CALCULATION OF VIBRATIONAL LINE SHIFTS FOR MOLECULAR DIMERS*

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ABSTRACT

A method for calculating the shifts of vibrational excitation frequencies in molecular clusters is presented. It is based on second order non–degenerate perturbation theory and refers to early publications of Buckingham. The resulting formula involves off–diagonal cubic force constants thus accounting for coupling of the individual molecular normal modes. It is applied to the C–O stretching mode in methanol dimers and to all three modes in water dimers. The results are in good agreement with experimental values with exception of the ν_3–mode of the donor molecule in the water dimer where the perturbation approach was found to be not adequate.

INTRODUCTION

The study of vibrational frequency shifts in molecular spectra has been one of the most important tools in understanding the intermolecular forces in liquids. This is especially true for hydrogen–bonded molecules with O–H groups which play an important role in solvation problems [1]. The difficulty, however, is that the experimental data is often not sufficient to unravel details of the very complex processes occurring in liquids. To obtain more specific information the frequency shift of a special intramolecular motion of such a molecule is measured in various polar and non–polar solvents and solutions of proton donor and acceptor molecules [2–5]. In this way results were obtained demonstrating the cooperative effect of hydrogen bonding in alcoholic solutions [5] and the spectral line shift upon H–bonding by proton donor and acceptor molecules [3]. This procedure then allows one

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Dedicated to Professor W.A.P. Luck

to derive at least qualitative conclusions about the behavior of these molecules and the nature of the forces [4].

Recently spectroscopic information on special vibrational modes of small water and methanol clusters became available from which direct information on the intermolecular forces can be obtained. Here we would like to refer to measurements of the O—H stretching vibrations of water by infrared [6—8] and CARS spectroscopy [9]. Similar results have been obtained for the C—O stretching vibration of methanol which has been measured as a function of cluster size both for vibrationally cold [10] and warm [11,12] species by combining the IR predissociation technique with the generation of size selected neutral clusters in a scattering process [13,14]. Here we mainly focus on the calculation of the shift of this intramolecular frequency in methanol dimers, for which the experiments show an interesting splitting into two lines which are red— and blue—shifted compared to the gas phase monomer frequency. The understanding of these frequency shifts in terms of the intermolecular interaction will then enable us to compare the result with those obtained in liquids [3] and to improve the simulation of liquids.

There is a number of publications concerned with the calculation of vibrational line shifts in clusters. One possibility is to calculate an ab initio potential surface and to determine directly the cluster geometries and vibrational frequencies [15,16]. This is a very time consuming task, especially if the calculations are carried out beyond SCF level. Another method is to start from a well established empirical potential model and then combining variational methods to obtain the instantaneous intramolecular frequencies with a classical simulation to model the thermal averaging [17] or carrying out a quantum simulation serving both purposes at a time [18]. Our much simpler approach is in the spirit of ideas going back to Buckingham [19,20] who calculated line shifts of molecular vibrations in the presence of solvent molecules using second order perturbation theory. His method is easily applicable to molecular clusters and can be used to compare calculated with experimental spectra which appear in increasing number in the literature. In the next section we present the formula and discuss the necessary input information, the intramolecular force field and the empirical model potentials. The results for methanol and water dimers are given in the following sections and will be discussed in the last section.

A METHOD FOR CALCULATING VIBRATIONAL LINE SHIFTS

The Intramolecular Force Field

The most fundamental prerequisite for the numerical treatment of vibrational line shifts occurring upon cluster formation is the knowledge of the intramolecular force field governing the vibrational—rotational spectra of the isolated molecule. We follow the

treatment of Papoušek and Aliev [21] which in contrast to the classical work of Wilson, Decius, and Cross [22] also gives an exhaustive description of the effects of anharmonicity which plays an important role for the examples discussed below.

Definition of Internal Coordinates

The procedure for the quantitative description of vibrations of a molecule consisting of N atoms starts with the definition of internal coordinates. A favorable choice is the use of valence coordinates such as bond lengths and different kinds of valence angles. The 3N–6 coordinates (3N–5 for a linear molecule) can be written as a Taylor series in terms of the 3N cartesian components d_{ap} of the vectors of displacement from the equilibrium geometry

$$R_k = \sum_{a,p} B_{k,ap}\, d_{ap} + \frac{1}{2} \sum_{a,p} \sum_{b,q} B_{k,ap,bq}\, d_{ap}\, d_{bq} + \cdots , \tag{1}$$

where the indices a and b denote the different atoms, while the indices p and q stand for x,y,z. The tensor elements B_{kap} and B_{kapbq} can be evaluated by taking the 1st and 2nd derivatives of the (generally curvilinear) internal coordinates with respect to the d_{ap}. In harmonic force field calculations it is sufficient to cut off the expansion after the first term on the right–hand side of Eq. (1). The coefficients B_{kap} are identical to the first 3N–6 rows of the B–matrix encountered in the standard definition of (rectilinear) internal coordinates [22]. In this case the B–matrix is augmented by six rows giving the coefficients of the Eckart conditions [23].

For anharmonic problems where finite amplitudes are considered it is necessary to include also higher terms of Eq. (1) to account for the fact that the atoms are moving on curved paths during angular vibrations. Aside from yielding a simpler form for the potential energy (smaller off–diagonal terms), these coordinates are solely geometrically defined and do not depend on the atomic masses or on isotopic substitution. They can be related to the normal coordinates Q_r by a nonlinear transformation

$$R_k = \sum_r L_{k,r}\, Q_r + \frac{1}{2} \sum_r \sum_s L_{k,rs}\, Q_r\, Q_s + \cdots . \tag{2}$$

The coefficients L_{kr} are identical to the L–matrix obtained when solving the harmonic problem, which also yields the rectilinear normal coordinates Q_k. The second order tensor elements L_{krs} can be obtained from

$$L_{k,rs} = \sum_{a,p} \sum_{b,q} B_{k,ap,bq}\, m_a^{-1/2}\, m_b^{-1/2}\, \ell_{ap,r}\, \ell_{bq,s} , \tag{3}$$

where m is the atomic mass and ℓ is defined by the matrix product

$$\ell = M^{-1/2} B^T (L^{-1})^T \quad . \tag{4}$$

Although this method of calculating the L–tensor elements involves multiple summations and requires more storage, it is much easier to implement as a computer code than the more sophisticated method proposed by Hoy et al. [24], who give special formulae for certain kinds of internal coordinates. Although their formulae are quicker to evaluate, we decided not to use them, since, unlike in a fitting procedure, we had to calculate the tensor elements only once for each molecule.

The Potential Energy Function

The intramolecular potential energy V can be expanded in terms of the internal coordinates introduced above

$$V = \frac{1}{2} \sum_{ij} f_{ij} R_i R_j + \frac{1}{6} \sum_{ijk} f_{ijk} R_i R_j R_k + \dots \, , \tag{5}$$

where the force constants f_{ij}, f_{ijk} are defined in the usual manner as derivatives of V with respect to the internal coordinates R taken at the equilibrium geometry. This representation is often found in publications of ab initio force fields. For spectroscopic applications, however, it is conventional to express the force field in terms of normal coordinates

$$V = \frac{1}{2} \sum_i \lambda_i Q_i^2 + \frac{1}{6} \sum_{ijk} \Phi_{ijk} Q_i Q_j Q_k + \dots \, ,$$
$$\tag{6}$$

or more conveniently in units of wavenumbers (cm^{-1})

$$V/(hc) = \frac{1}{2} \sum_i \omega_i q_i^2 + \frac{1}{6} \sum_{ijk} \phi_{ijk} q_i q_j q_k + \dots \, , \tag{7}$$

in which q_i stands for dimensionless normal coordinates [21]

$$q_i := (2\pi c \omega_i / \hbar)^{1/2} Q_i \quad , \tag{8}$$

and where the harmonic frequencies ω_i and the cubic force constants ϕ_{ijk} are given in wavenumbers. This convention will be followed through the rest of the present paper.

Now it is desirable to find a transformation from the internal coordinate force constants f_{ij}, f_{ijk} to the normal mode coordinate force constants λ_i and Φ_{ijk}. This can be attained by substituting Eq. (2) into Eq. (5):

$$\lambda_r = \sum_{i\,j} f_{ij} L_{i,r} L_{j,r} \tag{9}$$

and

$$\Phi_{rst} = \sum_{i\,j\,k} f_{ijk} L_{i,r} L_{j,s} L_{k,t} + \sum_{i\,j} f_{ij} (L_{i,rs} L_{j,t} + L_{i,rt} L_{j,s} + L_{i,st} L_{j,r}) \tag{10}$$

One interesting property of this non-linear transformation has to be mentioned: The cubic constants Φ_{ijk} used in the lineshift formula put forward in the next chapter depend on both quadratic and cubic constants f_{ij} and f_{ijk}. Consequently, to obtain the normal coordinate force field up to 3rd order, L- and B-tensor elements up to 2nd order have to be evaluated.

The Buckingham Formula

Long before cluster spectroscopy became available, shifts of spectral lines due to the vibrational excitations of molecules soluted in liquids were observed. The first quantitative studies were published by Buckingham [19,20], who explained line shifts as well as changes of intensities and line shapes in terms of the interaction potential of solute and solvent molecules. He proposed to treat the interaction of a solute molecule with its environment as a perturbation acting on isolated molecules. As a reference Hamiltonian for the description of vibrations of the solute molecule the harmonic oscillator approximation is chosen

$$H_0/(hc) = \frac{1}{2} \sum_i \omega_i (p_i{}^2 + q_i{}^2) \quad , \tag{11}$$

where the summation extends over all 3N-6 normal modes of an N-atomic molecule and where q_i and p_i stand for the dimensionless normal coordinates defined in Eq. (8) and their conjugate moments, respectively. The perturbation H_a arising from the anharmonic terms of the intramolecular force fields (omitting higher than cubic terms) is taken from the second term on the right-hand side of Eq. (7). Similarly, the intermolecular potential ΔE is expanded in terms of intramolecular normal coordinates of the solute molecule

$$\Delta E = \Delta E_0 + \sum \frac{\partial(\Delta E)}{\partial q_i} q_i + \frac{1}{2} \sum \frac{\partial^2(\Delta E)}{\partial q_i \, \partial q_j} q_i \, q_j + \cdots . \tag{12}$$

Note that the derivatives of ΔE which is a function of both all intermolecular and all intramolecular coordinates, have to be calculated with keeping the intermolecular coordinates which describe the cluster configuration constant. In the following we denote them by primes: $\Delta E_i'$ and $\Delta E_{ij}''$.

To evaluate them one needs a parameterization of the intermolecular potential energy surface that also depends on the (intramolecular) normal coordinates. The conventional method for achieving that is the use of site–site–potentials. In this approach the total interaction of two molecules is taken as a sum of the interaction energies of all pairs of potential sites located on either molecule. By assigning potential sites to nuclei and/or binding electrons the anisotropy of a pair potential can be modeled without using complicated terms for the orientational dependence and, therefore, also large (biochemical) molecules can be modeled [25]. Another advantage is that the potential parameters for certain sites may be identical for different molecules thus allowing for the transferability of these parameters. An example for this is the methanol pair potential [26] used in the following section. The dependence of the pair interaction energy on the normal coordinates is then easily calculated by translating the potential sites. The cartesian components of these displacements can be obtained by inverting the linear parts of Eq. (1) and (2) adhering to the Eckart conditions [23] to keep the center of mass and the orientation of the molecule constant.

Then vibrational energy levels can be calculated using standard second order non–degenerate perturbation theory [27]: For the solute molecule we take $H_a + \Delta E - \Delta E_0$ as perturbation operator, for the isolated molecule we take H_a only. This is done for the ground state and the state in which only the i–th mode is excited to $n_i = 1$. Taking the appropriate differences, yields for the shift $\Delta \omega_i$ (in wavenumbers) of the corresponding spectral line

$$\Delta \omega_i = \frac{1}{2} \left[\; \Delta E_{ii}'' - \sum_{j=1}^{3N-6} \frac{\phi_{iij}}{\omega_j} \Delta E_j' \right] / (\mathrm{hc}) \; . \tag{13}$$

Note that here the spectral line shift is given in terms of dimensionless normal coordinates as suggested by Westlund et al. [28]. The first term on the right–hand side represents the change of the force constant of the ν_i–mode arising from the intermolecular forces. The negative of the first derivatives $\Delta E_j'$ occurring in the second term can be interpreted as generalized forces corresponding to the intramolecular normal coordinates which are induced by the intermolecular forces. The sign and the size of their contribution to the line shift is proportional to the cubic anharmonic force constant ϕ_{iij}. If the ϕ_{iij} is negative (as is usually the case for diagonal stretching force constants ϕ_{iii}) a positive force ($\Delta E_j' < 0$) causes a red shift because in this case the curvature of the ν_i–potential decreases with increasing value of

the ν_j—normal coordinate. The summation over j indicates that the lineshift of the i—th mode is coupled through the ϕ_{iij} to all other symmetry allowed normal modes. This coupling makes the interpretation more complex than for the case of diatomic molecules [19].

THE METHANOL DIMER

As a first test the Buckingham formula is applied to methanol dimers. Recently published spectra of mass—selected clusters (dimer to hexamer) in the region of the ν_8—band (1033.5 cm^{-1}, A'—symmetry) exhibit interesting structures for these hydrogen—bonded complexes [11]. The dimer spectra measured most precisely for cold clusters [10] are splitted into two lines, one shifted by 18.1 cm^{-1} to the blue, the other shifted by 7.0 cm^{-1} to the red with respect to the monomer absorption frequency. It is subject of this chapter to assign these two lines to the (hydrogen—)donor and acceptor and to compare them with the values calculated using two different intermolecular potential energy surfaces.

The intramolecular force field is taken from a publication of Schlegel et al. [29], who calculated a force field from ab initio SCF data using a standard 4—31G basis set. It includes the cubic force constants f_{iij} and some of the quartic force constants f_{iiii}. Although deviations to experimental frequencies are relatively large (48.5 cm^{-1} for the O—H stretching frequency, 12.5 cm^{-1} for the C—O stretch), it gives many anharmonic force constants which are not available from fits to experimental spectra. Furthermore, the absolute frequencies are not of big importance for the calculations of line shifts. The quadratic and cubic force terms of the force field were transformed non—linearly according to Eq. (9) and (10) to obtain normal coordinate force constants. To check the transformation, anharmonicity constants χ_{ii} are calculated [30] and compared to those published together with the force field [29].

Two different models of the intermolecular pair potential will be discussed: These are the OPLS—potential of Jorgensen [26] and the PHH—potential of Pálinkás et al. [31]. Both represent the potential energy surface by three sites on each molecule, one for the methyl group CH_3, one for the oxygen, and one for the hydroxyl hydrogen atom. Note that two other potentials, the empirical EPEN/2—model [25] and the quantum mechanical QPEN—model [32], are not considered because both involve potential sites for binding and lone pair electrons thus making it more difficult to describe the pair potential as a function of the intramolecular normal coordinates. The PHH—potential is constructed from a modified version [33] of the water potential of Stillinger and Rahman [34] and the methyl group potential of Jorgensen [35]. The OPLS—potential is fitted to experimental liquid data, describing the interaction of the molecules A and B by a Coulomb term for all pairs of sites plus a Lennard—Jones potential for the heavier sites

$$\Delta E_{AB} = \sum_{i \epsilon A} \sum_{j \epsilon B} \frac{1}{4\pi\epsilon_0} \cdot \frac{q_i q_j}{r_{ij}} + \frac{A_{ij}}{r_{ij}^{12}} - \frac{C_{ij}}{r_{ij}^6} , \qquad (14)$$

where r_{ij} stands for the distance between the sites i and j and where the standard combination rules $A_{ij} = (A_{ii}A_{jj})^{1/2}$ and $C_{ij} = (C_{ii}C_{jj})^{1/2}$ are used. The parameters A and C are related by $A_{ii} = 4\epsilon_i\sigma_i^{12}$ and $C_{ii} = 4\epsilon_i\sigma_i^6$ to the Lennard–Jones parameters ϵ and σ given in Table 1. The gas phase bond lengths and angle used here are 94.5 pm and 143.0 pm for the O–H and C–O bond length, respectively, and 108.5⁰ for the COH angle.

TABLE 1: Parameters of the OPLS–potential for methanol

site	q_i/e	σ_i/pm	$\epsilon_i/kJ \cdot mol^{-1}$
CH$_3$	+0.265	384	0.799
O	−0.7	307	0.711
H	+0.435	–	–

Dimer configurations are calculated by minimizing the binding energy using a downhill–simplex algorithm [36] while keeping the monomer units rigid in their equilibrium geometry. The structures obtained for the two potential models are very similar: The hydrogen bond O–H···O is linear with an O–O distance of 274 pm for the OPLS–model and 285 pm for the PHH–model. The typical dimer configuration is shown in Fig. 1. The binding energies ΔE_0, however, differ by about 20%: The well depths are −28.53 kJ/mol for OPLS and −23.44 kJ/mol for PHH. The difference is mainly caused by the different
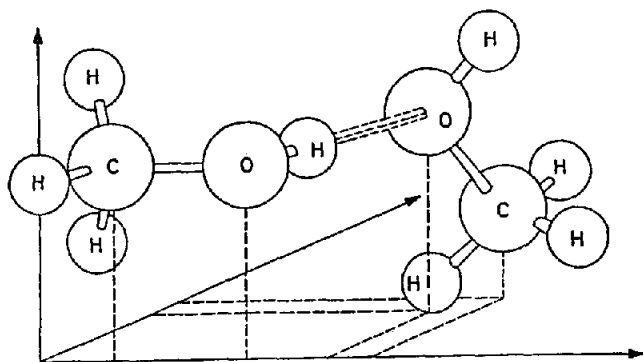

FIGURE 1: The methanol dimer

electrical charges assigned to the potential sites resulting in a different value for the (static) monomer dipole moment ($7.41 \cdot 10^{-30}$ Cm vs. $6.44 \cdot 10^{-30}$ Cm).

The shifts of the ν_8—excitation line calculated for these dimer configurations are shown in Table 2. The values obtained for both potentials differ only very little and are in good agreement with the experimental values. It is evident that the red shifted line corresponds to the acceptor, the blue shifted to the donor. In addition, the calculations are able to qualitatively reproduce the size of the shift: While the predicted red—shift of 4 cm^{-1} is 3 cm^{-1} smaller than the experimental one, the prediction for the blue shift is even better: The difference is 28% for the OPLS—potential and only 6% for the PHH—potential. Both results are surprisingly good if one takes into account how many different terms contribute to Buckingham's formula.

TABLE 2: Calculated binding energies[a] and line shifts[b] of the ν_8—mode using two different intermolecular potentials for the methanol dimer

	PHH	OPLS	experiment[c]
$\Delta E_0 / kJ \cdot mol^{-1}$	−23.44	−28.53	−
donor	+17.1	+23.1	+18.1
acceptor	−4.0	−4.1	−7.0

[a] The binding energies are calculated keeping the monomer units at their equilibrium geometry.

[b] line shifts are given in cm^{-1}

[c] Ref. [10]

In what follows we want to examine these contributions more in detail. For this analysis we chose the OPLS—potential because of its considerably simpler analytical form. Aside from the first term on the right—hand side of Eq. (13), proportional ΔE'', we have to consider those summands in the second term with large values of ϕ_{iij}. For the shift of the C—O stretching frequency (i=8) these are the cubic force constants ϕ_{881}, ϕ_{886}, ϕ_{887}, and ϕ_{888} amounting +253, +79, +130, and −279 cm^{-1}, respectively. They represent the anharmonic coupling of the C—O stretch to the O—H stretch (ϕ_{881}), the O—H bend (ϕ_{886}), and the CH$_3$—rock (ϕ_{887}), and the diagonal cubic force constant (ϕ_{888}) of the C—O stretch, itself. The individual contributions to the shift of the donor and the acceptor molecule are listed in Table 3. They are also split up into contributions from the three different potential terms in Eq. (14), that is the Coulomb term and the repulsive and attractive part of the Lennard—Jones potential.

The most striking fact when comparing the different columns of Table 3 is that the electrostatic forces dominate the line shift. The exchange and dispersion forces represented by the Lennard–Jones potential in Eq. (14) only play a role for the terms involving $\Delta E_8'$ and $\Delta E_8''$, while for the other terms they are almost negligible. On the one hand, this accounts for the preponderantly electrostatic character of the hydrogen–bond and, on the other hand, they might be due to the simple potential model omitting a Lennard–Jones potential for the O–H and the H–H interaction.

TABLE 3: Analysis of the main contributions[a] to the line shift of the ν_8–mode in the methanol dimer using the OPLS–potential

contribution	donor			acceptor		
	Coul.	Rep.	Attr.	Coul.	Rep.	Attr.
$+1/2 \cdot \Delta E_{88}''$	+8.2	+2.5	−0.5	+2.7	+3.5	−0.5
$-1/2 \cdot \phi_{888} \cdot \Delta E_8'/\omega_8$	−17.8	+4.2	+0.1	−24.8	+10.0	−2.0
$-1/2 \cdot \phi_{881} \cdot \Delta E_1'/\omega_1$	+18.0	+0.8	−0.2	+3.7	−0.5	+0.2
$-1/2 \cdot \phi_{886} \cdot \Delta E_6'/\omega_6$	+2.0	+0.8	−0.1	+2.8	−1.1	+0.3
$-1/2 \cdot \phi_{887} \cdot \Delta E_7'/\omega_7$	+4.3	+0.7	−0.1	+0.8	+0.9	+0.2
Sum	+14.9	+9.1	−0.9	−14.8	+12.4	−1.8

[a] all numbers are given in cm^{-1}

When comparing the rows of Table 3 corresponding to the different terms of Eq. (13) one finds that the contribution from the coupling of the ν_8–mode (C–O stretch) to the ν_1–mode (O–H stretch) is as important as the first two terms describing the dependence of the pair potential on the ν_8–coordinate itself while coupling to the ν_6– and ν_7–mode is found to be of less influence on the resulting line shifts.

Now the individual terms summed up in Eq. (13) will be discussed in more detail under special consideration of what causes the pronounced difference in the line shifts of the donor and the acceptor molecule. The first two contributions to the line shifts arising from the ν_8–potential itself can be explained most easily by regarding the methanol molecule to be like a diatomic consisting of the methyl group (CH$_3$) and the hydroxyl group (OH) with the ν_8–coordinate being the distance between them. The mutual attraction of the hydroxyl groups stretches both C–O oscillators which results in a red shift, because, for a negative cubic force constant ϕ_{888}, the local curvature of the C–O potential decreases with increasing C–O distance. These red shifts are similar for donor and acceptor yielding −13.5 cm^{-1} and

−16.8 cm⁻¹, respectively. It is interesting to investigate the contributions from different pairs of sites to these numbers. The repulsive O−O potential is overcome by the approximately twice as large attraction of the O−H potential which in the OPLS−potential is described by an electrostatic potential only.

Aside from changing the C−O bond lengths, the binding of the hydroxyl groups also makes the C−O potential steeper ($\Delta E_8''$) and thus causes a blue shift of 10.2 cm⁻¹ for the donor and 5.7 cm⁻¹ for the acceptor. To understand this discrepancy one has to visualize the ν_8−mode more closely. The C−O stretch is coupled to the COH bend with a relatively large amplitude. Accordingly, the ν_8−vibration of the donor is hindered more strictly than that of the acceptor molecule in which the hydrogen atom does not participate in the binding.

The third major contribution to the dimer line shifts is due to the coupling to the O−H stretching mode. We find that both in the donor and acceptor $\Delta E_1'$ is negative which leads to an increase of the O−H distance. Naturally, this effect is considerably more pronounced for the donor, where for the PHH−potential model the O−H bond length was found to be 2 % larger than in the gas phase monomer [31]. The remarkbly large value for the donor ($\Delta E_1' = -565$ cm⁻¹) is mostly caused by the strong H··O attraction ($\Delta E_1' = -964$ cm⁻¹) which is only partly compensated by the repulsion of the donor hydrogen by the methyl group and the hydrogen atom of the acceptor. The large positive force constant ϕ_{881} = 253 cm⁻¹ indicates that this elongation of the O−H bond makes the C−O oscillator more rigid thus resulting in blue shift of 18.6 cm⁻¹ for the donor and 3.4 cm⁻¹ for the acceptor. Hence it follows that mostly this coupling to the O−H stretch is reponsible for the total blue shift of the donor line.

When examining the contributions of the individual site−site potentials one disadvantage of the OPLS potential model is evident: The OH−interaction does not have a Lennard−Jones potential and, therefore, is purely electrostatic and strongly attractive. A further disadvantage is the omission of an induction term. This part of the potential is known to be the major contribution of the three−body interactions which has already been included in simulations of liquid water [37] and of SF₆−dimers [38].

THE WATER DIMER

As a further test the Buckingham formula is applied to the water dimer . This system has been subject to many experimental and theoretical studies. We use the semiempirical RWK2 model for the intermolecular pair potential by Reimers et al. [39], which has been fitted to a wide range of gas, liquid, and solid state properties. The potential energy surface is modeled by three sites located on the atoms of each molecule. An additional dummy charge is located on the bisector of the HOH angle in order to reproduce the electrostatic dipole and quadrupole moment of the water molecule. Aside from Coulomb terms for all pairs of sites there is a repulsive exponential term for the H−H interaction and a Morse

potential for the O—H interaction. The O—O repulsion is described by an exponential term, the attraction by individually damped dispersion terms proportional to R^{-6}, R^{-8}, and R^{-10}. The dimer structure (C_s—symmetry) is very similar to that of the methanol dimer, the hydrogene bond is almost linear with an O—O distance of 277 pm.

We chose the intramolecular force field of Hoy et al. [24]. It is fitted to harmonic frequencies, anharmonicity constants and vibration—rotation interaction constants and reproduces the experimental gas phase frequencies to within 0.5 %. The force constants (up to quartic) are already given in normal coordinates , so there was no need to carry out the non—linear transformation.

From these input data we calculate frequency shifts in the dimer for all three fundamentals. The results are presented in Table 4 where we compare them with results from infrared absorption spectra [7] and infrared predissociation spectra [8] in the region of the ν_1— and ν_3—mode (3500–3800 cm^{-1}) and to matrix isolation spectra of dimers trapped in Ar— and N$_2$—hosts [40] in the region of the ν_2—mode ($\approx$1600 cm^{-1}). With the exception of the ν_3—line of the donor molecule the trends of the experimental line shifts are qualitatively reproduced, but the agreement is less impressive than in the case of the methanol dimer. Note that except for the ν_3 donor mode the agreement with the experimental values is not so much different than for the considerably more sophisticated quantum simulation of Coker and Watts [18], who employed the same intermolecular potential model.

TABLE 4: Results for the water dimer[a]

Mol	Mode	this work	Qu—MC	Experiment
Don	ν_1 sym. str.	−143	−122	−125[c],−112[d]
Don	ν_2 bend	+33	+15	+16,+24[e]
Don	ν_3 asym. str.	−143	−35	−26[cd]
Acc	ν_1 sym. str.	−27	−47	−57[cd]
Acc	ν_2 bend	−2	−5	−2,+6[e]
Acc	ν_3 asym. str.	−24	−42	−34[c],−26[d]

a Line shifts are given in cm^{-1}, taken with respect to monomer frequencies of 3657, 1595, 3756 cm^{-1}

b Quantum—Monte Carlo simulation, Ref. [18]

c Ref [8]

d Ref [7]

e Ref [9]

DISCUSSION

Although the Buckingham formula given by Eq. (13) was originally developed for the simulation of solvent effects [19,20], it may be generally applied to shifts of vibrational lines of molecules weakly interacting with their environments. In the present paper we make use of this method for molecular clusters as has already been done for methyl cyanide tetramers [41]. Moreover, calculated lineshifts of small clusters are expected to be more sensitive to details of the potential energy surface than liquid spectra where both spatial and thermal averaging has to be accounted for. It has to be noted that the Buckingham formula is based on non–degenerate perturbation theory and hence is only formally correct for treating non–degenerate vibrational modes of a molecule embedded in an environment of different isotopes or molecules, while for homogeneous clusters or for (symmetric) molecules with degenerate normal modes degenerate perturbation theory should be applied. Examples for the use of degenerate perturbation theory can be found in several publications about the vibrational line shift of the triply degenerate ν_3–mode of sulfur hexafluoride . Eichenauer et al. [42] simulated the shift in SF_6–$(Ar)_n$ clusters, while van der Bladel and van der Avoird [38] calculated the shift in SF_6–dimers. In the latter case the spectra are dominated by the resonant dipole–dipole interaction which is not accounted for in the framework of of non–degenerate perturbation theory. We estimated the contribution of this effect for the methanol dimer. Using the experimental value for the ν_8–transition dipole moment of $0.807 \cdot 10^{-30}$ Cm [43] which is well reproduced by the OPLS potential we obtain a line shift of -2.1 cm^{-1}. This value is smaller than most of the other contributions to the line shift. Therefore, we conclude that the Buckingham formula is still a good approximation for the methanol dimer.

Furthermore, the methanol results are in remarkable agreement with the conclusions of Kabisch and Pollmer [3]. They measured the line shift of the CO–stretching mode of liquid methanol in various non–polar organic solvents ranging from CH_2Cl_2 to $(CH_3)_2CO$ and concluded that the frequency decreases upon H–bonding by the lone pairs, while it increases upon bonding by the hydroxyl proton. They also found that the latter shift is larger (13 cm^{-1}) than the former one (4 cm^{-1}). The present study of methanol dimers confirms these results and demonstrates that it is the direct interaction with the hydrogen bonded neighbours which causes the observed frequency shifts.

Limitations of the method can be deduced from the results for the water dimer where we are concerned with OH stretching frequencies. There the shifts are about one order of magnitude larger than those of the CO stretch in the methanol dimer. While in the acceptor molecule of the water dimer the structure of the normal modes is essentially left unchanged, it is known that in the dimer the coupling of the OH oscillators which for the free water molecule leads to the asymmetric and symmetric stretching modes breaks down because of the strong asymmetry of the hydrogen bond [15,17]. In that case the molecule is desribed more adequately in terms of a "free" and a "bridge" oscillator. In an ab initio study the

frequency of the first one was found to be almost unchanged for cluster sizes ranging from n=2 to 4, and resembling the monomer ν_3–frequency of the monomer, while the latter one shows a large red shift increasing with the cluster size [15]. This behaviour cannot be correctly reproduced by an approach based on perturbation theory because the intermolecular potential affects large changes of the overall forces acting on the H atom. This is the reason for the large discrepancy between our calculated ν_3 donor frequency and the experimental one. This failure is regarded to be typical for stretching frequencies of X—H bonds inside a hydrogen bond but for all other cases the assumption of the intermolecular forces being much smaller than the intramolecular ones is still valid and the Buckingham formula is claimed to be a useful tool for the calculation of vibrational frequency shifts in molecular clusters.

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