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Determination of the reduced matrix elements using accurate *ab initio* wavefunctions: Formalism and its application to the vibrational ground state (000) of $H_2{}^{16}O$

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ABSTRACT

The calculations of the reduced matrix elements for 441 rotational collisional transitions for rotational quantum numbers of the lower state up to $J''=20$ in the vibrational ground state of $H_2{}^{16}O$ are presented using effective and *ab initio* wavefunctions. Effective wavefunctions are derived from a Watson A-reduced Hamiltonian with the effective parameters determined by Matsushima et al. [Matsushima et al., J Mol Struct 1995;352–353:371]. The *ab initio* wavefunctions used in this study are from the work of Partridge and Schwenke [Partridge, H, Schwenke, DW. J Chem Phys 1997;106:4618]. The comparison of the reduced matrix elements obtained by both methods is described. It is demonstrated that, even for the rotational band, the effective wavefunctions show problems for some states.

1. Introduction

The transition moments of optically or collisionally induced transitions are fundamental quantities in physics, as their squares are proportional to the probability of a transition for the interaction under consideration [1]. The Wigner–Eckart theorem [see Appendix A of Ref. [2] and references therein] states that, for the interaction operator expressed under the form of an irreducible tensor, the transition moments can be written as the product of two parts, one depending of the projection of the magnetic quantum numbers, the other being independent of them. The first part can be expressed as a Clebsch–Gordon coefficient (or a Wigner 3-j symbol, equivalently [2]) whereas the second is the so-called the reduced matrix element (RME). Transition moments, and therefore reduced matrix elements, are involved in a wide range of physical problems, including the determination (empirically or calculated) of intensities [1,3–8], the calculations of optical cross-sections for collisionally induced transitions (line shape parameters) [9–14], the modeling of planetary atmospheres [7], the radiative transfer theory [15], Non-LTE applications [4,16,17], *etc.* For an optical transition from a lower state i to an upper state f, the square of the dipole transition moment for a given electrostatic interaction (dipole, quadrupole, *etc.*) is related to the oscillator strength, to the Einstein A coefficients for spontaneous emission and to the intensities [4,5]. The intensities and the optical transition moments (in general for the electric dipole interaction), or equivalently the A coefficients, can be found in a number of line lists and databases [18–24], widely used for spectroscopic applications. In semi-classical theories [9–14] used for the calculations of the line shape parameters, the optical cross-sections can be expressed as the product of terms describing the relative motion between the perturber and the radiator (resonance function), and the reduced matrix elements for both the perturber and the radiator. In this work the focus is on the reduced matrix elements describing the collisionally induced transitions from a lower state i and an upper state i'.

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The calculation of the reduced matrix elements requires the evaluation of the matrix element of the (optical or collisional) operator representing the interaction between the wavefunctions for the lower and upper ro-vibrational states. The wavefunctions for a given ro-vibrational state of an asymmetric rotor can be obtained by diagonalizing the Watson Hamiltonian (WH) [25] in a symmetric top basis. In a few studies the effective constants of the reduced Watson Hamiltonian were obtained non-empirically from the potential energy surface [26–28]. However, these parameters are generally obtained through fits of experimental data in a narrow spectral region. This empirical procedure has a number of difficulties and problems of extrapolation to other spectral regions or to higher rotational quantum numbers [29], the extrapolation for isotopic substitutions (in particular those changing the symmetry, as H←→D) [30], the possible correlation between the determined parameters [31], the possible interactions with "dark" states (states non experimentally observed) [32,33], *etc.* In addition, the Watson Hamiltonian model is derived for isolated vibrational states and the consideration of vibrational interactions are more complicated [34,35]. In an attempt to solve this problem, the empirical studies add terms describing the Coriolis, Darling–Dennison, and Fermi resonances [31,36] but with empirically determined parameters to the Hamiltonian. However, as the energy increases the importance of the various resonances becomes more important, and the determination of the empirical parameters is an ill-posed problem. Also, effective models are based on perturbative expansions (contact transformations [26,28,30,36]) that suffer from slow convergence for light asymmetric rotors [26,37].

The wavefunctions can also be obtained from first principles using techniques based on the variational principle for the nuclear motion [7,23,38,39]. These calculations aim to provide "exact" solutions (within the Born–Oppenheimer approximation, and the numerical procedure employed) to the Schrodinger equation using an exact kinetic operator and a potential energy surface (PES) [7,40–43]. The PES are generally obtained by *ab initio* calculations and fitted to experimental energy levels [23,44] in order to reach the required accuracy. One important feature of these methods is that due to the "exact" nature of the solutions all resonances are automatically included. However their precise form depends strongly on the potential energy surface used and they can be hard to model correctly. Table VI of Ref. [23] shows the entropy of mixing of the $J=0$ levels of H_2O computed with the potential from that work. The (000) level is well isolated from other levels and has insignificant resonance mixing with other levels. The variational calculations use only rigorous quantum numbers and symmetry proprieties; hence linking "global" and "spectroscopic" (*i.e.* normal modes) assignments can be difficult. A review of advantages and inconveniences of each method can be found in Ref. [45].

The reduced matrix elements are related to the probability of a transition between a lower state i and an upper state i' [1]. Using the Wigner–Eckart theorem, sum rules on the sum of the square of the projection of the RMEs can be derived (see Appendix B). For line shape problems, these sum rules depend of the order of the interaction under consideration and are independent of the ro-vibrational collisionally connected states. Hence the sum rules provide a check of the calculations based on physical proprieties. The sum rules are also useful to check the assignments of quantum numbers to the *ab initio* levels.

Due to its importance in Earth's atmosphere and in the interstellar space [46,47], this paper focuses on collisionally induced transitions for the main isotopologue of water, $H_2{}^{16}O$, and in particular on its vibrational ground state, (000). The ground state is generally considered an isolated band as no vibrational resonances are involved. Hence, small differences are expected between the reduced matrix elements obtained using *ab initio* and effective wavefunctions. This paper presents the calculation of the reduced matrix elements using the two forms of wavefunctions as described below. The dipole, quadrupole, octupole, and hexadecapole ($\ell=1$ to $\ell=4$ [2]) interactions are considered. The comparison of the reduced matrix elements using *ab initio* and effective wavefunctions, within the domain of validity of the fit of the constants and in extrapolated ranges, is presented.

2. Theory

2.1. The intermolecular potential

For line shape calculations, the intermolecular potential for a H_2O–A_2 collisional system can be expressed in the following tensorial form [2,48]:

$$V=\sum_{\substack{\ell_1\ell_2\\ \ell}}\sum_{\substack{n_1\\ m_1m_2\\ m}}\sum_{w,q}\frac{U(\ell_1\ell_2\ell,n_1wq)}{R^{q+\ell_1+\ell_2+2w}}C(\ell_1\ell_2\ell,m_1m_2m)D^{\ell_1}_{m_1n_1}(\Omega_1)D^{\ell_2}_{m_20}(\Omega_2)Y_{\ell m}(\omega) \tag{1}$$

where $C(\ell_1\ell_2\ell;m_1m_2m)$ is a Clebsch–Gordan coefficient, D is a Wigner D-matrix, $\Omega_1=(\alpha_1,\beta_1,\gamma_1)$ and $\Omega_2=(\alpha_2,\beta_2,\gamma_2)$ are the Euler angles describing the molecular fixed axis relative to the space fixed axis. ℓ_1, ℓ_2 and ℓ are the *rank* of the D-matrices and spherical harmonic, m_1, m_1, and m are the projection along the space-fixed axis and n_1 is the projection along the body-fixed axis, and w (an integer) is from the expansion of Sack [49] to map the atom–atom distance r_{ij} to the center of mass separation R. $\omega=(\theta,\varphi)$ describes the relative orientation of the centers of mass, and Y_{lm} is a spherical harmonic function. The $U(\ell_1\ell_2\ell,n_1wq)$ are coefficients of the spherical expansion of the potential and $\ell_1+\ell_2+2w$ is called the *Order* of the expansion of the potential, q is 1 for electrostatic interactions and 6 or 12 for the atom–atom interactions. Note the potential is comprised only of rotational operators. Here we are concerned with the Wigner-*D* matrix of the active molecule (water), $D^{\ell_1}_{m_1n_1}(\Omega_1)$.

The development is based on the conventions of Gray and Gubbins [2] and references therein (see Appendix A of Gray and Gubbins for details). The conventions used in this work are as follow: the choice of the body fixed axis system is the I^r representation [50] of the water molecule, passive rotations, and the Condon and Shortley phase convention. Caution must be taken not to make