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Citation: J. Chem. Phys. **145**, 120901 (2016); doi: 10.1063/1.4962907
View online: http://dx.doi.org/10.1063/1.4962907
View Table of Contents: http://aip.scitation.org/toc/jcp/145/12
Published by the American Institute of Physics

THE JOURNAL OF CHEMICAL PHYSICS **145**, 120901 (2016)

Perspective: Accurate ro-vibrational calculations on small molecules

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(Received 15 June 2016; accepted 5 September 2016; published online 22 September 2016)

In what has been described as the fourth age of quantum chemistry, variational nuclear motion programs are now routinely being used to obtain the vibration-rotation levels and corresponding wavefunctions of small molecules to the sort of high accuracy demanded by comparison with spectroscopy. In this perspective, I will discuss the current state-of-the-art which, for example, shows that these calculations are increasingly competitive with measurements or, indeed, replacing them and thus becoming the primary source of data on key processes. To achieve this accuracy *ab initio* requires consideration of small effects, routinely ignored in standard calculations, such as those due to quantum electrodynamics. Variational calculations are being used to generate huge lists of transitions which provide the input for models of radiative transport through hot atmospheres and to fill in or even replace measured transition intensities. Future prospects such as the study of molecular states near dissociation, which can provide a link with low-energy chemical reactions, are discussed. *Published by AIP Publishing.* [http://dx.doi.org/10.1063/1.4962907]

I. INTRODUCTION

Quantum chemistry has for the last fifty years placed tremendous emphasis on solving the molecular electronic structure problem but the nuclei in molecules also move. Observing these moving nuclei is at the heart of high resolution spectroscopy and their energy levels also provide the means of quantifying a wealth of thermodynamic properties via the partition function.[1] Traditionally nuclear motion was treated using perturbation theory based on harmonic vibrational motion and rigid rotational motions. This model provides much of the language of spectroscopy, and approaches based on it are continuing to be developed, for example, through the use of quartic force fields[2] and vibrational second-order perturbation theory (VPT2).[3] However, the harmonic-oscillator rigid-rotor model is firmly rooted in the notion of small amplitude motion about an equilibrium geometry, so it must be limited in its region of applicability: it must break for all systems as they are excited towards dissociation.

Nuclear motion methods based on direct solution of the time-independent Schrödinger equation are increasingly being used to compute rotation-vibration energy levels for a range of states up to and even above dissociation for important small molecules. While such computations used to require a national supercomputer,[4,5] they can now be performed on a good workstation.[6–8] Increasingly nuclear motion calculations are becoming the primary source of information on small molecules as the results of these calculations are competitive with or, in some cases, more reliable than measurements. In this context, I note that the value for "spectroscopic accuracy" of 1 cm^{-1} oft-quoted by theoreticians appears to have been chosen more for quantum chemical convenience than because it is a true, or indeed useful, value. Rotation-vibration spectra can only be considered to be high resolution at accuracies approaching 0.01 cm^{-1}, a value I would suggest should be used for "spectroscopic accuracy." This perspective will discuss situations where theory is competitive with or replacing observation as the primary source of data. In other words, this perspective will address situations where first principles calculations are replacing experiment for key data because either they can be computed more accurately or are too difficult to measure reliably. In this context, I note that if one is providing computed data for use in models or other applications, then it should also be incumbent on the provider to also supply some estimated associated uncertainty of these data.[9,10] The perspective will also mention some key areas in small molecule spectroscopy where high accuracy remains a distant goal.

The nuclear motion methods used to solve spectroscopic problems are generically known as variational methods. This is because, at least in their early implementations, they involved obtaining direct solutions of the nuclear motion Schrödinger equation using suitable basis functions to represent the wavefunction. Within the limitations of the Born-Oppenheimer (BO) approximation, these solutions are variationally exact for a given potential energy surface (PES).[11] The name variational has stuck even though many codes now adopt the grid-based discrete variable representations (DVRs) to represent the vibrational wavefunctions.[12] DVR methods are not strictly variational and can show convergence from below,[13] but have proved robust and reliable in practical calculations. Development and improvement of these methods continues apace[14] and the whole area of high accuracy treatment of nuclear motion calculations has been dubbed the fourth age of quantum chemistry.[15]

For the purposes of this perspective, I will take small molecules to mean ones containing up to five atoms. For these systems, the use of variational nuclear motion methods almost always means that the errors arising from these nuclear motion calculations reflect the underlying inaccuracy of the PES

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employed and, possibly, issues with the BO approximation. I will consider in turn the small but growing number of cases were full *ab initio* treatments are providing benchmark accuracy, the more standard case which makes use of experimental data to help provide accurate results, and finally I consider future prospects and, in particular, states around the dissociation limit and the link with chemical reactions. Before doing this, I will outline the various motivations for performing such calculations.

II. USES OF BOUND STATE NUCLEAR MOTION CALCULATIONS

Like others, I originally started performing nuclear motion calculation to test potential energy surfaces. High resolution spectroscopy can obtain transition frequencies with exquisite precision[16] and therefore provides a stringent test of potentials. For some time now, this process has routinely been treated as an inverse problem with nuclear motion calculations used to determine spectroscopically accurate PESs using observed data.[17–22] This procedure is now the main source of high-accuracy PES and has got to the point that the most accurately determined geometry for the water molecules comes from a refined PES;[23] other structural determinations are also increasingly relying on high accuracy theoretical calculations.[24,25]

Even without the need for refining the PES, variational nuclear motion calculations have been used to predict[26] and assign[27,28] spectra. They have also been used to probe the fundamental behaviour of molecules revealing the clustering of energy levels at high rotational angular momentum,[29,30] the rearrangement of the levels around the monodromy point which occurs when a bent molecule becomes linear,[31] and the quantal behavior of classically chaotic systems.[32] More recently such calculations are playing a role in guiding observations of processes important for fundamental physics such as a possible change with time in the proton-to-electron mass ratio.[33,34]

Explicit summation of energy levels can be used to give temperature-dependent partition functions and other thermodynamic properties such as the specific heat.[1,35] These data can be combined to give equilibrium constants as a function of temperature.[36] For high temperatures, typically $T \gg 1000$ K, experience shows that it is necessary to include, at least approximately, all states in the summation and that this can give results that differ significantly than those based on summing levels from simpler models.[37] Methods are available which help to avoid the need to actually explicitly compute all the levels.[38] In a similar fashion, the wavefunctions can be used to provide thermal averages of various properties.[39]

In the area of astrophysics, cold interstellar clouds are well-known to be a reservoir of cold molecules and unusual chemistry. High-level theoretical methods are now being used to aid the prediction and detection of exotic interstellar species.[44–47] Such calculations also yield accurate dipole moments which are necessary for abundance determination and often not known empirically.

Molecules, however, are also important in hotter bodies such as the atmospheres of planets, exoplanets, brown dwarfs ("failed stars"), and stars cooler than our Sun. In these bodies, radiative transport through these atmospheres, which may be much hotter than the Earth's, plays a crucial role in determining its properties. A ground-breaking study was made by Jørgensen *et al.*[48] in 1985; they computed an extensive, if not accurate by modern standards, list of spectral lines for hot (2000 K) HCN. They showed that use of this line list in a model atmosphere of a "cool" carbon star made a huge difference: extending the model atmosphere by a factor of 5, and lowering the gas pressure in the surface layers by one or two orders of magnitude. Subsequent calculations on water showed that it has a similar line blanketing effect in oxygen-rich cool stars.[49] This has led to the computation of extensive line list of transitions for hot molecules by a number of groups.[19,50–55] Recent work has particularly focussed on providing line lists for hot methane,[51,56–58] the use of which has also been shown to have a dramatic effect on models of astronomical objects,[43] see Fig. 1. Although the driver for computing hot line lists has largely been astronomical applications, there are actually many terrestrial applications in areas such as combustion, environmental monitoring, and plasma discharge studies for which they are also routinely being used. These line list can also be used to give other properties such as cooling functions[59] and radiative life times of individual states.[60] They also can form the input to models of electric-field interactions with polar molecules such as strong-field induced ro-vibrational dynamics and optoelectrical Sisyphus cooling.[61]

While much attention is focused on the calculation of energy levels and hence transition frequencies, most practical applications also require transition intensities. As discussed below, the provision of transition intensities is becoming an

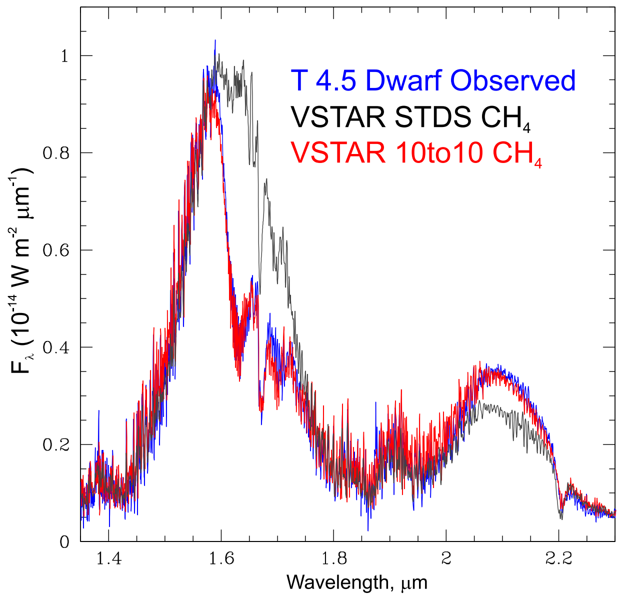

FIG. 1. Infrared spectrum of a T-dwarf 2MASS J055591915–1404489 as observed using the Infrared Telescope Facility (IRTF)[40] as modelled using the code VSTAR[41] and the empirical spherical top data system (STDS)[42] for methane or using the 10to10 methane variational line list.[43]

increasingly important reason for performing nuclear motion calculations.

III. HYDROGENIC SYSTEMS AS BENCHMARKS

Since the pioneering work of Kolos and Wolniewicz,[62] H_2 has always provided the *ab initio* benchmark for high-accuracy spectroscopic studies. Recent theoretical calculations on the frequency of the fundamental vibration of H_2 agree with observation within their mutual uncertainty of 2×10^{-4} cm^{-1}.[63] This work demonstrates what is needed for the precise *ab initio* determination of ro-vibrational energy levels. It transpires that the non-relativistic problem can be solved equally accurately using a direct fully nonadiabatic approach[64] or using the more traditional BO separation approach of solving the frozen geometry electronic structure problem[65] augmented by diagonal (adiabatic)[66] and off-diagonal (non-adiabatic)[67] corrections to the BO approximation. Rather remarkably, the current largest source of uncertainty is the treatment of quantum electrodynamic (QED) effects;[68] in this it echoes high precision calculations on the isoelectronic helium atom.[69] The spectrum of H_2 provides another probe of possible electron-to-proton mass variation,[70] a phenomenon whose strength is sensitive to terms which arise from BO breakdown.

For diatomic systems, high-accuracy studies are increasingly becoming based on the use explicitly correlated Gaussians to treat both the electronic and nuclear motion simultaneously.[71] However, this methodology has yet to make significant impact on polyatomic systems, even ones containing few electrons such as H_3^+. Here a more pragmatic model based on high-accuracy electronic structure calculations using explicitly correlated Gaussians[72] and a simplified treatment of non-adiabatic effects using effective vibrational and rotational masses[73] has been found to provide excellent predictions of ro-vibrational transition frequencies[74] and intensities.[75] This work demonstrated the importance for high accuracy of both using an extensive grid of points in the electronic structure calculation and being careful in how they are fitted to the functional form used to represent the PES.[76] The subsequent focus in these studies has been on including QED effects[77] and improving the treatment of non-adiabatic effects.[78–80] The recent high-precision spectra recorded for H_3^+ and its isotopologues[81,82] will in due course serve as benchmarks against which improved *ab initio* procedures can be tested.

While improving the accuracy with which *ab initio* calculations can predict measured high resolution spectra of H_3^+ and its isotopologues has made steady progress, the problem of treating the spectrum of these species near dissociation remains unsolved. The dense and complicated near-dissociation spectrum of H_3^+ and its isotopologues was systematically recorded by Carrington and co-workers for a decade starting from 1983.[84–86] Figure 2 shows a small (0.12 cm^{-1}) region of the near-dissociation spectrum of H_3^+ illustrating the density of lines and their variable widths, which reflects the different decay lifetimes of the various states. This spectrum was recorded by monitoring by the dissociation of the molecular ion into $H_2 + H^+$ and thus records transitions to temporarily bound states sitting above dissociation. Attempts to model these spectra quantum-mechanically have so far given little insight into the underlying physical processes involved and certainly provide nothing approaching any line assignments.[87–89]

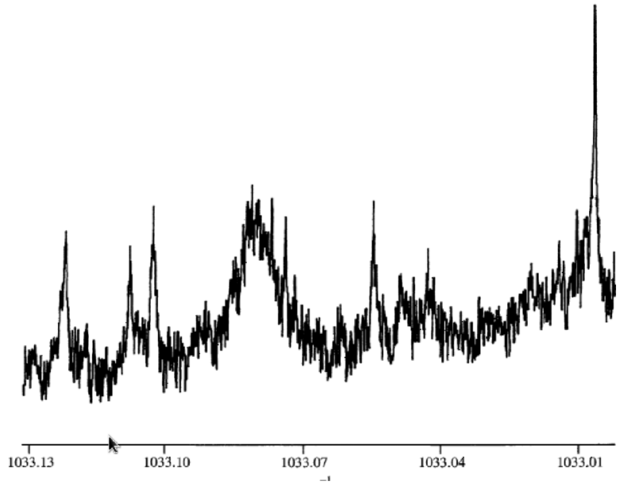

FIG. 2. A small portion of the photodissociation spectrum of H_3^+; as reported by Kemp *et al.*[83] Reproduced with permission from F. Kemp, C. E. Kirk, and I. R. McNab, Philos. Trans. R. Soc., A **358**, 2403 (2000). Copyright 2000 The Royal Society.

Before moving to larger systems, it is worth mentioning the intriguing H_5^+ system. This four-electron ion does not provide a benchmark for accuracy but instead provides a fundamental fluxional system in which the atoms freely interchange even at energies easily probed by spectroscopy. The stable CH_5^+ ion provides a similar system.[90,91] Accurate representation of the rotation-vibration states of H_5^+ and its multiple isotopically substituted forms has proved very challenging. In particular, new methods of treating the ro-vibrational symmetry of these fluxional systems have had to be developed.[92,93] Obtaining reliable analytic fits to a PES, which shows ten[94–96] energetically accessible stationary points, have proved difficult.[97] These systems display unusual spectroscopic properties[98] and new methods for treating the nuclear motion problem have been developed.[99–105] Work on these fluxional system is far from complete.

IV. HEAVIER SYSTEMS

The standard form for storing spectroscopic data is usually referred to as a line list. A line list comprises two components: (a) a list of energy levels which can be used to give transition frequencies and (b) a list of transition probabilities. For very large lists it is recommended that these are stored separately to minimize disk usage.[106,107] For both energies and intensities, calculations start from electronic structure calculations giving an initial *ab initio* PES and dipole moment surfaces (DMSs). There is increasing evidence that best results require the consideration of effects, such as QED,[108] which are usually considered to be too small to be important for chemically important molecules. Furthermore, even if the PES only provides a starting point for a fit to spectroscopic data, this fit improves fairly systematically as the *ab initio* model used as the starting point is improved.

The basic procedure for systematically improving *ab initio* PESs is the use of the focal-point analysis (FPA)[109] or closely related variants. In this procedure a base (focal point) calculation is performed at some high but affordable level of theory. The magnitude of the effects neglected or approximated in focal point calculation is corrected individually by performing additional calculations. These calculations consider effects such as extrapolation to the complete basis set limit, core correlation, high-order correlation, scalar relativistic effects, QED correction, spin-orbit effects, and corrections to the Born-Oppenheimer approximation. The top-up calculations are performed using a mixture of larger (variational) calculations and perturbation theory as is appropriate for each effect. Examples are given in the papers cited elsewhere in this perspective.[109–114] Of course, for simpler systems with fewer electrons, more of these effects can be included in the base calculation; for example, starting from an all-electron calculation eliminates the need to consider separately correlation of the core electrons.

Nuclear motion calculations on *ab initio* PES's for systems containing more than H atoms rarely reproduce observed transition frequencies to much better than 1 cm^{-1}.[22,110,112,113] However there are well-worked procedures for improving the PES by fitting to spectroscopic data.[21,115–117] Features of these procedures include the use of the Hellmann-Feynman theorem to avoid the computation of derivatives of the energy with respect to parameters of the PES by numerical finite differences, the inclusion of rotationally excited states as fits to vibrational energy levels alone is prone to give false minima in the fit,[118] and the use of the initial *ab initio* points to constrain the fit[117] which helps to stop the PES from becoming unphysical in regions where it is not determined by the available experimental data. Spectroscopically determined PES's are capable of reproducing the observed data with accuracies approaching 0.01 cm^{-1}. There are residual issues with how to deal with issues arising from failure of the BO approximations with some fits simply using a single PES to represent all isotopologues[21] and others explicitly considering non-BO terms as part of the fit.[116]

Finally, for larger molecules, where it can be difficult to employ large enough basis sets to fully converge the nuclear motion calculation, some of these convergence errors are either knowingly or unknowingly absorbed into the spectroscopically determined PES. Such effective PES's have been found to be very useful,[119] but, of course, cannot straightforwardly be used with other basis set parameters or indeed other nuclear motion programs.

For the DMS, the strategy is somewhat different and it is usual to simply use a high-quality *ab initio* surface. Indeed the evidence is that this produces better results than empirical fits,[120] although care must be taken to base the surface on a sufficiently high quality electronic structure calculation.[121] and an appropriate, dense grid of points.[122] Dipole moments can usually be computed as expectation values of a given wavefunction but can also be calculated using finite differences between energies perturbed by a small electric field. The Hellmann-Feynman theorem shows that these two methods are equivalent for exact wavefunctions. High accuracy tends to favor the use of finite differences despite the extra computational cost: the finite difference method is more accurate but, perhaps more importantly, as an energy-based method it allows small corrections to the DMS to be introduced along the lines of the FPA procedure used for PES[123,124] even for corrections which use first-order perturbation theory.

V. LINE LISTS FOR HOT MOLECULES

As mentioned above, there is a major demand from astrophysics and elsewhere of comprehensive lists of transitions for hot species which is important in the atmospheres of cool stars and extrasolar planets. Many of these species are closed shell polyatomic molecules composed of elements such H, C, O, N and S. My own ExoMol project[125] has already produced more than 20 such line lists, see the work of Tennyson *et al.*[106] for a review of the current status. Other groups notably from Reims[55] and NASA Ames[126,127] are also computing line lists for hot species, with more experimentally driven line list being provided by Bernath and co-workers.[128,129] Amongst the theoreticians is a certain consensus on how best to perform such calculations. There are reviews available detailing how to compute accurate rotation-vibration line lists,[130,131] so here I will just give a few examples which illustrate strategic issues.

Figure 3 illustrates the results achievable by comparing the computed spectrum of H_2O_2 with measured spectra currently available in the HITRAN database:[132] the main source of spectroscopic data for atmospheric models. The APTY H_2O_2 variational line list[133] is based an empirically adjusted version of a high quality *ab initio* PES[134,135] and a completely *ab initio* DMS.[136] It contains around 20×10^9 transitions and is designed to be complete for wavenumbers up to 6000 cm^{-1} and temperatures up to 1250 K.

This perspective gives little technical discussion of the nuclear motion programs employed in the calculations. This is because these programs generally give very precise solutions to the nuclear motion problem and, when inter-comparisons have been performed, the codes have been shown to give the same results for a given PES[21,54,110] or DMS.[54,137] However, hot molecules probe many vibrationally and rotationally excited levels and the resulting lists of transitions between these levels can be huge. Programs have therefore had to be adapted to cope with both the numerical and computational demands of these calculations.[138] In particular my group has developed methods of using graphical processing units (GPUs) to accelerate the computation of the many billions of transitions needed.[139] The speed-ups from this approach are large and should aid studies on larger molecules, such as hydrocarbons beyond methane, which are thought to be important in the atmospheres of hot Jupiter exoplanets.

The line lists generated to model the spectroscopic behavior of small molecules are so large because as the temperature rises, the number of states involved in transitions grows rapidly. Tests on methane[43] showed that good results

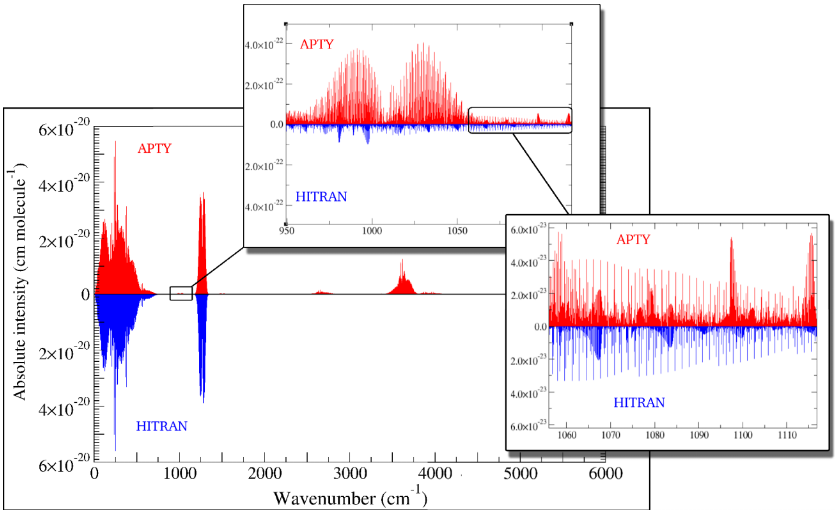

FIG. 3. Comparison of the 296 K absorption spectrum of hydrogen peroxide generated using the APTY variational line list[133] and taken from the 2012 release of HITRAN database.[132] Note that HITRAN currently contains no lines for H_2O_2 at wavenumbers higher than 1500 cm^{-1}.

illustrated in Fig. 1 could only be obtained by retaining 3.2×10^9 out just under 10×10^9 transitions provided by the full 10to10 line list. This meant the explicit consideration of transitions four orders-of-magnitude weaker than the standard intensity cutoff used by the HITRAN database. Figure 4 shows the temperature dependence of the absorption spectrum of H_2S as modelled by the AYT2 line list[140] which contains 114×10^6 vibration-rotation transitions computed using an empirically adjusted PES[140] and an *ab initio* DMS.[141] The shape of the spectrum changes significantly with temperature as the transitions involving highly excited rotational states and vibrational hot bands act to smooth out the sharp peaks and troughs observed at low temperatures.

To avoid leaving the impression that accurate results can be obtained in all cases, it should be noted that inclusion of a transition metal atom, even in a diatomic molecule, makes the solution of the electronic structure problem very much harder. As discussed at length elsewhere,[142–144] limitations on the accuracy of the *ab initio* potential functions in this case makes it difficult to use such calculations in a truly predictive fashion.

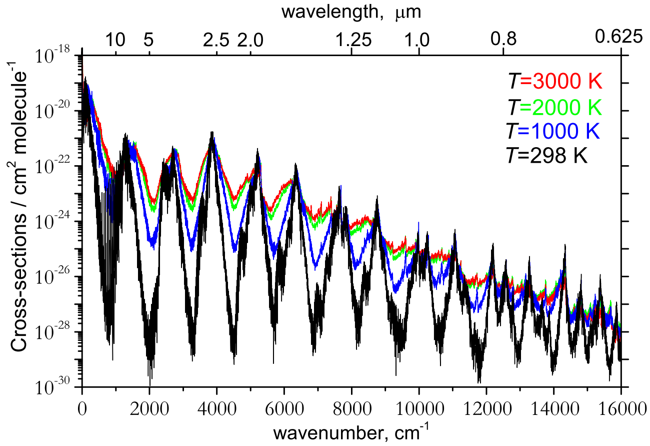

FIG. 4. Temperature-dependent spectra of H_2S generated using the ATY2 line list.[140] Note how the depth of the minima (windows) decreases monotonically with temperature.

VI. TRANSITION INTENSITIES

Extensive line lists, which contain tens of billions of transitions, may be useful for astrophysics where observations are rarely made at very high resolving power. However, remote sensing studies of our own atmosphere are often made at resolutions approaching that obtainable in the laboratory. Frequencies from variational nuclear motion calculations are rarely able to match these accuracy requirements but the same is not true for computed transition intensities. It is much more challenging experimentally to measure precise, absolute transition intensities; the success of remote sensing missions such OCO2[145] demands more precise transition intensities than are available in standard data compilations such as HITRAN 2012.[132]

Theory has long provided transition intensities for species, such H_3^+, for which measurements were not available.[146] Recently, however, it has become apparent that it is possible to predict transition intensities to within 1% or better based on the use of high accuracy *ab initio* DMS[124,147] and the judicious use of wavefunctions from variation nuclear motion calculations.[148,149] One major advantage of this approach is that transition intensities for isotopically substituted species can be computed with some confidence at a similar level of accuracy. Thus, for example, recent calculations have provided transition intensives for the important, radio-active trace species $O^{14}CO$ with what can be assumed to have same accuracy as those computed for the main, $O^{16}CO$, isotopologue.[150]

The *ab initio* computation of precise transition intensities requires some adaption to standard procedures used for both electronic structure and nuclear motion calculations. In particular it is becoming apparent that the calculation of accurate dipole moments requires extending the treatment of correlation more by, for example, using larger reference spaces in multi-reference configuration interaction (MRCI) treatments.[124] For reliable results, it is essential that dipole moment surfaces are smooth[122,151] and that reliable surfaces can only be obtained by using very extensive grids of points.[22] An uncertainty quantification procedure[10] has been developed for transition intensity calculations based on calculations with multiple PES and DMS.[148] I would expect the use of this procedure to become more widespread. Finally, I note that the use of computed transition dipoles for modeling electric-field effects requires retention of the phase information in the dipoles.[61] This information is lost when the dipoles are used to compute Einstein A coefficients or transition intensities, which are the standard quantities stored in data compilations. Changes to compilations of theoretical transition information are therefore needed to accommodate for this use.

VII. FUTURE DIRECTIONS

The discussions above have essentially concentrated on spectra at infrared (or possibly visible) wavelengths for molecules with thermally occupied levels. However, there are circumstances where it is desirable to move beyond this region, not least because not all observed spectra are thermal in origin.[152] Laboratory rotation-vibration spectra of water have been observed in the near ultra-violet[153] and there is increased interest in the atmospheric consequences of absorption by ro-vibrational excitation of water at even shorter wavelengths than this.[154,155] There are variational line lists which cover these wavelengths[156,157] but tests show that while it is possible to obtain reasonable predictions for transition frequencies with a good PES, it is hard to get reliable predictions for the transition intensity.[155] It would appear that this problem is associated with difficulties in obtaining a suitable DMS function. In particular other studies have already shown that computed transition intensities are sensitive to the fit of the DMS to the *ab initio* data even at visible wavelengths,[122,123,158] and that calculations of these high overtone transitions require care with the numerics.[151] So far, despite use of extended grids of *ab initio* dipoles, a satisfactory fit has not been found for the water dipole moment which allows the stable computation of transition intensities for the nine or ten quanta overtone transitions that occur at ultraviolet wavelengths.

Moving further up the energy levels, Boyarkin, Rizzo and co-workers performed a series of multi-photon experiments which probed rotation-vibration levels of water below,[159–163] above[114,164] and, indeed, at dissociation.[114,165] These experiments have the major advantage over the near-dissociation experiments on H_3^+ that their multiphoton nature both greatly simplifies the resulting spectrum and makes the assignment of the rotational quantum numbers to the final state relatively straightforward. Variational calculations on the bound levels gives good general agreement[166] with the observations although the differences increase markedly just below dissociation suggesting that the PES in this region is less accurate than at lower energies. Thus far global water potentials have not included the effect of spin-orbit coupling,[167] which is known to be unimportant at low energies[168] but almost certainly becomes significant near dissociation. Theoretical studies of the spectra above dissociation remain more preliminary.[6,7]

The ability to compute levels above dissociation raises a direct link not only with photodissociation but also with reactive scattering at low energies. The idea of using variational rotation-vibration calculations extending above the dissociation limit as a basis for theoretical studies of cold and ultra-cold reactions is currently being explored within my group.[169]

ACKNOWLEDGMENTS

I thank various members of the ExoMol group for letting me use their work in this article; in particular, I thank Ahmed Al-Refaie and Sergey Yurchenko for help with the illustrations and Laura McKemmish for helpful comments on my manuscript. Much of my work discussed here was supported by the ERC under the Advanced Investigator Project No. 267219 and the UK research councils NERC (under Grant Nos. NE/J010316 and NE/N001508) and STFC (under Grant Nos. ST/I001050, ST/M001334, and ACLP15).

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