

The Infrared Absorption Spectrum of Water

D. F. Coker, J. R. Reimers and R. O. Watts

Electron and Ion Diffusion Unit, Research School of Physical Sciences,
Australian National University, P.O. Box 4, Canberra, A.C.T. 2600.

Abstract

A combination of quantum calculations and Monte Carlo methods is used to predict the infrared absorption spectrum of the water monomer, water dimer and the pure liquid. Full quantum calculations using internal coordinates are used to fit three Morse oscillators to the fundamental and overtone vibrations of the water monomer. This intramolecular potential is then combined with an accurate intermolecular surface to calculate the dimer spectrum from a normal mode analysis and from classical trajectory studies. The liquid state spectrum is obtained using a Monte Carlo simulation program together with a sequence of normal mode analyses of representative molecular configurations. Results are in good agreement with available experimental data suggesting that the potential energy surfaces used are reasonably accurate.

1. Introduction

If an accurate theory of the structure and properties of water is to be developed, it is important that the potential energy surfaces for the monomer and dimer be known. Many methods have been applied to the estimation of these surfaces, including both *ab initio* quantum calculations (Popkie *et al.* 1973) and semi-empirical methods (Watts 1977; Reimers *et al.* 1982). The usual method for developing an empirical intramolecular surface is to fit predicted vibrational spectra to experimental results (Wilson *et al.* 1955). For intermolecular potential surfaces a more substantial set of calculations involving gas, liquid and solid properties has to be undertaken (Watts and McGee 1976). As one example, Reimers *et al.* (1982) developed a semi-empirical effective pair potential for the rigid water dimer by fitting thermodynamic data for gas, liquid and solid phases. Recently Reimers and Watts (1982*a*, 1982*b*) have determined a potential surface for the water monomer by fitting three Morse functions to vibrational transitions in the infrared spectrum. In the present paper we review this work and show how the two surfaces may be combined to predict the infrared spectra of the water dimer and the liquid.

The standard method for predicting the infrared spectrum of a single molecule is based on a normal mode analysis. It is assumed that in the region of the minimum the potential energy surface is to lowest order quadratic in atomic displacements. The force constants can then be determined by fitting the eigenvalues of the resulting secular equations to the infrared fundamentals (Wilson *et al.* 1955). A more realistic surface can be obtained by including higher order terms in the expansion in atomic displacements. The required eigenvalues are then obtained from those of the harmonic potential by perturbation theory. An alternative approach is to represent the atomic

interactions by Morse oscillators, or similar functions (Huffaker 1976*a*, 1976*b*, 1980), and fit the resulting eigenvalues to experiment by varying the Morse parameters. If properly carried out, this route can give a surface, for diatomics, that is accurate for all eigenvalues up to dissociation (Huffaker 1977). Reimers and Watts (1982*b*) have used this second approach to determine a reasonable representation of the monomer potential surface.

Although an approach similar to that outlined for the monomer can be used to study the spectral properties of van der Waals dimers, it is generally unproductive, primarily because it is very difficult to measure the vibrational fundamentals. High resolution spectra can be obtained from measurements on supersonic expansions (Gough *et al.* 1977; Miller 1980), but bulk gas measurements show only a broad rotational-vibrational band structure. One method for modelling the second situation is to artificially broaden the transitions predicted by a normal mode analysis. A second method is to use a classical trajectory calculation together with a Monte Carlo average over initial conditions to determine a set of possible dimer motions. The vibrational spectrum can then be determined using linear response theory, whereby the Fourier transform of the dipole-dipole autocorrelation function gives the required results (Berens and Wilson 1981). A third approach that has been applied to the liquid phase for polar systems (Watts 1981) is to calculate the trajectories when an interaction with an external periodic field is included in the Hamiltonian. If the response to the field (dipole polarization for the infrared spectrum) is calculated, the power absorption and the spectrum can be determined. All three methods have been studied for the water dimer and, as will be shown, the predicted spectra are similar.

It is not an easy matter to predict the infrared spectrum of a liquid. Standard methods for solids, based on normal mode calculations (Born and Huang 1954), require that the displacements of atoms from their lattice sites be small. This assumption clearly fails for a liquid, where there are no proper phonon modes. It is possible to use a molecular dynamics simulation together with linear response theory to obtain the required spectrum from the dipole-dipole autocorrelation function (McQuarrie 1976). This approach is very expensive to implement, particularly if the low frequency spectrum is required. A similar criticism can be made of the method based on applying a frequency dependent external field (Watts 1981) and measuring the corresponding polarization. The method used here is approximate and is based on a normal mode analysis. Although it does not give a complete description of the vibrational modes in the liquid, the method does give a good representation of vibrational bands in the range 500–4000 cm^{-1} .

2. Water Monomer

The normal mode method for determining the vibrational spectrum of a system begins by expanding the total potential energy in a Taylor series in terms of the atomic displacement from equilibrium sites. As the first derivative terms in the expansion are zero, truncation of the expansion at second order results in a surface which is quadratic in displacements. Standard methods (Wilson *et al.* 1955) can then be used to describe the resulting system in terms of a set of independent harmonic oscillators. Quantum mechanical perturbation theory can then in turn be applied to describe the eigenvalues and eigenfunctions of the original Hamiltonian in terms of the corresponding properties of the harmonic oscillator Hamiltonian. Although this approach is mathematically appealing, there are severe computational problems.

In particular, the expansion of the required eigenfunctions in terms of Hermite polynomials converges slowly. For example, if the first 20 vibrational levels for water are to be calculated accurately, the harmonic basis set extends to at least 560 Hermite polynomials. Clearly it would be advantageous to use a more rapidly convergent basis set.

It is not difficult to find reasons for the slow convergence of the harmonic oscillator basis set. For example, the correct interaction potential is a long way from being harmonic and higher order terms in the Taylor expansion are significant even in the ground vibrational state. Also, the harmonic oscillator is not capable of describing vibrations where the molecule is close to dissociation. Under these conditions the normal mode description itself breaks down and it is better to describe the molecular motions in terms of bond displacements. There are distinct advantages in using a basis set from a model that gives a good zeroth order description of both the potential surface and the higher energy motions. A local coordinate description, based on Morse oscillators, meets these requirements admirably. Such an approach has been applied to the bond stretching modes of water by Watson *et al.* (1981), who based their work on the analysis of Wallace (1975).

There are many possible choices of local coordinate and we use a set based on the internal valence coordinates. Suppose R_0 and θ_0 are the equilibrium bond length and bond angle respectively and then we define the mass-independent coordinates

$$s_1 = R_1 \cos \frac{1}{2}(\theta - \theta_0) - R_0, \quad (1a)$$

$$s_2 = R_2 \cos \frac{1}{2}(\theta - \theta_0) - R_0, \quad (1b)$$

$$s_3 = \{(R_1 + R_2)/R_0\} \sin \frac{1}{2}(\theta - \theta_0), \quad (1c)$$

with R_1 , R_2 and θ the two O-H bond lengths and the HOH bond angle respectively. A significant advantage of using these local coordinates is that within the constraints of the Born-Oppenheimer approximation the potential surface is transferable between isotopes (Hoy *et al.* 1972).

The intramolecular interaction is written as a sum of three Morse functions

$$\phi(s_1, s_2, s_3) = \sum_{i=1}^3 D_i \{1 - \exp(-a_i s_i)\}^2, \quad (2)$$

with D_i and a_i adjusted to fit experimental data. For water, the two stretch modes s_1 and s_2 are identical so that $D_1 = D_2$ and $a_1 = a_2$ and there are four fitted parameters. This should be compared with models based on Taylor expansions where there are sometimes 16 or more harmonic and anharmonic force constants (Eisenberg and Kauzmann 1969; Whitehead and Handy 1975). The values of D_i and a_i determined by Reimers and Watts (1982a) by fitting to 56 H₂O, HDO and D₂O band origins are $D_1 = D_2 = 131.1404 \text{ kcal mole}^{-1}$, $D_3 = 99.0249 \text{ kcal mole}^{-1}$ and $a_1 = a_2 = 2.134980 \text{ \AA}^{-1}$, $a_3 = 0.703372 \text{ \AA}^{-1}$.

A Morse function gives a good description of bond stretching motions in that it accounts for the strong repulsion between atoms at short separations as well as allowing for molecular dissociation. Our use of this function to describe a bending mode is less obvious in that the bond angle θ is constrained to the range $(0, 2\pi)$ and, for water, there is an inversion symmetry to be considered. As the coordinate

s_3 also includes some stretching characteristic, and as we were primarily concerned with lower quantum excitations, we were able to develop methods for minimizing any problems due to periodicity. A full account is given elsewhere (Reimers and Watts 1982a).

One advantage of using a normal mode analysis is that the kinetic energy operator is diagonal in the normal coordinates. This advantage no longer exists when a local coordinate description is used. Reimers and Watts (1982a) have shown that the full Hamiltonian for nonlinear molecules in local coordinates is given by

$$\hat{H} = \frac{1}{2}(\hat{\mathbf{\Pi}} - \hat{\boldsymbol{\pi}}) \cdot \boldsymbol{\mu} \cdot (\hat{\mathbf{\Pi}} - \hat{\boldsymbol{\pi}}) + \frac{1}{2}\hat{\mathbf{P}} \cdot \mathbf{G} \cdot \hat{\mathbf{P}} - \frac{1}{8}\hbar^2 \text{Tr}(\boldsymbol{\mu}) + \phi(s), \quad (3)$$

where $\boldsymbol{\mu}$ is related to the inverse of the moment of inertia matrix, $\hat{\mathbf{\Pi}}$ is the angular momentum operator conjugate to the angles describing rotation of a fixed-molecule frame of reference, $\hat{\boldsymbol{\pi}}$ is an angular momentum operator resulting from vibrational motion, $\hat{\mathbf{P}}$ is the linear momentum operator conjugate to the rectilinear components of the internal coordinates s , and \mathbf{G} the Wilson G matrix is related to the matrix transforming cartesian coordinates to local coordinates. Without entering into details, the first term in equation (3) contains most of the centrifugal and Coriolis contributions to the kinetic energy, the second term represents the vibrational kinetic energy, and the third is a mass dependent term that can be considered an additional contribution to the potential energy. Watson (1968) has discussed this term in detail. The fourth and last term in (3) is the intramolecular potential energy, in our case a sum of three Morse oscillators. This Hamiltonian includes coupling between the vibrations and rotations due to a number of effects. In particular, centrifugal, and Coriolis effects cause the molecule to be distorted and vibrations change the moment of inertia matrix. The major contribution in this coupling comes from the term $\hat{\boldsymbol{\pi}} \cdot \boldsymbol{\mu} \cdot \hat{\boldsymbol{\pi}}$.

We calculated the eigenvalues and eigenfunctions of the full Hamiltonian using variational theory with three independent Morse oscillators as the reference state. This is done by writing the reference Hamiltonian as

$$\hat{H}_0 = \sum_{i=1}^3 \frac{1}{2}G_{ii}P_i^2 + D_i\{1 - \exp(-a_i Q_i)\}^2, \quad (4)$$

where Q_i are the rectilinear components of s_i . All rotation-vibration coupling together with kinetic energy coupling between the local coordinates is ignored. The eigenfunctions of \hat{H}_0 are known analytically, the rotational basis set being that of a rigid rotor and the vibrational set a product of the eigenfunctions of the Morse oscillator (Morse 1929; ter Haar 1946). The eigenfunctions of the full Hamiltonian are then written as a linear combination of the reference system eigenfunctions and the required eigenvalues determined using standard methods. A basis set including all combinations of seven excitations (120 functions), for the reference system, gives convergent eigenvalues for all possible excitations up to five quanta (56 levels) for the full Hamiltonian. The numerical problems associated with using a set of Laguerre polynomials as the basis set are similar to those for the Hermite polynomials used in the normal mode approach. However, the improvement in convergence is dramatic.

Table 1 gives the observed and predicted vibrational frequencies for H_2O together with their assignments in terms of both local and normal modes. Morse potential

parameters were fitted to this data, together with corresponding data for HDO and D₂O. Overall, the agreement with experiment is very acceptable with the average deviation for a total of 56 states from all three isotopes being 3.5 cm⁻¹. The largest deviations from experiment occur for the bond stretch modes which invariably occur as a symmetric-antisymmetric combination of stretches in the two bonds. These two states are degenerate in the reference state and this degeneracy is lifted by off-diagonal terms in **G** and couplings with the centrifugal and Coriolis terms in the kinetic energy. Such terms give rise to a splitting that is about half that observed experimentally. The additional splitting arises from terms in the potential energy surface that depend upon the coordinates of all three atoms. It is clear from the results in Table 1 that the rising non-pairwise additive terms are small.

Table 1. Vibrational band origins for H₂O and their assignments in local and normal modes

Local	Assignments			Frequencies (cm ⁻¹)	
	C ^A	Normal	C ^A	Calc.	Obs.
000	100	000	98	0	0
001	100	010	98	1595	1595
100s	100	100	85	3669	3657
100a	100	001	92	3719	3756
002	100	020	92	3150	3132
200s	93	200	66	7213	7201
200a	100	101	68	7229	7250
110	93	002	82	7401	7445
101s	99	110	82	5266	5235
101a	100	011	93	5306	5331
003	99	030	79	4663	4667
300s	97	300	43	10593	10600
300a	98	201	42	10596	10613
210s	97	102	45	10881	10869
210a	99	003	64	10971	11032
201s	94	210	65	8808	8761
201a	99	111	69	8819	8807
111	72	012	83	8986	9000
102s	99	120	73	6820	6775
102a	99	021	92	6850	6872

^A The contribution (%) of the stated assignment to the converged basis set.

The extent to which the reference system matches the correct basis set is indicated in Table 1. An assignment of reference system states to several eigenvalues is given for both the Morse oscillator reference system and the normal coordinate basis. With few exceptions a single local coordinate reference state accounts for well over 95% of the character. For the normal coordinate reference system, only the ground state and one or two of the first quantum states approach this value. All other states, particularly those involving two or more quanta, have substantial mixing with reference system states representing higher excitations. This difference emphasizes the fact that an accurate description of the first 20 vibrational states requires a harmonic oscillator basis of at least 560 eigenstates or a Morse oscillator basis of 56 eigenstates.

Table 2. Rotational energy levels for H₂O

Values are given with respect to the band origins. Assignments are given in terms of quantum numbers J and K , while the symbols s and a refer to combinations of $\pm K$ states

Assignment		Frequencies (cm ⁻¹)		Assignment		Frequencies (cm ⁻¹)	
State	C ^A	Calc.	Obs.	State	C ^A	Calc.	Obs.
<i>Vibration origin: 000</i>				<i>Vibration origin: 100s</i>			
$A = 28.97 \quad B = 14.13 \quad C = 9.30$				$A = 28.61 \quad B = 13.87 \quad C = 9.14$			
11s	100	23.5	23.8	11s	100	23.1	23.3
11a	100	38.1	37.1	11a	100	37.5	36.2
10	100	43.1	42.4	10	100	42.4	41.4
22s	85	69.4	70.1	22s	85	68.1	68.8
22a	100	80.2	79.5	22a	100	78.7	77.8
21s	100	95.1	95.2	21s	100	93.5	93.5
21a	100	138.5	134.9	21a	100	136.3	131.5
20	85	139.6	136.1	20	83	137.9	132.8
<i>Vibration origin: 001</i>				<i>Vibration origin: 100a</i>			
$A = 33.48 \quad B = 13.75 \quad C = 9.27$				$A = 28.57 \quad B = 13.75 \quad C = 9.01$			
11s	100	23.0	23.8	11s	100	23.3	23.6
11a	100	42.2	40.3	11a	100	37.5	35.7
10	100	47.2	45.8	10	100	42.3	41.0
22s	83	68.2	70.2	22s	85	68.7	69.1
22a	100	83.3	82.4	22a	98	79.0	77.6
21s	100	98.2	98.1	21s	100	93.9	93.3
21a	100	155.1	147.6	21a	100	136.0	129.8
20	83	155.9	148.8	20	85	137.1	131.4

^A The contribution (%) of the stated assignment to the converged basis set.

The inclusion of full centrifugal and Coriolis terms in the Hamiltonian enabled the rotational fine structure to be examined. Table 2 gives the predicted and observed rotational frequencies, with respect to the band origins, for several vibrational states of H₂O. Agreement between calculated and experimental levels is generally good for H₂O, HDO and D₂O (Reimers and Watts 1982*b*). It is interesting to examine the dependence of the rotational levels on the vibrational state. Such levels are relatively insensitive to excitations that are primarily concentrated in the bond stretching modes. However, the bending modes have rotational levels that are much more sensitive. This is readily understood in terms of the rotational constants A , B and C also given in Table 2. The constant A increases markedly as the bending mode is excited, because this type of motion decreases the moment of inertia with respect to the molecular axis perpendicular to the symmetry axis. As a consequence the rotational levels become more widely separated. The major contribution to the differences between observed and calculated rotational levels is attributed to the fact that A is consistently 5–10% too large.

3. Water Dimer

The dimer spectrum can be predicted if both the intramolecular and intermolecular potentials are known. We have outlined the development of the first surface in the previous section. For the intermolecular potential surface we use a semi-empirical model developed by Reimers *et al.* (1982) that is a modification of a model described

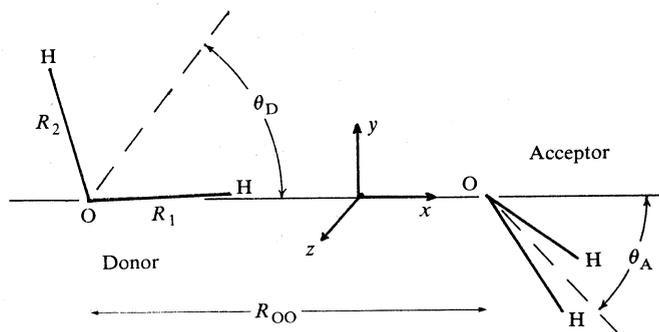


Fig. 1. Geometry of the water dimer. (For values of distances and angles see Table 3.)

ν	Mode		Symmetry	Frequencies (cm^{-1})		
	Donor	Acceptor		Monomer Morse	Dimer Morse	Dimer Harmonic
1			a''	-	115	115
2			a'	-	169	169
3			a''	-	219	219
4			a'	-	272	269
5			a'	-	483	482
6			a''	-	782	780
7			a'	1640	1621	1650
8			a'	1640	1682	1708
9			a'	3830	3520	3780
10			a'	3830	3797	3843
11			a''	3886	3852	3951
12			a'	3886	3872	3920

Fig. 2. Fundamental vibrations of the $(\text{H}_2\text{O})_2$ dimer calculated using a normal mode analysis.

for the vibrating dimer by Watts (1977). The Reimers *et al.* surface is based on the best known dispersion coefficients (Margoeflash *et al.* 1978), a damping term for the dispersion at short distances (Doukatis *et al.* 1982), and three atom-atom short range terms containing empirically determined parameters. Parameters were obtained by fitting the monomer dipole and quadrupole moments, the second virial coefficient of steam, and the static lattice energy, structure and bulk moduli of ices I-h, VII and VIII. Calculations of the structure and thermodynamic properties of liquid water, as well as molecular beam scattering data, showed that the effective pair potential is reasonably accurate.

We obtained a full potential surface for distorting water molecules by combining the monomer potential with the dimer surface. Our calculations are based on the assumption that the pairwise additivity of intermolecular potentials can be extended to the separate determination of the inter- and intramolecular terms. The results obtained suggest that this approximation is reasonably accurate, at least for the water dimer.

Table 3. Structure of H₂O monomer and dimer

The terms 'donor' and 'acceptor' molecule are defined in Fig. 1. Distances are in Å and angles in degrees

	Donor			Acceptor			R_{oo}	θ_A	θ_D
	R_1	R_2	θ	R_1	R_2	θ			
Monomer	0.9572	0.9572	104.52	0.9572	0.9572	104.52	—	—	—
Dimer	0.9788	0.9568	103.75	0.9606	0.9606	104.61	2.745	53.45	53.75

Initially, the dimer vibrational spectrum was determined from a normal mode analysis. Two water molecules were placed in the hydrogen bonding configuration shown in Fig. 1. A local minimum in the potential surface was found by allowing all atomic coordinates to relax. The resulting dimer structure belongs to the C_s point group. As shown in Table 3, the intramolecular structure of both molecules is distributed from the monomer result. A normal mode analysis was then made using the intramolecular Morse potentials developed by Reimers and Watts (1982*b*) and the intermolecular pair RKW potential of Reimers *et al.* (1982). Results for the calculations together with the monomer normal mode vibrations predicted by the Morse interactions are given in Fig. 2. No attempt has been made to obtain accurate eigenvalues for the full potential surface. In the case of the monomer, the eigenvalue of the bending mode is 46 cm^{-1} lower than the normal mode frequency, the symmetric stretch is 183 cm^{-1} lower, and the asymmetric stretch 131 cm^{-1} lower. We expect the eigenvalues for the six higher frequency dimer modes to be lowered similarly in an exact calculation.

The water dimer has twelve fundamental vibrations, six of which are associated with monomer modes. These monomer modes occur in pairs and their degeneracy is broken by the intermolecular interactions. All six low frequency modes are associated primarily with relative motions of the two molecules and are not very sensitive to the form of the intramolecular potential. Two of the high frequency modes are derived from the (monomer) intramolecular bending motion (ν_7 and ν_8), two from the (monomer) symmetric stretch (ν_9 and ν_{10}) and two from the (monomer)

asymmetric stretch (ν_{11} and ν_{12}). It is convenient when discussing these vibrations to use the terms 'donor' (D) and 'acceptor' (A) molecules as defined in Fig. 1.

Both bending modes ν_7 and ν_8 in Fig. 2 are shifted with respect to the monomer value. The acceptor molecule has a bending frequency ν_7 lowered by about 20 cm^{-1} and the donor molecule mode ν_8 is raised by around 40 cm^{-1} . Hence the intermolecular forces weaken the acceptor bend and strengthen the donor bend. In the case of the acceptor molecule, both stretching frequencies ν_{10} and ν_{11} are lowered by around 34 cm^{-1} . They retain their form as symmetric and antisymmetric O-H stretches respectively. The two stretching modes in the donor molecule, ν_9 and ν_{12} , behave quite differently. First, the symmetries of the two modes are now the same and ν_9 is almost entirely due to the motion of the hydrogen atom involved in the hydrogen bond, whereas ν_{12} is associated with the vibration of the other hydrogen atom. Next, the hydrogen bonded atom oscillates at a frequency that is 310 cm^{-1} lower than the monomer mode, whereas the other stretching frequency is lowered only by 14 cm^{-1} . The lowering of ν_9 by 300 cm^{-1} is observed in the infrared spectrum of liquid water, as will be discussed in the next section. This can be understood by examining the effective potential for the O-H stretch. Fig. 3 shows this potential for the two modes in the monomer and dimer. Clearly, the dimer hydrogen bonded atom moves in a much broader potential well than it does in the monomer. This is a direct effect of the strong O-H intermolecular attraction.

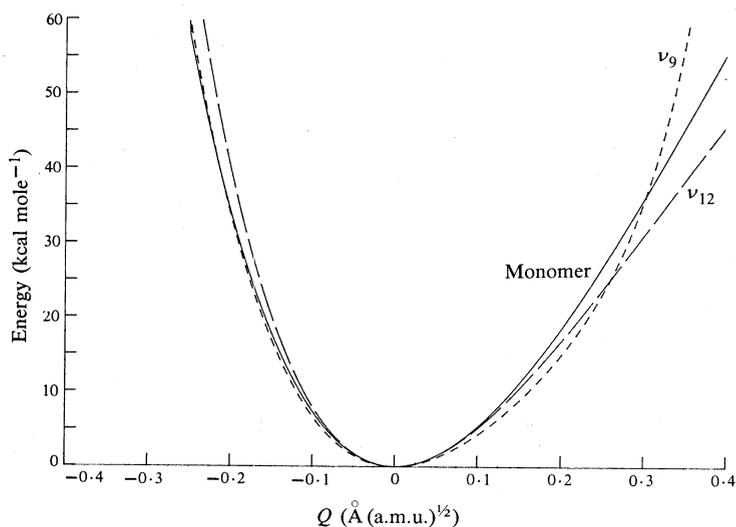


Fig. 3. Potential energy as a function of normal mode displacement for the monomer (symmetric stretch) and the dimer (modes ν_9 and ν_{12}) using the RKW2+Morse potential.

The six low frequency modes correspond to intermolecular vibrations and are assigned as in Fig. 2. Modes ν_4 , ν_5 and ν_6 are all directly concerned with hydrogen bond distortions, and cover the O-O stretch, and the O-H-O bending modes that are in-plane and out-of-plane respectively. It is of particular interest that the two bending modes are stiffer than the stretch, indicating that the 'hydrogen bond' is

fairly directional. The modes ν_2 and ν_3 correspond to the acceptor molecule rocking and rolling about its symmetry axis, and the lowest energy mode ν_1 is the hydrogen bond torsional motion.

Experimentally, it is difficult to prepare isolated water dimers for spectroscopic studies, the best methods being based on free jet expansions (Dyke 1977; Dyke *et al.* 1977; Odutola and Dyke 1980). Under such conditions there is substantial cooling of the internal modes of the molecules in the jet. The water dimer is expected to be at a vibrational temperature of about 50 K (35 cm^{-1}), and there will be significant excitation of the low frequency modes and corresponding broadening of the spectral lines. It is useful under such conditions to study the structure and dynamics of the dimer using classical trajectory methods (Bernstein 1979). We have developed programs that enable us to study collisions between vibrationally excited water molecules, vibrational predissociation of vibrationally excited van der Waals dimers, and the effect of external fields on the internal motions. The numerical algorithms are based on multi-time-step integration that largely uncouples the vibrational motions of the atoms from the much slower translational motions of the molecules (Reimers and Watts 1983). Trajectories are followed with greatly improved efficiency compared with the usual single time-step methods. All classical trajectory studies reported in this section are based on the dimer intermolecular potential together with a harmonic intramolecular potential. Studies with the full intramolecular surface are currently in progress.

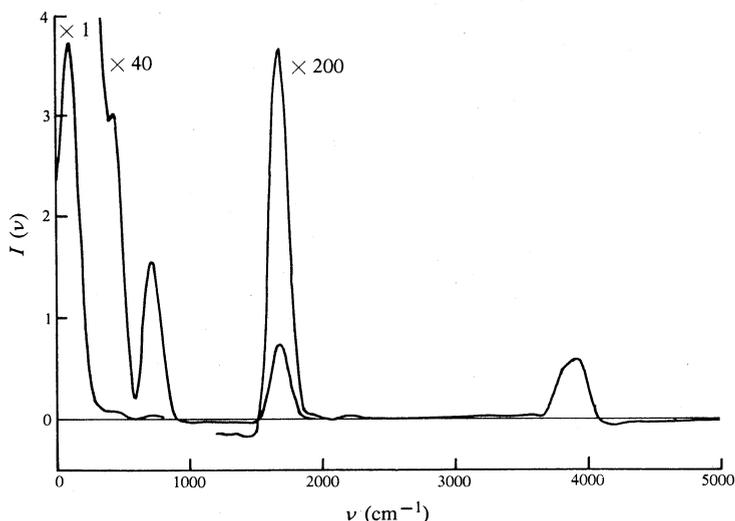


Fig. 4. Dimer vibrational spectrum obtained from the Fourier–Laplace transform $I(\nu)$ of the dipole autocorrelation function using the RKW2+harmonic potential at 50 K.

The most common method for obtaining the infrared spectrum from classical trajectories is based on linear response theory (McQuarrie 1976). This theory relates the spectrum to the Fourier–Laplace transform of the dipole autocorrelation function

$$I(\nu) = \int_0^{\infty} \langle \boldsymbol{\mu}(0) \cdot \boldsymbol{\mu}(t) \rangle \exp(-i\nu t) dt, \quad (5)$$

where $\mu(t)$ is the dipole moment of the system at time t . The average is over a Boltzmann distribution of initial conditions, which we generate at 50 K using a Monte Carlo algorithm. Both high and low frequency noise is caused by the requirements that a discrete time step be used and the time integral be truncated. The direct effect of this noise was removed by windowing techniques (Bracewell 1978). The results we give were obtained from 4×10^4 trajectories. Trajectories were followed for about 2.5×10^{-13} s, giving a resolution of 133 cm^{-1} in the spectrum.

The resulting spectrum for the range $0\text{--}5000 \text{ cm}^{-1}$ is given in Fig. 4. The spectrum consists of four broad bands. One below 600 cm^{-1} is attributed to the low frequency dimer modes ν_1 , ν_2 and ν_3 identified from the normal mode analysis. A band centred on 700 cm^{-1} is attributed to the hydrogen bond stretch and bending modes $\nu_4\text{--}\nu_6$. Intramolecular bending modes are active between 1500 and 1800 cm^{-1} and finally the stretching modes are observed between 3500 and 4000 cm^{-1} . Our resolution was not sufficient to distinguish between the two types of stretching motion. In all cases, the times are broadened by thermal averaging.

The method of non-equilibrium molecular dynamics is a useful approach to calculating time-dependent properties of dense fluids (Hoover *et al.* 1980). It has been successfully applied to the frequency-dependent dielectric properties of simple diatomic systems (Watts 1981) and to the prediction of Raman scattering spectra of liquid halogens (Evans *et al.* 1982). The method consists of including a frequency-dependent field in the equations of motion and calculating the response. Vibrational fundamentals can be identified by observing the response to a frequency-dependent electric field of a dimer that is initially stationary. Thermal effects are included by averaging the response (which can be either the induced dipole moment or the power absorbed) over a Boltzmann distribution of initial conditions.

An understanding of the observed effects is obtained by considering a single harmonic oscillator in an applied field $F(t) = f \cos vt$. The classical Hamiltonian is

$$H = (p^2/2m) + \frac{1}{2}kx^2 + xF(t), \quad (6)$$

and we consider the equations of motion both when the field is on-resonance $\nu = \nu_0$, with $\nu_0 = (k/m)^{\frac{1}{2}}$, and when it is off-resonance. When the field is on-resonance, the total energy will increase as

$$E = (f^2/8m)(t^2 + \nu^{-2} \sin^2 vt + t\nu^{-1} \sin vt), \quad (7)$$

so that for t reasonably large E will increase quadratically. When the field is off-resonance the response becomes sinusoidal at the sum and difference frequencies $\nu + \nu_0$ and $\nu - \nu_0$. Anharmonic terms will give similar effects if they are small or if the excitation is not allowed to grow too large. We determined the vibrational spectrum of the dimer by studying the response of an initially motionless system and following the induced motions. If the field was on-resonance, integration of the equations of motion was stopped when the total energy reached $h\nu$, and if the field was off-resonance, trajectories were followed for about 10^{-11} s. By varying the frequency and polarization of the applied field it was possible to identify a number of fundamental and overtone frequencies.

Fig. 5a shows the energy as a function of time induced by a field polarized in the y direction (see Fig. 1) and oscillating at a frequency of 3900 cm^{-1} . The oscillatory behaviour is clearly identified and the distribution of energy among normal modes shows that there are strong beats at difference frequencies of $\nu_{11} - \nu = 22 \text{ cm}^{-1}$ and

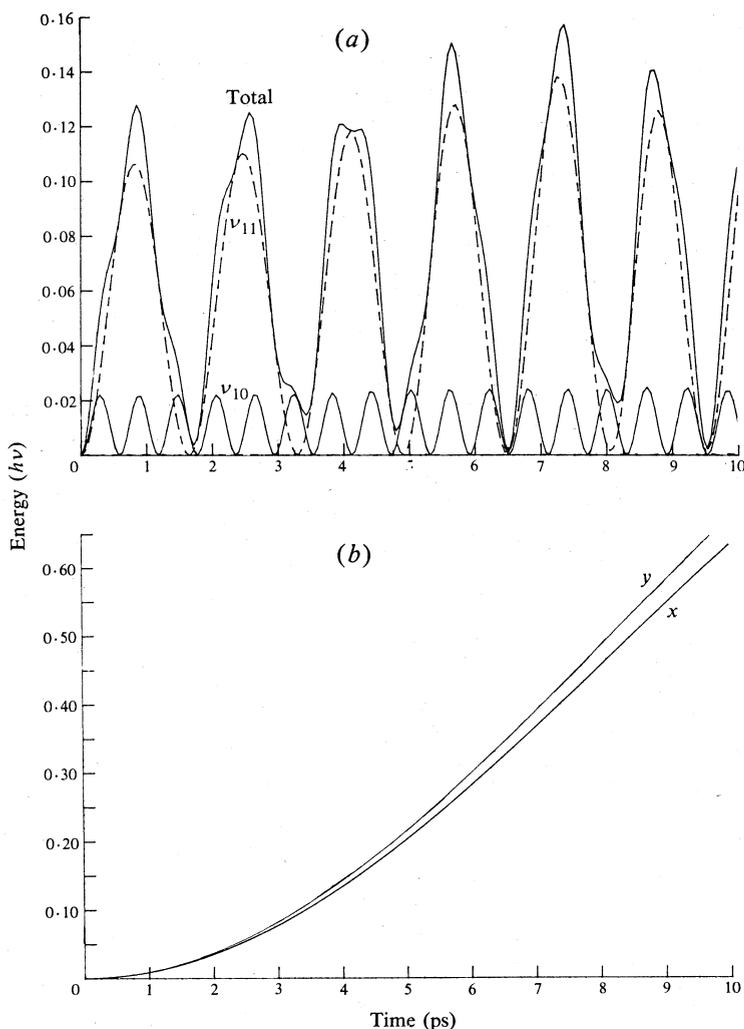


Fig. 5. Energy as a function of time using the RKW2+harmonic potential for a water dimer in an applied electric field: (a) The field of strength 0.050 V \AA^{-1} is polarized in the y direction and has a frequency of 3900 cm^{-1} . Contributions from two nearby vibrational modes ν_{11} and ν_{10} are indicated. (b) The field of strength 0.008 V \AA^{-1} is polarized in the x and y directions and has a frequency of 3922 cm^{-1} .

$\nu_{10} - \nu = -57 \text{ cm}^{-1}$. No beats were observed with the asymmetric stretch ν_{12} , although this is close to 3900 cm^{-1} , as its symmetry is such that it does not respond to fields polarized in the x or y directions. Fig. 5b shows the effect of changing the frequency so that the field is on-resonance at $\nu_{11} = 3922 \text{ cm}^{-1}$. The energy increases quadratically and any beats with other nearby modes are lost in the size of the resonant response. A detailed analysis of these types of response enables both the fundamental and overtone spectra to be determined.

It is important to consider the relative efficiency of these three methods for determining the dimer spectrum. A full quantum calculation is, in principle, the

correct method for calculating the fundamental and overtone frequencies. However, such calculations are very time consuming for a system having twelve vibrational modes together with three rotations, and requires a large basis set if accurate eigenvalues are to be obtained. Linear response theory relies upon the use of classical mechanics and is subject to considerable unwanted noise in the Fourier transform. In addition, in its usual form it is only capable of describing the fundamentals. It has the advantage that Boltzmann averaging is included so that band shapes can be obtained with reasonable accuracy. However, at low temperatures the method gives very poor results for the intensities due to the neglect of zero point motion. The non-equilibrium calculations, which also include Boltzmann averaging, represent a fast method for determining the properties of a small region of the spectrum but require very extensive calculations before the full spectrum is obtained.

4. Liquid Water

Two of the methods used to predict the dimer spectrum, namely linear response theory and non-equilibrium molecular dynamics, can be directly applied to the liquid. However, if reasonable resolution of the spectrum is required, a complete study using either method demands an excessive amount of computing. Consequently we have obtained results using an approximate method that can be expected to give a reasonable estimate of the liquid infrared spectrum, particularly in the range 500–4000 cm^{-1} . Although we have only considered the fundamental vibrations, the method can in principle be applied to overtone bands.

The approximation starts by generating a long sequence of possible liquid configurations using a Monte Carlo method (Barker and Watts 1969; Watts 1974). At regular intervals the system is frozen and a normal mode analysis made for the spectrum of one water molecule, under the assumption that the rest of the lattice can be regarded as an external inhomogeneous field. This approximation accounts for nine vibrational modes: three intramolecular modes (ν_7 , ν_8 and ν_9) and six modes (ν_1 – ν_6) associated with the vibration and libration of the molecule in its lattice. Clearly, this approximation neglects most of the low frequency lattice modes, including all phonon-like modes, and only approximates coupling between low and high frequency modes. However, it is expected to be fairly accurate at higher frequencies where, at least in the liquid, it is reasonable to assume that the lattice modes are largely uncoupled from the molecular modes. An additional assumption, that has particularly severe consequences for the three lowest frequency modes, is that the molecule is at a local minimum in its multi-dimensional potential surface. Although there are effects at all frequencies, this approximation sometimes leads to negative eigenvalues for the lowest frequency modes.

The Monte Carlo method (Watts 1974) was used to generate a sequence of 10^6 possible configurations for 64 water molecules interacting through the inter- and intramolecular potentials described earlier. Standard periodic boundary conditions (Watts and McGee 1976) were used to reduce the effects of finite system size. After every 500 configurations, 20 molecules were chosen at random and their nine vibrational frequencies calculated using a normal mode analysis as described above. The resulting eigenvectors, assumed to be the corresponding harmonic oscillator functions, were used to calculate oscillator strengths for every mode. A histogram of the frequencies, with 20 cm^{-1} resolution, gave the predicted density of states, and

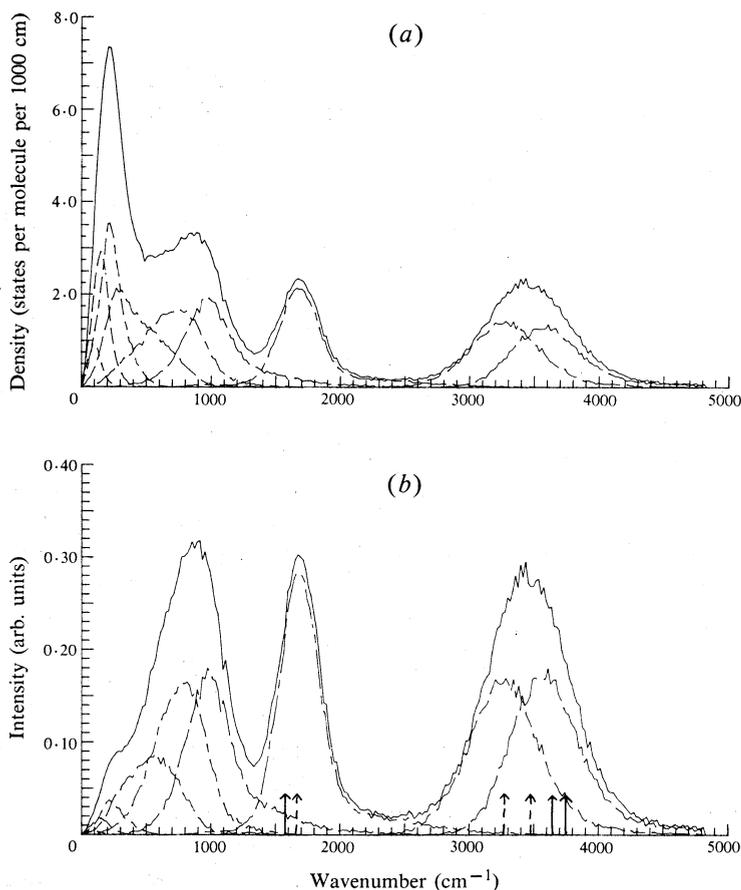


Fig. 6. Liquid water at 298 K: (a) Density of states together with an analysis into normal modes. (b) Oscillator strength distribution, where the solid arrows indicate monomer frequencies and dashed arrows maxima in the experimental infrared absorption spectrum for the liquid.

a corresponding histogram of oscillator strengths as a function of frequency gave the predicted infrared spectrum.

The density of states calculated at 298 K is shown in Fig. 6a together with the individual contributions from the three highest vibrational frequencies. There are rather broad bands centred on 3500 and 1700 cm^{-1} , and there is a broad band of rotational-vibrational frequencies below 1000 cm^{-1} . Our analysis of the dimer spectrum associates the band in the range 500–1000 cm^{-1} with hydrogen bond bending and stretching motions. A detailed analysis of this band shows that there are two major contributors, corresponding to the in-plane and out-of-plane dimer modes discussed in Section 3. The band centred near 1700 cm^{-1} is almost entirely associated with the monomer bending mode, and has been significantly broadened by interactions with other molecules in the liquid. It is moved to higher frequencies by about 70–100 cm^{-1} , a shift that is observed experimentally in the infrared spectrum of water (Bailey *et al.* 1963). The broad band centred around 3400 cm^{-1} is associated with the two monomer stretching modes. From the analysis in Fig. 6a, we see that

the separation between these two modes is about 400 cm^{-1} , in agreement with the separation found from the dimer analysis given in the previous section. The positions of the two peaks at 3200 and 3600 cm^{-1} are close to observed structures in the infrared spectrum (Bayley *et al.* 1963).

The oscillator strength as a function of frequency is shown at a temperature of 298 K in Fig. 6*b*. Arrows indicate the positions of the monomer frequencies and of the band maxima in the liquid observed experimentally. Clearly, the positions of the predicted bands are, in general, in good agreement with observed band maxima. However, the two experimentally observed features in the band near 3400 cm^{-1} are closer than the maxima in the two components obtained from our analysis. Although our spectrum is not well resolved near the maximum, the structure in the combined band, which corresponds to the experimental observation, is closer to the measured data. Overall, agreement between theory and experiment for band positions is very pleasing.

Calculated intensities and bandwidths are less satisfactory. The ratio of the bending mode to stretching mode extinction coefficients is about one-third (Bayley *et al.* 1963), whereas our spectrum predicts about equal intensity. Similarly, the spectrum shown in Fig. 6*b* has a width at half maximum for both the bending mode and the stretching modes that is too large by $100\text{--}200\text{ cm}^{-1}$. This lack of agreement between observed and calculated intensities is, perhaps, to be expected as this property is very sensitive to the dipole moment function of the molecule. Although the monomer potential predicts that the dipole moment is a function of the internal state, it is likely that the predicted excited state values are incorrect.

Several interesting variations in the water spectrum occur if the temperature is altered. In particular, the distribution of intensity between the two maxima observed experimentally in the stretch band around 3400 cm^{-1} alters. At low temperatures the lower frequency maximum contains much of the intensity, whereas at high temperatures the other mode is more intense (Walrafen 1967). We have made calculations at other temperatures in order to examine this effect. An analysis of the density of states shows that at low temperatures the splitting between the two components is small, both ν_8 and ν_9 being in the range $3200\text{--}3400\text{ cm}^{-1}$. At high temperatures ν_9 moves to higher frequencies while ν_8 remains close to 3200 cm^{-1} . In addition the higher frequency mode becomes more heavily populated at the expense of the lower. Thus our results are in qualitative agreement with experiment. The problems associated with calculating intensities discussed in the previous paragraph remain.

Acknowledgments

We have benefited from discussions with Dr M. G. Sceats of the University of Sydney and Dr R. E. Miller of the Australian National University.

References

- Barker, J. A., and Watts, R. O. (1969). *Chem. Phys. Lett.* **3**, 144.
- Bayley, J. G., Kartha, V. B., and Stevens, W. H. (1963). *Infrared Phys.* **3**, 211.
- Berens, P. H., and Wilson, K. R. (1981). *J. Chem. Phys.* **74**, 4872.
- Bernstein, R. B. (1979). 'Atom-Molecule Collision Theory: A Guide for the Experimentalist' (Plenum: New York).
- Born, M., and Huang, K. (1954). 'Dynamical Theory of Crystal Lattices' (Oxford Univ. Press).

- Bracewell, R. (1978). 'The Fourier Transform and its Applications' (McGraw-Hill: Tokyo).
- Doukatis, C., Scoles, G., Machatti, S., Thakkar, A. J., and Zen, M. (1982). (to be published).
- Dyke, T. R. (1977). *J. Chem. Phys.* **66**, 492.
- Dyke, T. R., Mack, K. M., and Muentner, J. S. (1977). *J. Chem. Phys.* **66**, 498.
- Eisenberg, D., and Kauzmann, W. (1969). 'The Structure and Properties of Water' (Oxford Univ. Press).
- Evans, D. J., Gaylor, K. J., and Watts, R. O. (1982). (to be published).
- Gough, T. E., Miller, R. E., and Scoles, G. (1977). *Appl. Phys. Lett.* **30**, 338.
- Hoover, W. G., Evans, D. J., Hickman, R. B., Ladd, A. J. C., Ashurst, W. J., and Morgan, B. (1980). *Phys. Rev. A* **22**, 1690.
- Hoy, A. R., Mills, I. M., and Strey, G. (1972). *Mol. Phys.* **24**, 1265.
- Huffaker, J. N. (1976a). *J. Chem. Phys.* **64**, 3175.
- Huffaker, J. N. (1976b). *J. Chem. Phys.* **64**, 4564.
- Huffaker, J. N. (1977). *J. Mol. Spectrosc.* **65**, 1.
- Huffaker, J. N. (1980). *J. Chem. Phys.* **74**, 1217.
- McQuarrie, D. A. (1976). 'Statistical Mechanics' (Harper and Row: New York).
- Margoefash, D. J., Proctor, T. R., Zeiss, G. D., and Meath, W. J. (1978). *Mol. Phys.* **35**, 747.
- Miller, R. E. (1980). Ph.D. Thesis, Univ. of Waterloo.
- Morse, P. M. (1929). *Phys. Rev.* **34**, 57.
- Odutola, J. A., and Dyke, T. R. (1980). *J. Chem. Phys.* **72**, 5062.
- Popkie, H., Kistenmacher, H., and Clementi, E. (1973). *J. Chem. Phys.* **59**, 1325.
- Reimers, J. R., and Watts, R. O. (1982a). Complete molecular rotation-vibration Hamiltonian for nonlinear molecules in local coordinates, to be published.
- Reimers, J. R., and Watts, R. O. (1982b). The ro-vibrational spectrum of the water molecule calculated using local coordinates, to be published.
- Reimers, J. R., and Watts, R. O. (1983). The vibrational spectrum of the water dimer, to be published.
- Reimers, J. R., Watts, R. O., and Klein, M. L. (1982). *Chem. Phys.* **64**, 95.
- ter Haar, D. (1946). *Phys. Rev.* **70**, 222.
- Wallace, R. (1975). *Chem. Phys.* **11**, 189.
- Walrafen, G. E. (1967). *J. Chem. Phys.* **47**, 114.
- Watson, I. A., Henry, B. R., and Ross, I. G. (1981). *Spectrochim. Acta* **A37**, 857.
- Watson, J. K. G. (1968). *Mol. Phys.* **15**, 479.
- Watts, R. O. (1974). *Mol. Phys.* **28**, 1069.
- Watts, R. O. (1977). *Chem. Phys.* **26**, 367.
- Watts, R. O. (1981). *Chem. Phys. Lett.* **80**, 211.
- Watts, R. O., and McGee, I. J. (1976). 'Liquid State Chemical Physics' (Wiley-Interscience: New York).
- Whitehead, R. J., and Handy, N. C. (1975). *J. Mol. Spectrosc.* **55**, 336.
- Wilson, E. B., Decius, J. C., and Cross, P. C. (1955). 'Molecular Vibrations: The Theory of Infrared and Raman Vibrational Spectra' (McGraw-Hill: New York).