harmonic oscillator), Laguerre polynomials (Morse and spherical oscillator potentials), and Legendre polynomials (free rotors). This provides a direct link to methods based on the use of a discrete variable representation (DVR).

The DVR is a grid-based method which is particularly computationally effective for problems where many solutions are required. In the original DVR approach, the grid points are obtained as the zeroes of an orthogonal polynomial.[76] However, modern variants use other grids, such as potential-optimized DVRs which are adapted to the particular potential energy surface under consideration[77] and multidimensional adaptations.[78]

Two-Step Treatment of Rotation Motion

It is possible to solve the rotation–vibration Schrödinger equation in a single step. However, this leads to a problem in which computer time scales as J^3, where J is the total angular momentum quantum number. In practice, it has proved possible to formulate the problem so that scaling on both time and memory is, at least approximately, linear in J. Indeed, this linear scaling has even been found for rotationally excited calculations extending all the way to dissociation.[79]

The key to this linear scaling is to solve the problem in two steps.[80] The first step treats the projection of J onto the body-fixed z-axis, k, as a good quantum number; $J + 1$ effective "vibrational" problems are solved, one for each $|k|$. In the second step, the lowest solutions of the first-step problems are used as a basis for solving the full problem. This second step has diagonally dominant Hamiltonian matrix which is increasingly sparse as J increases. The efficiency of this method is greatly increased if k is an approximately good quantum number of the system and therefore the choice of appropriate body-fixed axes for the molecule becomes important. Use of this two-step procedure is the key to solving for high J states, which is necessary for hot molecules.[14] It should be noted that there are alternative methods for partitioning the vibration–rotation problem into two steps in use.[59]

ELECTRONIC MOTION

Figure 1 gives a simplified illustration of the steps necessary to calculate the rotation–vibration spectrum of a molecule from first principles; it implicitly makes the Born–Oppenheimer approximation. What Figure 1 illustrates is that calculating the instantaneous dipole moment of the system simultaneously with the electronic energy allows for a treatment of the intensity problem.

Given that, for most studies on systems with less than five atoms, the nuclear motion part of a calculation can be solved rather accurately, the accuracy of the results of such a calculation is largely determined by the underlying potential energy surface. This surface, or at least a grid of points which can be used to define it, can of course be calculated *ab initio* using one of several electronic structure methods.

In contrast to the nuclear motion step of the problem, it is straightforward to write down the nonrelativistic, electronic Hamiltonian. However, finding even the lowest solution of this Hamiltonian is far from straightforward.

Conventional Methods

Neither the Hartree–Fock approximation, which assumes each electron moves in the average potential of the other electrons, nor density functional theory (DFT) which includes a significant portion of the electron–electron correlation for little extra computational cost, are capable of predicting vibration–rotation spectra in more than a semiquantitative manner. To obtain accurate potential energy surfaces, it is necessary to treat the correlated motions of the electrons using a higher level theory. To approach experimental accuracy, it is actually necessary to use both very large basis sets and to explicitly consider effects which are usually ignored.

It is the treatment of the electron correlation problem which usually makes the biggests demands on the calculation. There are two conventional high-level treatments of electron correlation which are generally favored when one is seeking highly accurate results. These are coupled clusters (CC) and multireference configuration interaction (MR-CI). Detailed

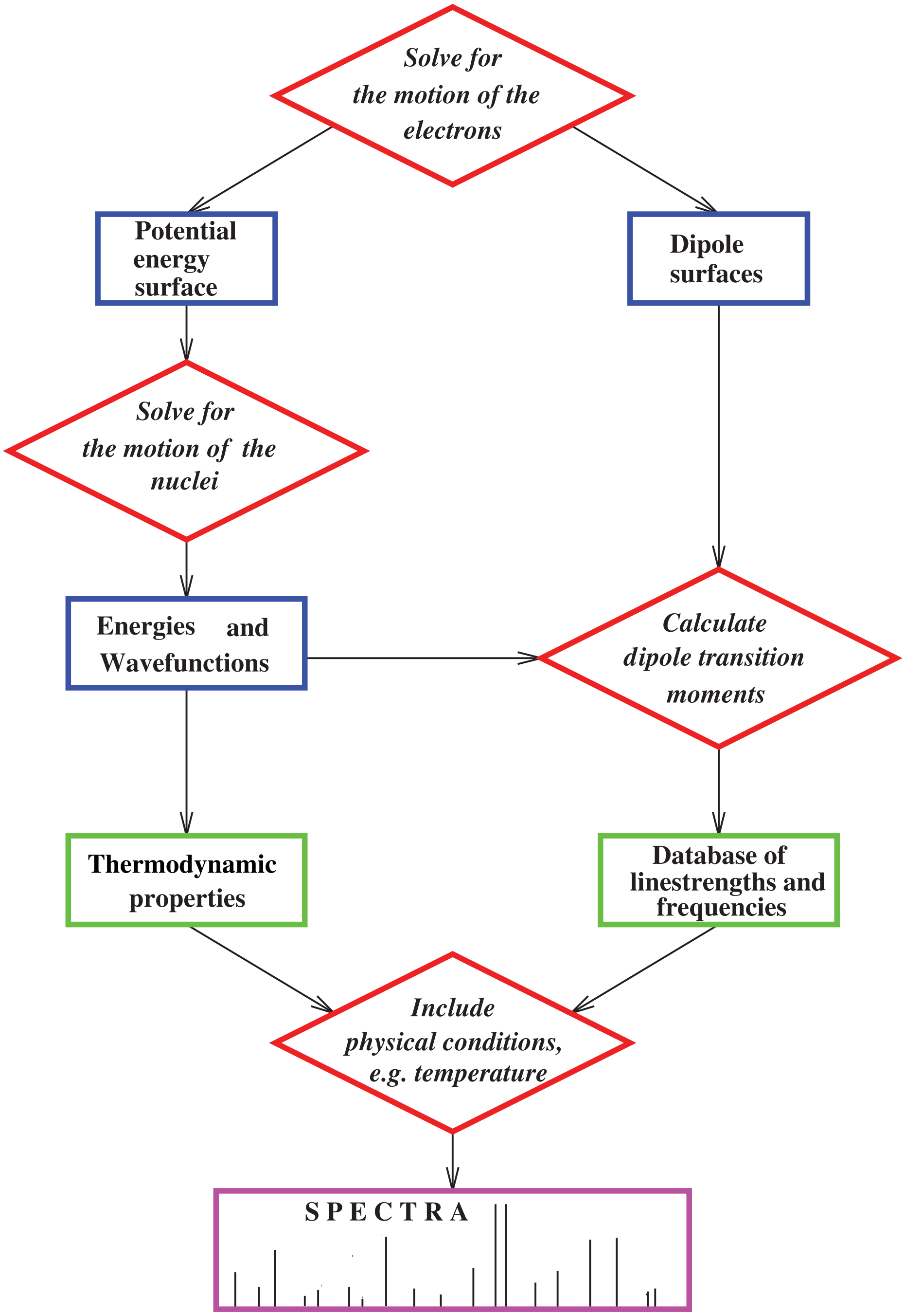

FIGURE 1 | Schematic figure showing the steps in a first principles calculation of the rotation–vibration spectrum of a molecule.

discussion of these methods can be found in standard quantum chemistry text books.[81] Hybrid MR-CC methods are also under active development.

CC and MR-CI methods differ in how they treat the configurations that result from redistributing (exciting) the electrons. CC methods use an exponential form for the electron excitation operator which has a number of theoretical benefits and has allowed the development of very efficient algorithms for building CC wavefunctions. The "gold standard" method is CCSD(T); this is the usual way of denoting a CC calculation that explicitly treats single and double excitations but only approximately allows for the contribution due to triple excitations via perturbation theory.

From the perspective of vibration–rotation spectroscopy, the main problem with CC approaches is that the expansion is based on excitation from a single electronic configuration reference state which is usually the Hartree–Fock ground state. This is very efficient for states whose electronic wavefunction is almost completely dominated by this configuration but it inevitably fails to correctly represent bond-breaking in most molecules.

Multireference methods avoid the problems caused by using a single reference configuration for the CI expansion by using a number of reference configuration. In these approaches, all the important configurations required for building up the zeroth-order wavefunction over all of the potential energy surface are included in the starting expansion. In the MR-CI method, single and double excitations are considered out of this multireference space. Again, it is possible to approximately allow for the effect of triple and higher excitations using perturbation theory, for example, using the so-called Davidson correction.[82] The MR-CI ansatz is clearly very powerful and can be used to model surfaces involving a significant degree of stretching, or indeed other complications. However, MR-CI calculations are computationally very expensive, which limits their use with appropriately sized basis sets for high-accuracy calculations to molecules with relatively few electrons. In this context, it should be noted that the 10 electron molecules: HF,[83] water,[4,10] ammonia,[4,12,84] and methane[85] form something of a benchmark set for theoretical vibration–rotation calculations.

A good CCSD(T) or MR-CI calculation can recover a significant fraction of the correlation energy. How much correlation energy is recovered, however, is strongly dependent on the quality of the one-particle basis functions used. Indeed, experience has shown that in actual calculations it is the convergence of the problem with the choice of one particle basis set that causes more problems than the actual choice of a an appropriate CI expansion.

Dunning and coworkers have systematized the generation of one-particle basis sets for use in correlation calculations. Their basis sets are based about the use of the designation "nZ" where n gives the number of Gaussian functions used to represent each physical orbital. Dunning basis sets are routinely available up to $n = 6$.[86] However, use of 6Z basis sets has been shown to be insufficient to converge the electronic energy sufficiently to give high-accuracy potentials. Indeed, the indications are that even $n = 7$ would not do this. A standard approach aimed at compensating for the effects of the basis set truncation is to perform a series of calculations with systematically larger basis sets and then extrapolate the results to what is known as the complete basis set limit.[87] The Dunning basis sets are particularly suitable for this as considerable care was taken in their generation to ensure that properties calculated using them vary smoothly with increasing n. Notwithstanding these considerations, extrapolation to the complete basis set limit in itself introduces some residual error in the calculation.[88]

Explicitly Correlated Methods

One way of improving the convergence on one-particle basis functions is to explicitly include the interelectron distance, r_{12}, in the functional form of the wavefunction. The integrals involved in such calculations are formidably difficult for many electron systems. However, Klopper and Kutzellnigg[89] developed a method of calculating these integrals using an extra (auxiliary) basis set. This has led to a rapid increase in the use of explicitly correlated methods.

As two electrons approach each other, their combined wavefunction should show a cusp. This cusp can be well represented by simple use of the electron–electron coordinate, r_{12}, but this can lead to problems with the wavefunction when the two electrons are well separated. These problems are solved using a function of the form $\exp(-r_{12})$ to represent the interaction. Very recently, methods, known generically as F12 methods,[90] have been developed which are based on the more appropriate use of functions of the electron–electron distance in the wavefunctions. These methods have been shown to have excellent basis set convergence properties. Very promising MRCI-F12 methods are just being developed[91] but are yet to be thoroughly tested.

Minor Corrections

The effective potential energy surface upon which the nuclei move depends on more than the simple nonrelativistic electronic energy. For calculations with an accuracy better than about 1 cm^{-1}, it is necessary to consider these small corrections which are usually ignored.

Chemical intuition is based entirely on the behavior of valence electrons. It would therefore seem natural that one should be able to freeze core electrons when constructing a potential energy surface. The core electrons dominate the absolute energy of a molecule but, if they remain unperturbed while the molecule vibrates, should not strongly influence the shape of the surface. For semiquantitative calculations, this is true, but for high-accuracy work it is essential to consider the correlation between the core and valence electrons. Whether this core-valence (CV) correction is included in the original electronic structure calculation by means of an all-electron CI calculation or added as a correction afterward depends on the details of the system under study and the methodology being employed.

The CV correction is probably the most important "minor correction" but even for light molecules the effect of relativity on the motion of the electrons cannot be neglected.[10,92] As working with the full Dirac equation is difficult, a practical strategy for light nuclei is to complete a comprehensive nonrelativistic (or Schrödinger) treatment of the problem and then to introduce relativistic effects using perturbation theory. Test calculations on water have shown that while the perturbation theory does not recover the absolute magnitude of the relativistic effects fully, it does a very good job of representing the shape of these corrections,[93,94] which is what is required for modeling spectra.

Within a perturbation theory framework there are a hierarchy of relativistic corrections that need to be considered. The largest contributions are generally taken to arise from operators which act on a single electron. These are the mass–velocity and the one-electron Darwin (D1) terms.[92] Collectively this one-electron correction is thus labeled as MVD1. The mass–velocity term is the leading term in a standard (i.e., nonquantum mechanical) relativistic treatment of rapid motion whereas the Darwin term, which normally acts to reduce the energy lowering of the mass–velocity correction, is a purely quantum mechanical effect with no classical analogue. For light molecules, the MVD1 correction can be calculated using perturbation theory and nonrelativistic wavefunctions as a routine and computationally cheap addition to an electronic structure calculation performed with standard quantum chemistry packages.

In cases where the MVD1 correction is large, and water is such an example,[93] it may be necessary to also consider two-electron corrections to the relativistic energy. The two-electron Darwin term (D2) has been calculated but has generally been found to be small. The other two-electron term of significance is the Breit correction, which arises from magnetic interactions that are not considered in the Dirac–Coulomb Hamiltonian. The Breit correction can be approximated by the simpler to calculate Gaunt correction although my experience is that the way these two terms contribute to a potential energy surface is sufficiently different that the saving engendered by using the Gaunt correction is not really worthwhile. The corrections can again be calculated using perturbation theory for light molecules.[92]

Further corrections to the Schrödinger treatment of electronic motion are spin–orbit interaction and the Lamb shift. Experience has shown that while spin–orbit interaction is important for heavy system (e.g., see Ref 95) and for open shell systems, its contribution to the spectroscopy of light, closed shell molecules can safely be ignored.[92] Perhaps rather surprisingly, this is not true for the Lamb shift, which arises from a quantum electrodynamic (QED) treatment of electronic motion and is therefore an addition to the Dirac equation. A full QED treatment of a many-electron molecule would be a ferocious undertaking and to my knowledge has yet to be attempted. Fortunately, it is possible to approximate the effect of QED using integrals already calculated as part of a perturbative treatment of the one-electron Darwin (D1) term.[3]

To illustrate the magnitudes involved, let me consider, for water, typical shifts in energy levels due to the various corrections.[10] For these purposes, comparisons are made with experimentally observed vibrational band origins up to 25,000 cm^{-1} above the ground state. Similar, but smaller, shifts are seen in the rotational levels with, say, $J = 20$. The MVD1 relativistic term has a strong influence on the bending states and its inclusion lowers overtone energies by up to 19 cm^{-1}, a further lowering by about 0.8 cm^{-1} arises from the Darwin term. The Briet correction raises levels by up to 6 cm^{-1} and the Lamb shift by a further 1.3 cm^{-1}. The adiabatic correction to the Born–Oppenheimer approximation contributes to a raising by up to 5 cm^{-1} while the nonadiabatic corrections leads to a lowering by up to 4 cm^{-1}. Although it may seem that many of these effects at least partially cancel, it must be remembered that this a multidimensional problem which means that something that lowers the energy of bending excitation does not counteract an effect which raises the stretching energy. Although a similar study of the isoelectronic HF molecule[83] produced qualitatively similar results, it should be noted that the barrier to linearity in water is particularly sensitive to relativistic effects.[4,93]

The most favorable triatomic case is H_3^+. In that case, the nonrelativistic electronic structure problem can be solved effectively exactly while the adiabatic correction shifts the band origins by up to 2 cm^{-1}. Nonadiabatic corrections, for which an effective but still *ab initio* procedure is available,[49] accounts for about 0.5 cm^{-1}. Relativistic corrections are small, yielding shifts of about 0.05 cm^{-1} but have still been found important in a recent, *ab itinio* study which

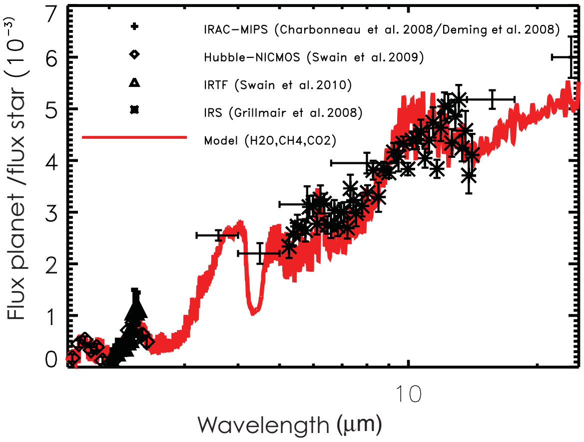

FIGURE 2 | Photometry and spectroscopy data for the Hot–Jupiter exoplant HD189733b recorded with multiple instruments and teams using Spitzer and Hubble Space Telescope (points with error bars), as well as ground-based instruments. The curve is a simulated emission spectrum containing H_2, H_2O, CH_4, and CO_2. (G. Tinetti, private communication (2010), based on data given in Ref 97.)

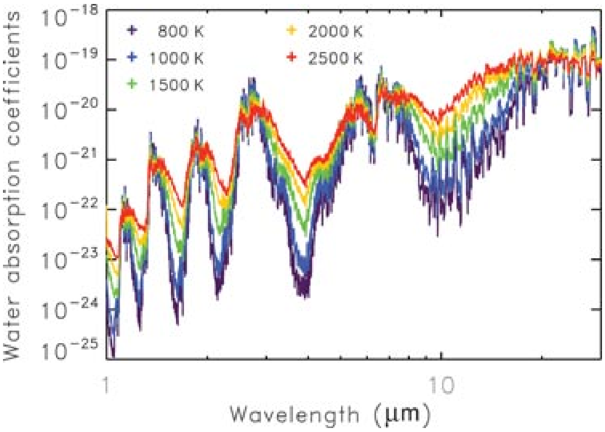

FIGURE 3 | Temperature-dependent spectrum of hot water as a function of wavelength in μm. Note that the absorption intensity, given in units of cm^{-1}/(molecule cm^{-2}), is plotted on a logarithmic scale. (After Ref 102.)

was able to reproduce transition frequencies in the visible to about 0.1 cm^{-1}.[9]

EXTENSIVE DATASETS

Both ground-based and space-borne telescopes have been and are continuing to develop fast, yielding not only high-resolution spectra but also probing astronomical objects that were not previously amenable to spectroscopic analysis. The wealth of observational discoveries requires significant quantities of fundamental data, especially in molecular spectroscopy. Planets and cool stars share some common fundamental characteristics: they are faint, their radiation peaks in the infrared and their atmosphere is dominated by strong molecular absorbers. Modeling planetary and stellar atmospheres is difficult as their spectra are extremely rich in structure and their ability to absorb light, or opacity,[96] is dominated by molecular absorbers (see Figure 2). Each of these molecules may have hundreds of thousands to many billions of spectral lines which, in turn, may be broadened by high-pressure and temperature effects. As discussed below, spectra of species prevalent in planetary and cool star atmospheres, such as water and methane, are important for many other applications.

Determining line lists for hot molecules experimentally is difficult because: (1) the sheer volume of data (billions of lines), (2) the difficulty in obtaining absolute line strengths experimentally in many cases, particularly for spectra recorded at elevated temperatures, (3) the need to have assigned spectra in order for the correct temperature dependence to be reproduced, (4) the need for completeness requires a large range of wavelengths; even at room temperature experimental line lists are often far from complete.[98] All this means a purely empirical strategy is unlikely to work. A more productive approach is therefore to build a reliable theoretical model for each molecule of importance based on a combination of the best possible *ab initio* quantum mechanical treatment which is then validated and, in most cases, tuned using experimental data.

So far only there have been a few attempts at constructing comprehensive rotation–vibration line lists for polyatomic molecules. Besides water, discussed in the following section, extensive and generally reliable line lists for H_3^+,[99] HCN/HNC,[11] CO_2,[100] and NH_3.[14] A first attempt at line list for methane was given by Warmbier et al.[101]

Water as an Example

Water is the best studied, and arguably the most important, polyatomic for which there is a line list available. It is instructive to consider the water line lists that have been calculated and how the methods for this have evolved.

A major aim for the study of water line lists is to model the way atmospheres of "cool" stars absorbed light, and indeed how other hot objects such as rocket exhausts emit radiation and cool. The absorption of light by water as function of temperature and wavelength is known as its opacity. An example is given in Figure 3 which illustrates that band structures, which are strong at lower temperatures, broaden as the temperature rises.

TABLE 2 | Summary of Calculated Water Line Lists

Name	Authors	Year Published	10^6 Lines	Nuclear Motion	Potential Energy Surface
HITEMP91	Wattson and Rothman[105]	1991	0.15	Variational, finite basis	Empirical
MT	Miller and Tennyson[106]	1994	6.2	Variational, finite basis	Empirical
VTP1	Viti et al.[107]	1997	0.23	Discrete variable representation	Empirical
PS or AMES	Partridge and Schwenke[13]	1997	300	Variational, finite basis	Tuned *ab initio*
SCAN	Jorgensen et al.[108]	2001	3000	Approximate	*Ab initio*
BT2	Barber et al.[11]	2006	504	Discrete variable representation	Tuned *ab initio*[109]

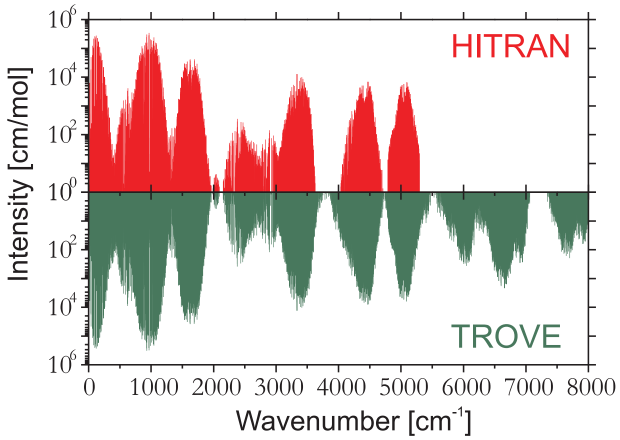

FIGURE 4 | Room temperature comparison of laboratory measured spectrum of ammonia, as taken from the HITRAN database,[110] with the line list calculated using the program 'TROVE'. (Reprinted with permission from Ref 98. Copyright 2009 American Chemical Society.)

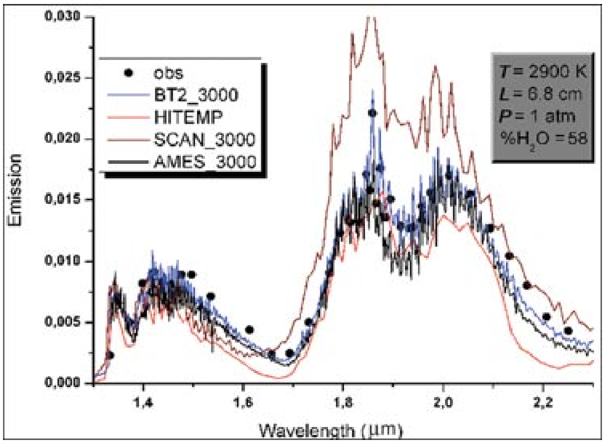

FIGURE 5 | Laboratory absorption spectrum of water at 2900 K (dots)[113] compared with available spectra synthesized by various line lists. The UCL line list BT2 gives the best results;[114] other line lists are as specified in Table 2 (S. Tashkun, private communication, 2006).

The first attempt to make a water opacity was actually done experimentally by Ludwig.[103] However, Ludwig's opacity overestimates the amount of absorption as the low resolution of his experiments gave a quasi-continuous function of wavelength rather than a highly structured function with gaps where the light can escape.[104] The calculated line lists, which are summarized in Table 2, do not suffer from this problem.

With the calculated line lists, the issues are threefold (1) the accuracy of the model which gives energy levels and wavefunctions, (2) the accuracy of the dipole surface used to generate transition probabilities and (3) the completeness of the data. Figure 4 illustrates the completeness issue for the case of ammonia.

Although the most accurate potential energy surfaces have been derived by tuning fits to high-accuracy electronic structure calculations to observed spectra,[111] tests have shown that purely *ab initio* dipole surfaces give the best results.[112] Indeed, dipole surfaces have been developed which are competitive with even the best experimental measurements[15]. Finally, while completeness of the data is greatly helped by the increase in computer power with time, it is clear that the ability to treat highly excited rotational states using the two-step procedure discussed above is a significant advantage.

The most recent of water line lists is the so-called BT2 list.[11] Figure 5 demonstrates the ability of BT2 to model a hot laboratory emission spectrum. BT2 is a computed list of all $H_2{}^{16}O$ infra-red transition frequencies and intensities constructed by considering all rotational states up to $J = 50$ and all energy levels up to 30,000 cm^{-1} above the ground state. The calculated energy levels and hence transition frequencies are based on a spectroscopically determined potential energy surface[109] which in turn used a high-accuracy *ab initio* potential energy surface[13] as a starting point which also included allowance for relativistic and non-Born–Oppenheimer effects.

Checks using the partition function[115] suggest the 504 million lines in BT2 provide a 99.99% water opacity complete up to 3000 K; above this temperature the completeness drops somewhat. The calculated energy levels and hence transition frequencies are stored in such a fashion that they can be improved using experimentally determined energy levels[116] (e.g., see the recent edition of the HITEMP database[114]). A procedure for systematically obtaining optimal experimental energy levels from spectra has been developed[117] and is being applied to water.[118,119]

Extensive line lists can be applied to a whole variety of problems. To illustrate this it is worth briefly considering some the problems that BT2 has been used to study. The BT2 line list was explicitly calculated for use in astrophysical studies and in that context has been used for:

- To show an imbalance between nuclear spin and rotational temperatures in cometary comae[120] and to assign a new set of, as yet unexplained, high-energy water emissions in comets[121];
- To detect and analyze water spectra in a variety of hot objects including the Nova-like (i.e., exploding) object V838 Mon[21] and the atmospheres of brown dwarfs;[122]
- To detect water on transiting extrasolar planets,[24] for which it was completely instrumental. It is notable that other available but less complete line lists did not contain good enough coverage of the many weak lines that become significant absorbers at high temperatures to make this detection securely;
- To model water spectra in the deep atmosphere of Venus;[123]
- As input for standard models of cool stars[122,124] and to determine their temperatures.[125]

However, the line list has rather wide application for other scientific studies including

- For construction of the temperature and concentration histories of water vapor within the expansion of a highly explosive detonation[126];
- For the design of high-temperature gas sensors[127];
- For high-speed thermometry and tomographic imaging in gas engines and burners[128,129] and for oxyfuel gas spectral radiation models[130];
- As input for an improved theory of line-broadening[17];
- To validate the data used in models of the Earth's atmosphere and, in particular, simulating the contribution of weak water transitions to the so-called water continuum[131];
- For analyzing room temperature[132,133] and hot[134] laboratory experiments.

CONCLUSIONS

The calculation of rotation–vibration spectra using first principles quantum mechanical procedures is a well-established method. It has moved from being something to study for the sake of developing methodologies to a procedure capable of generating results of genuine usefulness to scientists working in a variety of disciplines. Although it is still not possible to compute transition frequencies with the same accuracy as high-resolution experiments, rapid advances in theoretical methods are beginning to give results approaching this accuracy.

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