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Vibration–rotation transition dipoles from first principles

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ABSTRACT

The use of *ab initio* methods to calculate line positions and associated transition intensities for the infrared spectrum of small molecules has recently become common. The first principles calculation of transition dipoles, upon which the intensity is based, relies on three distinct steps: the quantum chemical calculation of the dipole moment surface at a grid of geometries, the accurate representation of this surface using an appropriate functional form and the wave functions used to represent the initial and final states, which in turn depend on the accuracy of the potential energy surface used to generate them. Each of these stages is discussed with a view to obtaining the highest possible accuracy. The prospect of computed transition intensities displacing measured ones as the primary source of such information is considered.

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1. Introduction

A detailed knowledge of molecular spectra is important for a large variety of remote sensing and radiative transport applications, which is of course why there are extensive compilations of spectroscopic data [1–4]. These applications all rely on the use of laboratory data to provide the position and intensity of the molecular transitions involved. Laboratory measurements generally provide line positions with a very high level of precision, something that has recently taken another significant step forward with the development of frequency combs [5], see Galzerano et al. [6] for example.

The accuracy obtained for measurements of line positions is rarely mirrored in the accuracy with which transition intensities are determined. Indeed, there are a variety of situations where measurements do not routinely provide absolute intensity data at all. These include many microwave spectra, most spectra of unstable species such as radicals and ions, and spectra recorded at high temperature under non-thermodynamic equilibrium conditions. For other species, water being a classic example, the provision of accurate line intensities is complicated by practical problems in determining the precise number density of the molecules in the line-of-sight [7]. There are very precise measurements of line intensities for water transitions in the infrared [8,9], but such measurements are performed using very specially developed methodologies which can then only be applied to a relatively few lines. Workhorse methods of populating databases, such as Fourier Transform Spectroscopy, usually only yields line intensities accurate to a few percent.

Theoretically the situation is somewhat different. Only for systems with very few electrons is it possible to compute transition frequencies with an accuracy approaching experimental [10,11]. This is not true for transition intensities where there is increasing evidence that the careful and systematic application of *ab initio* procedures described below can lead to predicted transition intensities of high accuracy. If accuracy can be achieved in first principles calculations which is similar to that obtained experimentally, then theoretical procedures have a number of distinct advantages. They can be applied uniformly to several isotopologues; they can be used to study lines not easily observed under equilibrium conditions, such as flourescence spectra in comets [12,13]; and they can be extended to cover hot vibrational bands and highly-excited rotational states, both of which become increasingly important at elevated temperatures.

The ability to predict spectra at high temperatures is being extensively exploited in the ExoMol project [14]. This project is dedicated to producing a spectroscopic database for the analysis and modeling of the spectra of exoplanets and other hot atmospheres. As a rotation-vibration line list for a single polyatomic molecule may contain billions of transitions [15,16], the ExoMol project relies on developing and solving a robust theoretical model for each molecule considered. While these calculations are performed using a variety of empirical data to obtain the best possible estimate of each line position, it has so far used entirely *ab initio* procedures to consider transition probabilities as represented by the Einstein-A coefficient.

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The transition dipole between two states can be written:

$$\mu_{if} = \sum_t \langle i|\mu_t|f\rangle \tag{1}$$

where for a vibration–rotation transition, the initial and final states are represented by nuclear motion wave functions $|i\rangle$ and $|f\rangle$, and the sum runs over the components of the internal dipole moment vector. Here I will consider only transitions between fully specified vibration–rotation states and not the simpler but approximate vibrational band intensities, which require the use of an Eckart-embedded coordinate system [17]. In the full vibration–rotation case, the dipole moment, μ, is the instantaneous, dipole moment of the molecule at a given nuclear configuration in any coordinate system and the integration runs over all nuclear-motion degrees-of-freedom. This formulation implicitly assumes the Born–Oppenheimer approximation. Given the transition dipole, it is straightforward to derive other measures of a transition probability such as the Einstein A-coefficient or the transition intensity [18].

A tutorial on theoretical methods for computing molecular rotation-vibration spectra has been given by Lodi and Tennyson [19] and a comprehensive survey of available, *ab initio* dipole moment surfaces for molecules with between 3 and 5 atoms has recently been the presented by Yurchenko [20]. Here I consider only the ingredients required to obtain accurate predictions of transition dipoles and hence intensities. These fall into three parts: electronic structure calculations, representation of the dipole moment surfaces or curve (DMS or DMC) and nuclear motion wave functions. I will consider each of these in turn.

2. Calculated dipole moments

2.1. Ab initio procedures

Standard electronic structure packages, such as MOLPRO [21], offer the possibility of computing the instantaneous electronic dipole moment for any given geometry for the molecule under consideration. In practice this can be done using two distinct methods. Given the electronic wave function, the dipole can be computed as an expectation value of the dipole operator. Alternatively, it can be obtained from the derivative of the electronic energy when the system is placed in a uniform, static electric field. The Hellmann–Feynman theorem suggests that the two methods should be equivalent [22]. However, this theorem only holds in general for exact wave functions. In practice, differences can be significant with values found to differ by more than 0.1 D for calculations on water with large basis sets and sophisticated CI models [23].

Experience suggests that the perturbation method yields better results in practical calculations with approximate electronic wave functions. This can be understood in terms of the convergence of the energy in a calculation, which is second-order, against the first-order convergence of the wave function. In addition, use of the perturbation method means that the contribution to the dipole moment due to effects for which only the energy is calculated can readily be considered. A number of effects can be treated in this fashion including relativistic corrections, the Born–Oppenheimer (BO) diagonal correction and higher-order configuration interaction corrections such as the Davidson correction. The disadvantage of the perturbation theory method over the use of expectation values is that it requires several calculations at each geometry with different electric fields and is therefore computationally more expensive.

Conventional wisdom holds that accurate dipole moment calculations require the use of large diffuse basis sets since the contributions from diffuse portions of the wave function are emphasized by the dipole moment operator. In practice, experience, in particular supported by detailed studies on the water molecules, suggests

that the dipoles moments are largely converged using basis sets of about 5-zeta quality [24,25]. This contrasts with the electronic energy, which is not satisfactorily converged even with a 7-zeta basis set [26]. Conversely there is strong evidence that for really accurate results it is necessary to extend standard treatments of the electron correlation problem [23] by, for example, using a larger than usual active space for the electron correlation problem. This, combined with the requirement to do several calculations at each geometry, discussed above, and the need for a finely space grid of dipole points, discussed below, can makes the calculation of high accuracy DMS for polyatomic molecules computationally expensive even for few-electron systems.

It is becoming increasingly standard to consider corrections to the dipole moment due to core correlation, relativistic effects and failure of the BO approximation. While the non-Born–Oppenheimer contribution is important for systems such as the HD molecule which have no permanent dipole within the BO approximation [27,28], it is generally less important for systems which already have a permanent dipole moment [29,30]. However core correlation and relativistic effects have both been found to make small but significant contributions to the DMS [24,25]. Interestingly, in the case of water, these two effects appear to essentially cancel [24]. The reasons for this remain unclear and the situation does not appear to apply to other similar molecules such as H_2S [25]. However, it would seem that including only one of these corrections may actually give worse results than including neither.

Table 1 compares the various contributions to the equilibrium dipole moment of water and H_2S taken from *ab initio* studies performed in my group [24,25,31]. The aim in each case was to obtain this dipole with an accuracy of better than 1 %. For water aug-cc-pCV5Z and aug-cc-pCV6Z CCSD (T) calculations were extrapolated to the complete basis set limit but this only changes the value by 0.00005 D. Additional corrections to the model only give minor contributions: spin–orbit coupling is estimated to contribute about 0.000005 D [23], while the Born–Oppenheimer Diagonal Correction (BODC, also known as the adiabatic correction) at equilibrium was computed by Hobson et al. [30] and amounts to 0.002 D. As can be seen, the contribution to the dipole due to vibrational motion of the nuclei is also small. This leaves the treatment of the electron correlation problem as contributing the largest uncertainty, with the MRCI value of Partridge and Schwenke [34] lying 0.01 D higher that of Lodi et al. [23], who used a larger active space for the electrons.

For H_2S the issues with computing a precise value for the equilibrium dipole moment are similar to those encountered in water. However for this system, the fundamental transitions are all rather weak; weaker than some of the combination bands for example. This can be associated with the behavior of the dipole moment surface which passes through zero for at geometries close to equilibrium, which gives rise to various intensity anomalies [35]. This behavior make the DMS very challenging to compute [25,36,37].

Table 1
Permanent dipole moments in Debye for water and H_2S. Uncertainties are given in parenthesis. The electronic structure calculations are performed at the equilibrium geometries; see the cited references for further details.

	H_2O [24]	H_2S [25,31]
Correlated calculation	1.8580(12)	0.9886
Core correlation correction	(0.0043)[a]	−0.0020
Relativistic correction	−0.0043(2)	−0.0160
Best equilibrium dipole	1.8578(14)	0.9706
Vibrational averaging	0.0002(1)	−0.0002
Final value for the ground-state dipole	1.8540(15)	0.9704
Experimental value	1.8546(6) [32]	0.978325(10) [33]

[a] Estimated since the correlated calculation result is for an all-electron study.