CALCULATIONS OF STRUCTURE AND IR FREQUENCY SHIFTS FOR SMALL H2O CLUSTERS

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Abstract
Calculated equilibrium structures and infrared spectra for water clusters composed of up to twenty molecules, using a quantum mechanical formalism based on second order perturbation theory, are reported. The frequency domain between 3000 and 4000cm-1, including the symmetric and asymmetric bond stretching modes and the first overtone of the angle bending mode, was investigated. The stretch modes are found to be redshifted, while the bending mode is blueshifted, the shift increasing with cluster size and showing a saturation tendency.

1. Introduction

Water is one of the most intensively studied substances, due to its special properties, many of them being related to the presence of hydrogen bonds. One of the most sensitive methods of probing the hydrogen bond network is vibrational spectroscopy. The spectral lines appear to be either redshifted (the stretch modes) or blueshifted (the bending mode) in comparison with those of the monomer. We have studied the frequency interval between 3000 and 4000 cm-1, comprising the symmetric and asymmetric stretch modes and the first overtone of the angle bending mode (all three modes being non-degenerate). There are only few experimental studies of water cluster spectra in this frequency range, among which the most accurate are those published by Buck et al. [0-0] and Huisken et al. [0]. Other experiments were carried out using less effective size-selection techniques. For example, Huang and Miller [0] have measured spectra only for the dimer, while Cocker et al. [0] have reported spectra for larger clusters, however with no size selection.

2. Theoretical methods

We have employed the minimal energy structures of the clusters calculated previously using a deterministic-stochastic method and two well known potential models(TIP4P [0] and TIP5P [0]) and we have calculated the infrared spectra using a quantum mechanics formalism based on second order perturbation theory [0,0].

This formalism 0,0,0 is based on the idea of treating the anharmonic contributions to the intramolecular force field and the intermolecular potential as perturbation of the molecular vibration, described in the normal mode approach. This formalism was successfully applied to several systems until now.00.

For a homogeneous cluster formed of n molecules, the first order frequency shifts $\Delta v_{mi}^{(1)}$ relative to a particular vibrational mode m of the monomer i have been shown to result from the eigenvalue problem

$$\sum_{m'\in\Gamma}\sum_{i'=1}^{n}\left(\frac{\partial^2 U}{2\partial q_{mi}\partial q_{m'i'}}-hc\Delta v_{mi}^{(1)}\delta_{mm'}\delta_{ii'}\right)c_{m'i',mi} \quad = \quad 0, \quad i=1,2,...,n.$$

(1)

The second order line shifts can be explicitly expressed as:

$$\Delta v_{mi}^{(2)} = \sum_{m',m''\in\Gamma}\sum_{i',i''}c_{m'i',mi}c_{m''i'',mi}^{*}\Delta v_{m'i',m''i''}^{(2)},$$

(2)

where the coefficients $c_{m'i',mi}$ are components of the eigenvectors yielded by the eigenvalue problem (1), and the partial contributions $\Delta v_{m'i',m''i''}^{(2)}$ are given by:

$$\Delta v_{m'i',m''i''}^{(2)} = -\frac{\delta_{i'i''}}{2hc}\sum_{r}\frac{1}{\omega_r}\frac{\partial U}{\partial q_{ri'}}\phi_{m'm''r}$$
$$+\frac{1}{4(hc)^2}\sum_{r\not\in\Gamma}\sum_{j}\frac{1}{\omega_m-\omega_r}\frac{\partial^2 U}{\partial q_{m'i'}\partial q_{rj}}\frac{\partial^2 U}{\partial q_{m''i''}\partial q_{rj}}$$
$$-\frac{1}{4(hc)^2}\sum_{r}\sum_{j}\frac{1}{\omega_m+\omega_r}\frac{\partial^2 U}{\partial q_{m'i'}\partial q_{rj}}\frac{\partial^2 U}{\partial q_{m''i''}\partial q_{rj}}.$$

(3)

Here ω_m and $\phi_{m'm''r}$ are harmonic frequencies and cubic force constants, respectively. The most significant second order contributions are generally due to the first term, coupling the generalized intermolecular forces $-\partial U/\partial q_{ri'}$ with the cubic intramolecular force constants $\phi_{m'm''r}$.

In the first step in our approach, the normal mode analysis of the water monomer is performed using the G-F method of Wilson 0. In the second step, the transformation of the intramolecular force field from valence to normal coordinates is accomplished by the L-tensor formalism of Hoy, Mills and Strey 0, yielding anharmonic monomer frequencies and transformed cubic force constants $\phi_{m'm''r}$.

The IR frequencies are obtained by adding the first and second order frequency shifts to the experimental monomer frequencies corresponding to each normal mode. The second

order frequency shifts couple the considered normal mode with the closest overtones, thus accounting also for the Fermi resonances. The line spectrum for a given cluster size was averaged over a Boltzmann ensemble of computed cluster configurations, averaged at 150K, consistent with experimental measurements.
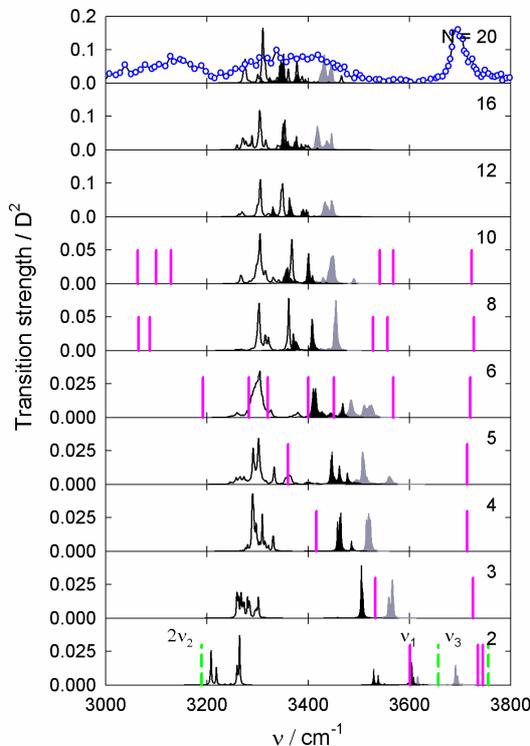
Figure 1. IR spectra for (H2O)n clusters. The dotted drop-lines in the lower panel represent the monomer frequencies, while the solid drop lines are the experimental frequencies of Huisken et al. 0 (up to the pentamer). The data for liquid water reported by Buck et al. 0 was depicted in the upper panel.

3. Results and discussion

The equilibrium structures of the water clusters ($n = 2-20$) have been determined by stochastic minimization of the total interaction energy, considering the clusters as being composed of rigid monomers. The methodology and results are presented in our previous paper.

We have carried out the frequency shift calculations using both potential models under consideration (TIP4P and TIP5P). In order to better describe the vibrational modes, we have used the atomic displacements provided by the normal-mode analysis of the monomer. For

38

the motion of the supplementary sites adopted a prescription according to which they move together with the oxygen atoms.

The TIP4P model renders more realistic values mainly because the supplementary site is positioned closer to the hydrogen atoms and the charges oscillate less, rendering more realistic variations of the dipole moment. The TIP5P model leads to an underestimation of the frequency shifts which can be accounted by the fact that in this model the charges are overspread. Also the TIP4P model is known to more accurately reproduce the dipole moment of water 0,0. However, for both potential models the frequency shifts show the same general tendencies, and further on only the results for TIP4P will be presented.

Figure 1 shows ensemble-averaged IR-spectra for the considered H_2O clusters obtained by applying the approach described above to the symmetric stretch mode ν_1, the asymmetric stretch mode ν_3, and the overtone $2\nu_2$ of the symmetric bending mode. While the two OH-stretch modes present a red shift that was expected, the overtone of the asymmetric bending vibration shows a pronounced blue shift. The shifts are due to the presence of the hydrogen bonds in the cluster.

The asymmetric stretch mode ν_3 exhibits the largest frequency shifts. This can be explained by the presence of hydrogen bonds that hinder the OH-stretch vibration. The symmetric stretch lines (ν_1) are the least intense, and are also less shifted that the asymmetric stretch lines. The lines corresponding to the bending mode overtone are the most intense of the spectra and also the least shifted, the bending mode being less perturbed by the presence of the other molecules in the cluster. The line shifts increase with cluster size, but for larger clusters the shifts tend to saturate, the spectrum appearing rather like a broad band than separate lines, in agreement with the liquid-state bands.

Our infrared spectra are compared with the experimental results for size-selected water clusters obtained by Huisken et al. ($n = 2 - 5$) 0 and Buck et al. ($n = 6 - 10$) 0-0. For clusters larger than the decamer there is no accurate size-selective study in literature. For the dimer and trimer our results are in good agreement with the experiments. For the tetramer and the pentamer the experimental lines assigned to the stretch modes are strongly redshifted to values that correspond rather to the bending mode overtone predicted by our calculations.

For the hexamer all our spectral lines have experimental counterparts. For larger clusters the results are not very reliable because they are at the limit of the size-selection technique and the measurement of cluster size is not very accurate.

4. Conclusions

We have computed infrared line shifts for water clusters formed of up to 20 molecules using two site-site intermolecular potentials(TIP4P and TIP5P).The best results were obtained for the TIP4P model, the TIP5P model rendering underestimated shifts, probably because the charges are overspread. The line shifts appear to increase with cluster size, tending to saturate for larger clusters. The largest shifts appear for the asymmetric stretch mode, while the bending mode overtone seems to be the least affected by the intermolecular force field.

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