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CALCULATION OF TRANSITION FREQUENCIES AND LINE STRENGTHS OF WATER FOR COOL STAR OPACITIES

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RESUMEN. Se presentan cálculos de la molécula de agua basados en primeros principios y usando diferentes superficies del potencial electrónico, como el primer paso en un cómputo más exacto de la opacidad del agua en estrellas frías tales como las enanas M.

ABSTRACT. First principles calculations for water, using a number of electronic potential surfaces, are presented as a first step towards the computation of an accurate water opacity for cool stars such as M dwarfs.

Key words: MOLECULAR PROCESSES – OPACITIES – STARS: ATMOSPHERES – STARS: LATE-TYPE – STARS: LOW-MASS

I. INTRODUCTION

In recent years it has become apparent that molecules can play an important, in some cases dominant, role in determining the opacities of stellar envelopes in cool stars (Gustaffson, 1988; Johnson, 1986). Several diatomic species are now included in models of stellar opacities (e.g. Jørgensen and Larsson, 1990). However, triatomic molecules may be even more important. Triatomics have a much greater density of states than diatomics; bending vibrational bands—generally lower in frequency than bond-stretching modes—may contribute enormously to 'filling in' spectral gaps. In carbon-rich stars, species such as HCN, C_2H and SiC_2 play an important role (Jørgensen *et al.*, 1985). For oxygen-rich stars such as M dwarfs, the most obvious candidate for producing a major contribution to the atmospheric opacity is the water molecule (Alexander *et al.*, 1989).

In this contribution to the Workshop on Astrophysical Opacities, we summarise preliminary calculations for water using four electronic ground-state potential energy surfaces which have been produced in recent years (Carter and Handy, 1987 (CH); Halonen and Carrington, 1988 (HC); Jensen, 1989 (J); Kauppi and Halonen, 1990 (KH)). For temperatures applicable to cool star atmospheres (up to 5,000 K) we consider it will be necessary to compute all levels up to 22,000 cm^{-1} above the ground state. Calculating all transition frequencies and line strengths up to 14,000 to 15,000 cm^{-1} (wavelengths longer than 0.7μm) will cover the near to far infrared spectral region for which water is likely to be the main source of opacity.

II. VARIATIONAL CALCULATIONS

Spectroscopists often use techniques based on perturbation expansions to calculate vibrational levels close to the ground state (e.g. Flaud *et al.*, 1983). This involves fitting measured levels using a perturbational Hamiltonian. The parameters obtained from the fit are then used to predict higher, unobserved, levels.

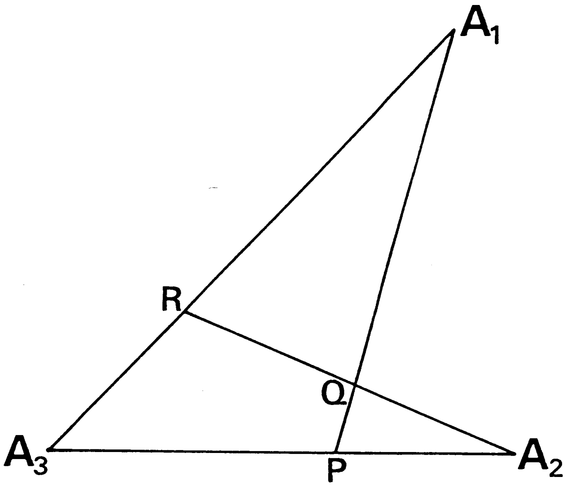

Figure 1: Sutcliffe-Tennyson co-ordinate system. Atomic positions are A_1, A_2 and A_3. The radial co-ordinates are A_1–P and A_2–R, and the included angle is A_1–Q–A_2. Parameters g_1 and g_2 allow P and R to be positioned at any point along the internuclear co-ordinates A_3–A_2 and A_3–A_1 respectively.

Rotational levels belonging to each vibrational manifold may similarly be computed for moderate angular momentum, J, levels. Such techniques, however, become inappropriate when the vibrational modes involve large amplitude motions and when the angular momentum is such that centrifugal distortion plays a major role. Additionally, perturbational approaches are based on an ideal model in which rotational and vibrational motions are uncoupled to first order. Ro-vibrational coupling is then added through coriolis contributions, again considered to be perturbations of the ideal rigid-rotor, harmonic oscillator system. At high energies, however, dealing with ro-vibrational coupling in this manner is inadequate.

More recently, a number of groups (Tennyson, 1986; Carter and Handy, 1986; Spirko *et al.*, 1985) have developed techniques for calculating triatomic energy levels based on variational techniques. In particular, Sutcliffe and Tennyson (1991) have produced a ro-vibrational Hamiltonian which is exact within the constraints of the Born-Oppenheimer approximation (which decouples **electronic** from **nuclear** motion in a molecule) and the limitations of the electronic potential energy surface available.

The Sutcliffe-Tennyson kinetic energy operator directly relates the cartesian positions of the nuclei of a triatomic molecule to a set of internal co-ordinates comprising two radial co-ordinates and the included angle. Rotation of the molecule-fixed internal co-ordinates in the laboratory frame is carried by the usual Wigner rotational matrices. This operator makes **no** ***a priori*** assumptions about ro-vibrational separation or equilibrium geometry. In addition, the operator includes parameters, g_1, g_2, which relate the radial co-ordinates to the bonds of the molecule in a flexible way (see Figure 1). This has computational advantages, especially for the accurate calculation of high vibrational energy levels.

A 'two-step' procedure is employed to calculate rotationally excited states. In the first step, k, the projection of the total angular momentum on the molecule-fixed z-axis, is taken as a good quantum number. The solutions of this calculation are taken as **new** basis functions for the second step, which allows for coupling between levels with different values of k. This method is efficient because (a) not all the solutions of the first step are required to get good solutions for the second step, and (b) the Hamiltonian matrix turns out to require only coupling between k and $k \pm 1$ levels, enabling efficient sparse matrix diagonalisers to be used.

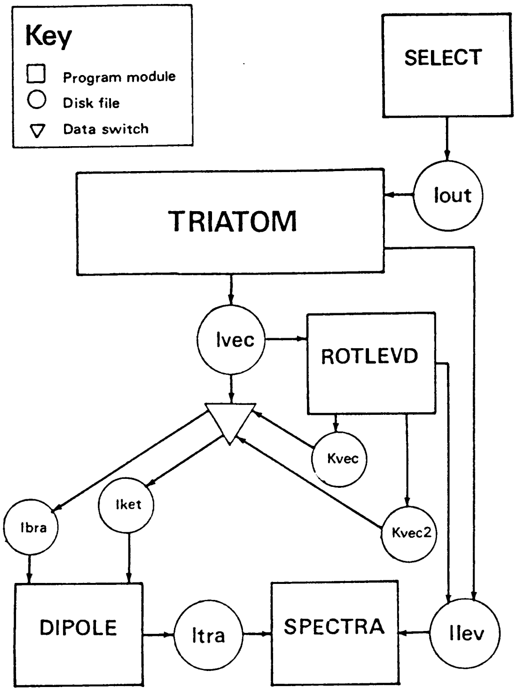

Figure 2: The TRIATOM program suite. The main driver program TRIATOM computes the vibrational part of the ro-vibrational problem, using basis functions provided by SELECT and an input potential energy surface. ROTLEVD produces fully coupled ro-vibrational eigenfunctions and energies. These are taken as input for DIPOLE, along with the vector dipole surface, to produce transition frequencies and line strengths. The final module SPECTRA produces predicted spectra at given temperatures, either in emission or absorption.

Ro-vibrational wavefunctions may be calculated by two essentially separate techniques. An approach using model basis functions as building blocks has been developed into a suite of 'user-friendly' programs (Tennyson and Miller, 1989). This suite, known as TRIATOM, contains modules to calculate ro-vibrational transition frequencies and line strengths from dipole moment surfaces as well as synthetic spectra (Figure 2). Once more, the suite does not involve any *a priori* assumptions about spectroscopic selection rules. Instead it allows whatever symmetry is inherent in the potential energy and dipole surfaces to express itself in the calculated line strengths. This method has proved successful in identifying weak and classically 'forbidden' transitions (Miller *et al.*, 1990).

A second, more recent, approach has been pioneered by Light and coworkers (Bacic and Light, 1990). Known as the Discrete Variable Representation (DVR), Light's technique calculates wavefunctions on a grid in co-ordinate space (as opposed to the basis function method, which can be considered to calculate wavefunctions on a grid in **function** space). This method is very efficient at building up wavefunctions for high-lying levels. Henderson and Tennyson (1991) have used this method to calculate all the bound vibrational states of H_3^+ (dissociation energy $\sim 36,000$ cm^{-1}). Work is currently underway to develop a suite of programs based on the DVR approach similar to the TRIATOM suite.

Table 1: Comparison of observed and calculated band origins for symmetric vibrational states of water. The states are assigned, where possible, using both normal mode, (v_1,v_2,v_3), and local mode, $[m,n]^{\pm}v_2$, notations. All band origins are in cm^{-1}. For observed band origins the calculated values are given as observed–calculated; otherwise the actual calculated band origin is given.

(v_1,v_2,v_3)	$[m,n]^{\pm}v_2$	Expt	CH	HC	KH	J
0 1 0	0 0^+ 1	1594.7	−0.7	−0.4	+1.0	+0.4
0 2 0	0 0^+ 2	3151.6	−0.4	+0.1	+2.8	−0.4
1 0 0	1 0^+ 0	3657.1	+0.7	−0.1	−3.7	+0.6
0 3 0	0 0^+ 3	4666.8	+1.3	+0.3	+3.9	−0.9
1 1 0	1 0^+ 1	5235.0	+0.5	+1.0	−0.9	+0.7
0 4 0	0 0^+ 4	6134.0	+4.8	−1.5	+2.7	−0.2
1 2 0	1 0^+ 2	6775.1	+3.1	+3.3	+4.8	+0.0
2 0 0	2 0^+ 0	7201.5	−2.9	−2.2	−8.3	−1.2
0 0 2	1 1^+ 0	7445.1	+2.4	+1.2	+3.5	+0.1
0 5 0	0 0^+ 5		7531.5	7551.0	7545.8	7539.9
1 3 0	1 0^+ 3	8274.0	+7.4	+5.5	+12.3	+0.7
2 1 0	2 0^+ 1	8761.6	−2.5	+0.2	−5.6	−1.4
0 6 0	0 0^+ 6		8850.0	8898.9	8889.3	8863.3
0 1 2	1 1^+ 1	9000.1	+2.5	−0.4	−3.0	−2.1
1 4 0	1 0^+ 4		9711.8	9719.8	9703.5	9719.9
0 7 0	0 0^+ 7		10054.1	10161.0	10131.7	10073.9
2 2 0	2 0^+ 2	10284.4	+3.0	+4.1	+2.4	−1.5
0 2 2	1 1^+ 2	10524.3	+6.7	+4.7	−2.5	−1.4
3 0 0	3 0^+ 0	10599.7	−8.8	−4.8	−8.1	−3.2
1 0 2	2 1^+ 0	10868.9	+11.9	−4.3	−2.0	−0.5
1 5 0	1 0^+ 5		11087.4	11117.5	11073.7	11082.4
0 8 0	0 0^+ 8		11201.0	11368.5	11300.7	11234.5
2 3 0	2 0^+ 3		11756.8	11759.1	11752.5	11766.3
0 3 2	1 1^+ 3		12000.9	11998.6	12012.2	12011.6
3 1 0	3 0^+ 1	12139.2	−7.9	−2.8	−10.5	−5.4
1 6 0	1 0^+ 6		12364.0	12451.3	12350.0	12340.8
1 1 2	2 1^+ 1	12407.6	+14.7	−3.4	−4.4	−1.0
0 9 0	0 0^+ 9		12458.5	12637.1	12548.2	12504.2
2 4 0	2 0^+ 4		13185.7	13194.0	13172.0	13195.9

Table 2: Comparison of calculated high energy band origins for symmetric vibrational states of water. The states are assigned as in Table 1.

(v_1,v_2,v_3)	$[m,n]^{\pm}v_2$	Expt	CH	HC	KH	J
			21316.3	21280.5	21289.6	21284.5
			21360.7	21427.1	21322.2	21332.5
			21366.4	21601.5	21361.5	21378.0
			21476.0	21725.9	21526.9	21545.1
			21563.1	21841.6	21716.7	21652.1
			21720.0	21871.0	21768.9	21757.7
			21793.7	21977.9	21837.3	21831.3
			21831.8	21994.6	21855.4	21842.8

III. TEST CALCULATIONS ON WATER

At equilibrium, the water molecule has C_{2v} symmetry, with an angle of about 105° between the two O–H bonds. However, the molecule can access linear geometries at energies around 12,000 cm^{-1} above the minimum, well below the maximum energy level we consider necessary to calculate for cool star opacities. Such large amplitude bending vibrations are almost certainly not amenable to perturbational calculations.

We have carried out rigorous testing of the four recent potential energy surfaces mentioned above (Fernley *et al.*, 1992). All of them perform reasonably well when compared with experimental data for vibrational levels lying below or just above the energy region at which linear geometries become accessible (Table 1). At higher energies it has proved impossible to assign the levels using the standard spectroscopic notations; in the absence of experimental data, we present the levels computed on each surface simply in ascending energy order (Table 2). Sample ro-vibrational energy levels for low-lying vibrational manifolds are presented in Table 3. The surface due to Jensen (1989) labelled J compares best with the available experimental data both for vibrational band origins and for low-lying rotational term values (Table 4).

So far we have not been able to test dipole surfaces to compare calculated line strengths with those observed (e.g. Mandin *et al.*, 1988). An SCF surface has been calculated by Rosenberg *et al.* (1976) for H_2O, but this was based on fitting values obtained at geometries for which the bending co-ordinate varied by only $\pm 6^o$ from equilibrium. As such, it is anticipated that serious modification of the dipole will be needed to allow for large amplitude bending motion. It may also be possible to contruct a water dipole, using a form similar to that used by Senekowitsch *et al.* (1989) for H_2S and fitting the expansion parameters to existing water intensity data. We also intend to test the dipole reported by Jørgensen in this volume.

IV. DISCUSSION

Carrying out our planned coverage of water energy levels and transitions, will involve calculating several million individual frequencies and line strengths, covering vibrational levels much higher than have been measured spectroscopically and rotational states with J possibly as high as 50. These data will be calculated accurately within:

i) the accuracy of the potential energy and dipole surface available;
ii) the number of basis functions/discrete variable points that can be fitted into available computer memories.

Table 3: Comparison of observed and calculated term values with J=1 for the lowest 10 vibrational states of water. The states are assigned using both normal mode, (v_1,v_2,v_3), and rigid rotor, notation. All term values are in cm^{-1}. For observed levels the calculated values are given as observed–calculated; otherwise the actual calculated term value is given.

(v_1,v_2,v_3)	(K_a,K_c)	Expt	CH	HC	KH	J
0 0 0	0 1	23.79	−0.05	−0.13	−0.04	−0.01
	1 1	37.14	+0.04	−0.03	−0.03	+0.06
	1 0	42.36	+0.00	−0.10	−0.06	+0.03
0 1 0	0 1	23.81	−0.06	−0.02	−0.07	−0.01
	1 1	40.22	+0.07	−0.33	+0.00	+0.04
	1 0	45.76	+0.03	−0.30	−0.03	+0.04
0 2 0	0 1	23.81	−0.07	+0.08	−0.11	−0.01
	1 1	44.46	+0.08	−0.76	+0.10	+0.07
	1 0	50.28	+0.04	−0.66	+0.04	+0.06
1 0 0	0 1	23.40	−0.05	−0.38	−0.05	−0.03
	1 1	36.24	+0.14	+0.30	+0.00	+0.00
	1 0	41.43	+0.08	+0.07	−0.04	−0.02
0 0 1	0 1	23.56	−0.09	−0.22	−0.04	−0.04
	1 1	35.77	+0.07	−0.10	−0.14	−0.03
	1 0	41.06	+0.02	−0.18	−0.12	−0.03
0 3 0	0 1	23.77	−0.09	+0.15	−0.18	−0.05
	1 1	50.66	+0.05	−1.40	+0.38	+0.13
	1 0	56.74	+0.02	−1.22	+0.28	+0.11
1 1 0	0 1	23.42	−0.09	−0.27	−0.07	−0.02
	1 1	39.17	+0.24	+0.10	−0.07	−0.04
	1 0	44.68	+0.16	−0.03	−0.11	−0.05
0 1 1	0 1	23.63	−0.08	−0.07	−0.02	+0.00
	1 1	38.52	+0.17	−0.43	−0.15	−0.05
	1 0	44.13	+0.10	−0.41	−0.14	−0.04
0 4 0	0 1	23.73	−0.08	+0.25	−0.24	−0.06
	1 1		60.75	62.98	59.58	60.43
	1 0	67.04	−0.03	−2.00	1.02	+0.29
1 2 0	0 1		23.53	23.59	23.52	23.44
	1 1		42.82	43.35	43.33	43.27
	1 0		48.72	49.22	49.18	49.08

Table 4: Statistical comparison of the 4 potentials for the 63 observed band origins and the rotational term values. Given are the mean (observed–calculated) error and standard deviation (σ), both in cm^{-1}.

Potential	Band origins		Term values	
	mean	σ	mean	σ
CH	4.1	11.5	0.10	0.35
HC	-1.2	7.2	-0.59	1.20
KH	0.2	10.3	-0.05	0.37
J	-1.1	6.4	0.01	0.14

An alternative strategy might be to calculate vibrational band origins and band intensities variationally, and then distribute rotational energy levels according to model Hamiltonians and band intensity, say, according to Hönl-London factors. Such an approach assumes that:

i) Rotational and vibrational motion can be separated effectively throughout the requesite energy range;

ii) Band intensities will determine the intensity of each individual ro-vibrational transition within that manifold.

Our experience with the H_3^+ molecular ion is that neither of these assumptions is valid at higher energies. (Indeed the term 'higher'—in the case of H_3^+—means just one quantum of vibrational energy and J values of 7 and above!) Present techniques of determining mean opacities for stars use approximations such as Opacity Distribution Functions (ODF, Jørgensen and Larsson, 1990). It may be argued that these are not sufficiently sensitive for very accurate calculations of molecular data, requiring large amounts of super-computer processing time, to be worthwhile. We consider, however, that this view is both misleading and shortsighted, even for work which continues to make use of ODF and even cruder approximations.

For example, effects such as 'intensity stealing' can cause 'dark bands' to become intense; this effect may not be uniform across the entire band, but may depend on individual rotational states. Thus spectral regions which might have been considered free from absorption may turn out to have considerable opacity. Similar processes can remove opacity from other spectral regions. It is also clear that any astronomical study which measures or predicts detailed spectral profiles for stars needs to have accurate molecular data as input, so that significant inferences about physical conditions within stellar atmospheres may be drawn. Finally, we are convinced that techniques of modelling cool star opacities will progress to the point where lack of good molecular frequencies and line strengths will be a limiting factor, rather than such data being an 'embarras de richesse'.

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