

Cite this: *Phys. Chem. Chem. Phys.*, 2011, **13**, 7760–7772

www.rsc.org/pccp

PAPER

Methanol in its own gravy. A PCM study for simulation of vibrational spectra

Ferenc Billes,^{*ac} Ildikó Mohammed-Ziegler^b and Hans Mikosch^c

Received 23rd July 2010, Accepted 11th January 2011

DOI: 10.1039/c0cp01297a

For studying both hydrogen bond and dipole–dipole interactions between methanol molecules (self-association) the geometry of clusters of increasing numbers of methanol molecules ($n = 1,2,3$) were optimized and also their vibrational frequencies were calculated with quantum chemical methods. Beside these B3LYP/6-311G** calculations, PCM calculations were also done for all systems with PCM at the same quantum chemical method and basis set, for considering the effect of the liquid continuum on the cluster properties. Comparing the results, the measured and calculated infrared spectra are in good accordance.

1. Introduction

Methanol is a very simple molecule (see Fig. 1). Therefore it is an ideal model compound to study the self-association and the interaction of a solute molecule with its “own” solvent environment.

Several articles dealt with the description of the structure of liquid methanol. The bulk methanol was simulated by means of molecular dynamics, sometimes supported with *ab initio* calculations.

In this paper, however, an alternative way is used: DFT calculations completed with PCM modeling are presented. By observing the coupling of methanol molecules with a hydrogen bond, the intermolecular hydrogen bond effect is revealed, while the methanol continuum as the environment of these coupled molecules can exhibit other intermolecular effects.

As can be seen from the literature, the structural studies of methanol have always been in the center of scientific interest. For instance, a relatively simple, mixed quantum mechanical/molecular mechanical (QM/MM) model—using AMBER force field—was described for liquid methanol by Morrone and Tuckermann,¹ in which the hydroxyl constituents were treated at an *ab initio* level using density functional theory (DFT).

The potential energy surfaces of methanol clusters $\{(\text{CH}_3\text{OH})_n, n = 2-12\}$ were studied by Boyd and Boyd² using density functional theory at the B3LYP/6-31G(d) and higher levels of theory. Cyclic clusters in which n methanol

molecules are joined in a ring structure formed by n hydrogen bonds are shown to be more stable than structures of the same number of methanol molecules where one or more methanol molecules are outside the ring and are hydrogen-bonded to oxygens of methanols in rings of $n-1$, $n-2$, and so forth.

Different structural and dynamical properties were modeled by MD calculations. Matsumoto and Gubbins³ carried out molecular dynamics (MD) simulations in order to observe the dynamics of hydrogen bonding in liquid methanol. A similar

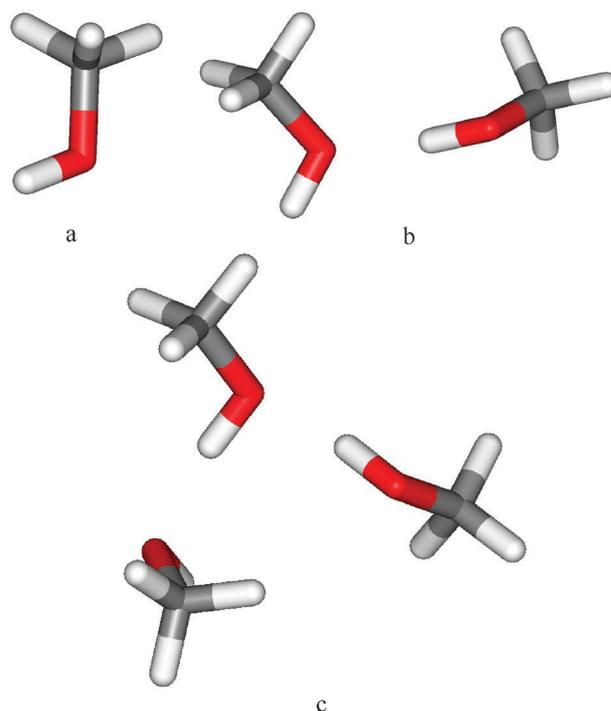


Fig. 1 Geometry of a methanol molecule and clusters consisting of two or three methanol molecules; a: monomer, b: dimer, c: trimer.

^a Department of Physical Chemistry and Material Science, Budapest University of Technology and Economics, H-1025 Budapest, Budafoki út 8, Hungary. E-mail: fbilles@mail.bme.hu

^b Validation Department, Gedeon Richter Plc. H-2510 Dorog, Esztergomi út 27, Hungary. E-mail: mohazihu@yahoo.com

^c Institute for Chemical Technologies and Analytics, Vienna University of Technology, A-1060 Vienna, Getreidemarkt 9, Austria. E-mail: hans.mikosch@tuwien.ac.at

study was aimed by Kosztolányi *et al.*⁴ when MD simulations were carried out. Pálkás *et al.*⁵ presented a new potential for the description of methanol–methanol interactions on the basis of a flexible three-site model, where the potential was derived from spectroscopic measurements. Then, a MD study was performed based on the new potential.

Four intermolecular potential models were used in the MD simulations of liquid methanol by Haughney,⁶ and several physico-chemical data were established on this basis. Bianchi *et al.*⁷ went further, MD simulations were carried out for liquid methanol using a six-site potential model. This potential model was originally derived using *ab initio* quantum chemical calculations. Zakharov *et al.*⁸ applied an OPLS potential model (by Jørgensen) for the MD simulation of methanol clusters. Sharma *et al.*⁹ described a canonical ensemble molecular dynamics simulations of liquid methanol, modeled using a rigid-body, pair-additive potential, those were used to compute static distributions and temporal correlations of tagged molecule potential.

The structure and topology of molecular clusters in liquid methanol were investigated by reverse Monte Carlo (RMC) simulation.¹⁰ Similarly, the thermodynamic and structural properties of methanol clusters were modeled by Monte Carlo simulations by Wright and El-Shall.¹¹

Moreover, a combination of MD and the quantum cluster equilibrium (QCE) model was applied for liquid methanol by Ludwig.¹² It was proved that liquid methanol is dominated by cyclic and/or lasso structures. A density functional theory (DFT) based MD study led to structural, dynamical and electronic properties of liquid methanol as reported by Handgraaf *et al.*¹³ This work was continued in the following paper,¹⁴ in which the dynamical, structural and electronic properties of liquid methanol were investigated by DFT method based on an MD study. The obtained data were compared to neutron diffraction measurement results.

Shilov *et al.*¹⁵ studied the long-range order in liquid methanol by Monte Carlo simulations, in NVT ensemble at 298 K using a cubic simulation box containing 500 molecules. In another paper,¹⁶ computer simulation results were used to compare the “discrete” and “continuum” methods for estimating dispersion contributions. Coordination number singularities caused by H-bonding were observed in liquid methanol. The formation of H-bonds in methanol was shown to “split” the first coordination sphere characteristic of simple liquids such as argon, into two spheres. As a consequence, the first and second coordination spheres of methanol gave comparable contributions to the dispersion component of intermolecular interaction energy. The primary liquid alcohols from ethanol to 1-hexanol were studied by Tomič *et al.*¹⁷ utilizing the configurational-bias Monte Carlo (MC) simulations of the modeled alcohols (transferable potential for phase equilibria-united atom model) and the small-angle X-ray scattering (SAXS) method. A novel approach for calculating the scattering intensities from the theoretically obtained MC data by utilizing the Debye equation and their further validation with experimental results were introduced.

As Zoranić *et al.*¹⁸ reported, the microstructure of neat methanol was successfully studied by MD simulations. The site–site radial distribution functions, the corresponding

structure factors, and an effective local one-body density function are shown to be appropriate statistical quantities to investigate the microstructure of any given liquid. The thermodynamic and structural properties of different models of liquid methanol were investigated by Costa *et al.*¹⁹ in the framework of reference interaction site model (RISM) theory of molecular fluids. These results were compared with MD results and Monte Carlo data with a special focus on hydrogen bonds.

Tsuchida *et al.*²⁰ also studied the properties of liquid methanol as well as of a single molecule by a combination of gradient-corrected density-functional theory, norm-conserving pseudopotentials, and the finite-element basis set. The structural and dynamical quantities were calculated through molecular dynamics simulations, and were compared with experiments, just to mention a few important results in this field.

A Carr-Parrinello MD simulation was performed by Pagliai *et al.*²¹ in order to observe the structure of fully deuterated liquid methanol. It was shown that the liquid is aggregated in the chains of hydrogen-bonded molecules.

A recent paper of Perchard *et al.*²² presented the spectral analysis of five isotopic species of methanol in the range of 11 000 cm⁻¹ and 200 cm⁻¹, complemented with their Raman spectra as well. The hydrogen bonding of supercooled methanol was analyzed by Palomar and Sesé,²³ thus the thermodynamic, structural, and dynamical properties could be observed. The influence of an electric field on methanol was simulated by MD calculations by Sun *et al.*²⁴ with the use of a three-site potential model.

The effects of different thermodynamic parameters on the Raman spectra were also observed. For instance, Pogorelov *et al.*²⁵ analyzed the temperature dependence of the Raman bandwidths for methanol and ethanol. Moreover, Torii²⁶ examined the pressure dependence of the liquid structure and the Raman noncoincidence effect of liquid methanol with the combination of molecular dynamics (MD) simulations and the intermolecular resonant vibrational interactions determined by the transition dipole coupling (TDC) mechanism (MD/TDC method).

Methanol diluted with different solvents was also extensively studied. In the paper by Takano and Houk,²⁷ the conductor-like polarizable continuum model (CPCM) was used to compute aqueous solvation free energy for a number of small molecules also including methanol. Dilute clusters of methanol and water were in the center of interest as Ruckenstein *et al.*²⁸ reported, and *ab initio* quantum mechanical methods were used to examine the clusters. Piletic *et al.*²⁹ applied frequency resolved pump–probe experiments to observe deuterated and normal methanol in tetrachloride solution of different concentrations.

Klein *et al.*³⁰ performed *ab initio* calculations for the ¹⁷O NMR-chemical shifts of water clusters using density functional theory (DFT) in which both water size and cooperative hydrogen bonding were taken into account. It was also shown that polarizable continuum models (PCM) using a self-consistent reaction field (SCRFF) failed to predict adequately ¹⁷O-chemical shifts in condensed phase.

Larsen *et al.*³¹ calculated the IR and Raman frequencies of several trimers and tetramers of methanol and its isotopomers,

CH₃OD, CD₃OH, and CD₃OD B3LYP and MP2 methods, using different basis sets. They compared the experimental OH stretch frequencies with the calculated ones.

Mó *et al.*³² dealt with the characteristics of a monomer, dimer and trimer of methanol. They calculated using the MP2 and B3LYP methods the bond characteristics and

Table 1 Optimized molecular parameters of the studied systems^{a,b}

| Parameter ^c | ma | mb | mma | mmb | mma | mmbb |
|------------------------|-------|-------|--------|--------|--------|--------|
| r (1,2) | 1.099 | 1.098 | 1.096 | 1.096 | 1.093 | 1.094 |
| r (1,3) | 1.099 | 1.098 | 1.096 | 1.095 | 1.095 | 1.094 |
| r (1,4) | 1.091 | 1.092 | 1.089 | 1.091 | 1.090 | 1.091 |
| r (1,5) | 1.421 | 1.424 | 1.430 | 1.430 | 1.441 | 1.439 |
| r (5,6) | 0.961 | 0.974 | 0.961 | 0.976 | 0.963 | 0.978 |
| r (5,12) | | | 1.879 | 1.794 | 1.821 | 1.771 |
| r (7,8) | | | 1.100 | 1.099 | 1.097 | 1.096 |
| r (7,9) | | | 1.099 | 1.099 | 1.097 | 1.097 |
| r (7,10) | | | 1.092 | 1.093 | 1.091 | 1.091 |
| r (7,11) | | | 1.416 | 1.420 | 1.422 | 1.427 |
| r (11,12) | | | 0.969 | 0.975 | 0.976 | 0.981 |
| r (11,18) | | | | | 1.837 | 1.810 |
| r (13,14) | | | | | 1.099 | 1.098 |
| r (13,15) | | | | | 1.100 | 1.099 |
| r (13,16) | | | | | 1.092 | 1.093 |
| r (13,17) | | | | | 1.416 | 1.421 |
| r (17,18) | | | | | 0.974 | 0.977 |
| φ (2,1,3) | 108.6 | 108.5 | 109.4 | 109.1 | 110.7 | 110.0 |
| φ (2,1,4) | 108.0 | 108.2 | 108.5 | 108.6 | 109.2 | 108.9 |
| φ (2,1,5) | 112.6 | 112.4 | 112.0 | 111.9 | 111.2 | 111.3 |
| φ (3,1,4) | 108.0 | 108.2 | 109.3 | 108.8 | 108.4 | 108.6 |
| φ (3,1,5) | 112.6 | 112.4 | 111.6 | 111.4 | 110.8 | 111.1 |
| φ (4,1,5) | 106.9 | 107.1 | 106.1 | 106.8 | 106.4 | 106.7 |
| φ (1,5,6) | 107.8 | 108.6 | 109.2 | 110.1 | 107.9 | 109.4 |
| φ (1,5,12) | | | 104.9 | 114.5 | 107.3 | 105.9 |
| φ (6,5,12) | | | 133.6 | 121.5 | 105.4 | 107.7 |
| φ (8,7,9) | | | 108.0 | 108.0 | 108.6 | 108.7 |
| φ (8,7,10) | | | 107.8 | 107.9 | 108.2 | 108.4 |
| φ (8,7,11) | | | 112.6 | 112.5 | 111.6 | 111.3 |
| φ (9,7,10) | | | 108.0 | 107.9 | 108.3 | 108.5 |
| φ (9,7,11) | | | 112.7 | 112.4 | 112.3 | 112.1 |
| φ (10,7,11) | | | 107.6 | 107.9 | 107.6 | 107.7 |
| φ (7,11,12) | | | 107.6 | 107.2 | 109.2 | 108.7 |
| φ (7,11,18) | | | | | 126.0 | 121.0 |
| φ (12,11,18) | | | | | 98.5 | 100.8 |
| φ (5,12,11) | | | 157.5 | 172.7 | 165.4 | 169.0 |
| φ (14,13,15) | | | | | 107.9 | 108.2 |
| φ (14,13,16) | | | | | 107.9 | 108.0 |
| φ (14,13,17) | | | | | 112.4 | 112.2 |
| φ (15,13,16) | | | | | 108.0 | 108.0 |
| φ (15,13,17) | | | | | 112.7 | 112.4 |
| φ (16,13,17) | | | | | 107.8 | 107.9 |
| φ (13,17,18) | | | | | 107.8 | 107.3 |
| φ (11,18,17) | | | | | 164.4 | 171.2 |
| θ (2,1,5,6) | 61.6 | 61.4 | 53.1 | 55.7 | 65.1 | 73.4 |
| θ (2,1,5,12) | | | -95.0 | -85.4 | -48.1 | -42.4 |
| θ (3,1,5,6) | -61.6 | -61.4 | -69.9 | -66.8 | -58.5 | -49.6 |
| θ (3,1,5,12) | | | 142.0 | 152.0 | -171.7 | -165.3 |
| θ (4,1,5,6) | 180.0 | 180.0 | 171.2 | 174.5 | -176.2 | -167.8 |
| θ (4,1,5,12) | | | 23.1 | 33.4 | 70.7 | 76.4 |
| θ (1,5,12,11) | | | -31.6 | -51.0 | 37.4 | 32.7 |
| θ (6,5,12,11) | | | -168.0 | 172.7 | -77.3 | -84.3 |
| θ (8,7,11,12) | | | -64.0 | -60.7 | -61.2 | -61.5 |
| θ (8,7,11,18) | | | | | -177.6 | -177.2 |
| θ (9,7,11,12) | | | 58.4 | 61.5 | 61.1 | 60.5 |
| θ (9,7,11,18) | | | | | -55.4 | -55.2 |
| θ (10,7,11,12) | | | 177.3 | -179.6 | -179.8 | 179.8 |
| θ (10,7,11,18) | | | | | 63.8 | 64.1 |
| θ (7,11,12,5) | | | -90.4 | -56.8 | -133.5 | -125.1 |
| θ (18,11,12,5) | | | | | -0.5 | 3.1 |
| θ (7,11,18,17) | | | | | 145.6 | 138.4 |
| θ (12,11,18,17) | | | | | 24.3 | 18.8 |
| θ (14,13,17,18) | | | | | 61.8 | 60.3 |
| θ (15,13,17,18) | | | | | -60.4 | -61.9 |

Table 1 (continued)

(a) Optimized geometric parameters; a comparison with results of other authors; DFT B3LYP

| Basis set | <i>r</i> (C–O) ^d | <i>r</i> (O–H) ^d | <i>r</i> (O...H) ^d | Trimer type | Reference |
|----------------|-----------------------------|-----------------------------|-------------------------------|------------------------------|-----------|
| 6-31G | 1.449 | 1.002 | 1.721 | triangle (udu [−]) | ref. 2 |
| | 1.447 | 1.002 | 1.736 | triangle (udu [−]) | ref. 2 |
| | 1.447 | 1.002 | 1.767 | triangle (udu [−]) | ref. 2 |
| 6-31 + G(d,p) | 1.425 | 0.98 | 1.873 | triangle (udu [−]) | ref. 2 |
| | 1.424 | 0.901 | 1.986 | triangle (udu [−]) | ref. 2 |
| | 1.424 | 0.979 | 1.876 | triangle (udu [−]) | ref. 2 |
| 6-311 + G(d,p) | 1.419 | 0.968 | 1.948 | “Y” like (No. 3) | ref. 32 |
| | 1.438 | 0.967 | 1.993 | “Y” like (No. 3) | ref. 32 |
| 6-311G** | 1.441 | 0.963 | 1.821 | see Fig. 2 | this work |
| | 1.422 | 0.976 | 1.837 | see Fig. 2 | this work |
| | 1.416 | 0.974 | — | see Fig. 2 | this work |

^a The number of the letters “m” indicates the number of molecules in the clusters. “a” stands for the isolated cluster. “b” for the cluster in continuum. ^b Distances in angstroms, angles in degrees. ^c r: bonds or interatomic distances. ϕ : valence angles. θ : dihedral angles; for numbering of the atoms see Fig. 2.; parameters in italics contain hydrogen bond. ^d Distances in angstroms.

most important geometric parameters of several dimer and trimer forms. They gave an approximate assignment of the vibrational frequencies.

In this work we applied a new concept exploiting the possibilities of quantum chemistry. In our model the intermolecular interactions were separated into intermolecular interactions and solvent continuum interactions. Two cluster series were built. One was discussed for the molecule–molecule interactions, the other for the separated cluster–solvent continuum ones.

During the stepwise building of the cluster three types of methanol molecules were observed, the isolated, a dimer with one hydrogen bond, and a trimer with common interaction. The building of the second cluster series makes possible the observation of the solvent effect on the aforementioned structures. The concept of our calculation series is suitable for the clear separation of the two effects.

2. Calculations

The Gaussian03 program package³³ was applied for quantum chemical calculations. The DFT Becke3LYP functional³⁴ was used with the 6-311G** basis set. The molecular geometries were optimized, Mulliken’s atomic net charges³⁵ and NBO natural charges³⁶ were computed. The second derivative of the molecular energy function to the Cartesian coordinates gave the vibrational force constants and the vibrational frequencies, infrared and Raman intensities and depolarization ratios.

The PCM model³⁷ was used in our calculations for representing the effects of the liquid continuum.

Internal coordinates were defined. Normal coordinate analysis was carried out. Arbitrary consistent scale factors of 0.95 were used for force constant scaling. This corresponds to a frequency scaling by $\sqrt{0.95} \approx 0.9747$. The potential energy distributions were also calculated. Home made programs were applied for these calculations.

Our model systems were the single methanol molecules, a cluster of two, and another one of three methanol molecules. Quantum chemical calculations were performed for these isolated systems and also for the same in methanol continuum.

The PCM calculations of the larger clusters yielded one imaginary frequency, the lowest. It was assumed that these results are close to the results for the stationary points, and hence these results were applied for assigning the vibrational modes in solution.

3. Results and discussion

Our main interest is the study of the effect of cluster structure and the continuum around the clusters on the vibrational spectra of methanol. Therefore the construction of a two- or three-member cluster model system was our first step. One molecule is appropriate to study the properties of the isolated molecules and the effect of the liquid continuum on it. With the second cluster molecule the hydrogen bond appears and thus it is possible to investigate both the hydrogen bond and the solvent effects. The insertion of the third methanol molecule produces a molecule with two hydrogen bondings. These are the simplest possibilities for the methanol–methanol interaction and at the same time one can also consider the solvent effect.

3.1 Optimized molecular geometry

Several geometric parameters are sensitive to the increase of the cluster, some others exhibit significant changes in the presence of the methanol continuum, and there exist also parameters which are sensitive to both effects. Table 1 presents the optimized parameters.

By using the parameters of the first molecule (atom 1 to 6, see Fig. 1 and 2), the C1–O5 distance is found sensitive to the size of the cluster, while the O5–H6 bond is affected by the methanol continuum.

The appearance of the second methanol molecule of the cluster enables the formation of a hydrogen bond between the C5 and H12 atoms. Both the extending of the cluster (the third molecule) and the liquid methanol environment reduce substantially this distance, however, the second one is the stronger effect. The angles O5–H6–O12 and O5–H12–O11 are also sensitive to both effects, like also the H6–O5–H12–O11 or the C7–O11–H12–O5 dihedral angles.

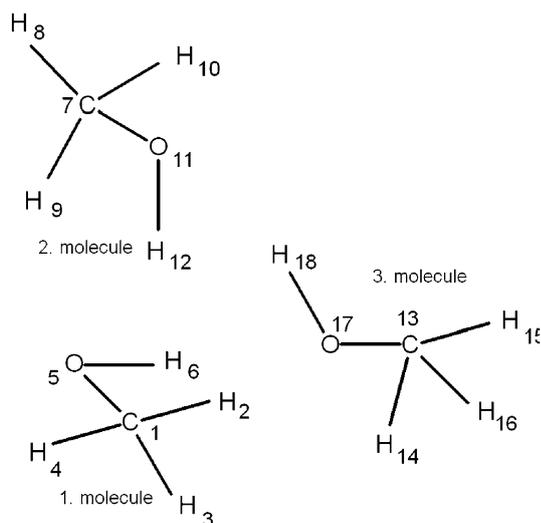


Fig. 2 Numbering of the cluster consisting of three methanol molecules.

The formed hydrogen bond has also a smaller effect on the structure of the second molecule (atoms 7 to 12) in comparison to the isolated molecule (atoms 1 to 6), comparing the C1–O5 and C7–O11, the O5–H6 and O11–H12 distances.

The further enlargement of the cluster with a third methanol molecule ensures the possibility of the formation of a second hydrogen bond. The O11–H18 bond is a little longer than the O5–H12 one. The liquid continuum has a weaker influence on the second one, than on the first one. Similarly, the building of the second hydrogen bond caused fewer changes in its environment than the first one. One can understand that the second hydrogen bond acts weaker on the first molecule than the second one. However, it is interesting that the solvent effect of the O11–H18 distance is less than that of the first hydrogen bond, O5–H12.

Table 1(a) is a supplement to Table 1. Here we compared literature data with our own results. The problem of the comparison is double. On the one hand the found trimer

forms differ from ours, on the other hand the applied DFT B3LYP basis set is also different from that applied in the literature. It is evident from the table that the intramolecular distances in the methanol molecules depend strongly on the chosen basis set. Moreover, the length of intermolecular O...H distances depends on the optimized structure. Additionally, their number depends also on the configuration of the model structure.

Summarizing, the effects of the hydrogen bonds and the solvent are essential for the structure of the cluster.

3.2 Atomic net charges

The calculated NBO natural charges are shown in Table 2.

The charges on the movable hydrogens (H6, H12, H18) became more positive both under the effect of molecular interactions and solvent effect. The behavior of the methyl hydrogens depends very strongly on their relative positions in the cluster. The charge of H2 is extremely high in the isolated trimolecular cluster (0.1883 a.ch.u.) but decreased to a relatively “usual” value under the solvent effect (0.1691 a.ch.u.) One can explain this phenomenon with the relatively short H2–O17 distance (2.431 Å). This distance increased under the solvent effect to 2.625 Å.

The solvent effect made C7 and C13 charges more negative. However, the C1 atom shows an opposite behavior in the trimolecular cluster.

The O11 and O17 atoms became more positive as results of both effects. However, the charge of the atom O5 did not change with addition of the third methanol molecule.

The Mulliken atomic net charges are listed in Table 3.

Although the values of the charges are different here, the tendencies of the charges are close to the NBO ones.

The charges of the movable hydrogen atoms became more and more positive, both effects act in the same direction. The charges of the methyl hydrogens depend on their relative positions, and the mentioned anomalous behavior of H2 is also reflected here. All the carbon atom charges cause similar shifts

Table 2 Calculated natural (NBO) atomic charges^{a,b}

| Ser. numb. | Atom type | ma | mb | mma | mmb | mma | mmmb |
|------------|-----------|---------|---------|---------|---------|---------|---------|
| 1 | C | -0.1856 | -0.1874 | -0.1894 | -0.1860 | -0.2010 | -0.1977 |
| 2 | H | 0.1443 | 0.1497 | 0.1540 | 0.1592 | 0.1883 | 0.1691 |
| 3 | H | 0.1443 | 0.1497 | 0.1526 | 0.1592 | 0.1540 | 0.1639 |
| 4 | H | 0.1684 | 0.1653 | 0.1834 | 0.1711 | 0.1700 | 0.1713 |
| 5 | O | -0.7117 | -0.7570 | -0.7426 | -0.7732 | -0.7439 | -0.7733 |
| 6 | H | 0.4403 | 0.4796 | 0.4582 | 0.5016 | 0.4584 | 0.5020 |
| 7 | C | | | -0.1831 | -0.1890 | -0.1821 | -0.1891 |
| 8 | H | | | 0.1391 | 0.1451 | 0.1508 | 0.1564 |
| 9 | H | | | 0.1399 | 0.1451 | 0.1482 | 0.1541 |
| 10 | H | | | 0.1606 | 0.1611 | 0.1669 | 0.1695 |
| 11 | O | | | -0.7451 | -0.7750 | -0.7727 | -0.7859 |
| 12 | H | | | 0.4724 | 0.4807 | 0.4858 | 0.4898 |
| 13 | C | | | | | -0.1810 | -0.1880 |
| 14 | H | | | | | 0.1435 | 0.1470 |
| 15 | H | | | | | 0.1370 | 0.1452 |
| 16 | H | | | | | 0.1597 | 0.1626 |
| 17 | O | | | | | -0.7614 | -0.7789 |
| 18 | H | | | | | 0.4796 | 0.4819 |

^a Atomic charge units. ^b The number of the letters “m” indicates the number of molecules in the clusters. “a” stands for the isolated cluster. “b” for the cluster in continuum.

Table 3 Calculated Mulliken atomic net charges^{a,b}

| Ser. numb. | Atom type | ma | mb | mma | mmb | mma | mmmb |
|------------|-----------|---------|---------|---------|---------|---------|---------|
| 1 | C | -0.1160 | -0.1157 | -0.1233 | -0.1160 | -0.1481 | -0.1406 |
| 2 | H | 0.0880 | 0.0965 | 0.1014 | 0.1108 | 0.1312 | 0.1048 |
| 3 | H | 0.0880 | 0.0965 | 0.1022 | 0.1118 | 0.1037 | 0.1183 |
| 4 | H | 0.1104 | 0.1070 | 0.1261 | 0.1164 | 0.1162 | 0.1211 |
| 5 | O | -0.4059 | -0.4752 | -0.4306 | -0.4788 | -0.4426 | -0.4863 |
| 6 | H | 0.2356 | 0.2908 | 0.2541 | 0.3157 | 0.2627 | 0.3208 |
| 7 | C | | | -0.1076 | -0.1176 | -0.1100 | -0.1238 |
| 8 | H | | | 0.0804 | 0.0875 | 0.0987 | 0.1087 |
| 9 | H | | | 0.0763 | 0.0870 | 0.0913 | 0.1019 |
| 10 | H | | | 0.0977 | 0.0994 | 0.1099 | 0.1154 |
| 11 | O | | | -0.4302 | -0.4835 | -0.4628 | -0.4859 |
| 12 | H | | | 0.2534 | 0.2673 | 0.2731 | 0.2826 |
| 13 | C | | | | | -0.1064 | -0.1208 |
| 14 | H | | | | | 0.0865 | 0.0939 |
| 15 | H | | | | | 0.0707 | 0.0868 |
| 16 | H | | | | | 0.0976 | 0.1023 |
| 17 | O | | | | | -0.4344 | -0.4673 |
| 18 | H | | | | | 0.2626 | 0.2681 |

^a Atomic charge units. ^b The number of the letters “m” indicates the number of molecules in the clusters. “a” stands for the isolated cluster. “b” for the cluster in continuum.

like in the NBO calculations. All oxygen atoms (even O5) show negative charge shifts under both the internal and the external effects.

3.3 Cluster energies

For cluster energy calculations, the clusters of one, two and three coupled methanol molecules are labeled by ma, mma and mmma, respectively. The same clusters in methanol solution are denoted by mb, mmb and mmmb, respectively.

The calculated molecular energies of the aforementioned clusters are listed in Table 4. Comparing the molecular energies of the clusters and the corresponding multiple of molecular energy of the isolated molecule (ma), the stabilization energies of the clusters are obtained. For the isolated clusters these energy differences give the building energy of the

solution. These energies were listed referring to one molecule of methanol.

Regarding the clusters in methanol solution their energies may refer to different bases. If their energies are compared with the molecular energy of the corresponding multiple to that of the isolated methanol molecule (*e.g.* mmb-2*ma) the total stabilization energy is received. Choosing the single methanol molecule in solution (*e.g.* mmb-2*mb) as basis, one has again calculated the building energies in methanol environment.

The differences between the molecular energies of the cluster in solution and that of an isolated one (*e.g.* mmb-mma) give the solution enthalpy.

All resulted energies are listed referring to one methanol molecule (last column in Table 4). All calculated energies increase (in absolute value) with the size of the cluster. On the contrary, the solvent effect energies corresponding to

Table 4 Methanol cluster energies and their energy differences^a

| Cluster | | Energy | | | Energies pro molecule/ kJ mol ⁻¹ |
|-------------------|------------------------------|-----------|---------------------|----------------------|--|
| Type ^b | Energy /MJ mol ⁻¹ | Type | Effect | kJ mol ⁻¹ | |
| ma | -303.9212 | | | | |
| mb | -303.9440 | mb-ma | Solvent effect | -22.8395 | -22.8395 |
| 2*ma | -607.8424 | | | | |
| 2*mb | -607.8880 | | | | |
| mma | -607.8747 | mma-2*ma | Building of cluster | -32.2795 | -16.1397 |
| mmb | -607.9078 | mmb-mma | Solvent effect | -33.1065 | -16.5533 |
| | | mmb-2*mb | Building of cluster | -19.7060 | -9.8530 |
| | | mmb-2*ma | Total stabilization | -65.3860 | -32.6930 |
| 3*ma | -911.7636 | | | | |
| 3*mb | -911.8320 | | | | |
| mma | -911.8427 | mma-3*ma | Building of cluster | -79.1625 | -26.3875 |
| mmmb | -911.8765 | mmmb-mma | Solvent effect | -33.7296 | -11.2432 |
| | | mmmb-3*mb | Building of cluster | -44.3720 | -14.7907 |
| | | mmmb-3*ma | Total stabilization | -112.8921 | -37.6307 |

^a 1 hartree corresponds to 2625.501 kJ mol⁻¹. ^b The number of letters “m” indicates the size of the cluster. “a” refers to isolated cluster. “b” to cluster in solvent.

one molecule decrease with increasing the size of the cluster. As result of these two effects, the total stabilization energies referring to one methanol molecule increase with the cluster size.

3.4 Vibrational force constants

The calculated vibrational force constants were scaled consistently with a factor of 0.95 for shifting the calculated frequencies into the region of real values.

Table 5 Definition of internal coordinates and diagonal vibrational force constants

| Ser. numb. | Internal coordinate Definition ^d | Diagonal force constants ^{a,b,c} | | | | | |
|------------|--|---|-------|-------|-------|-------|-------|
| | | ma | mb | mma | mmb | mma | mmb |
| 1 | r (1,2) | 4.716 | 4.729 | 4.830 | 4.825 | 4.930 | 4.880 |
| 2 | r (1,3) | 4.716 | 4.729 | 4.825 | 4.832 | 4.869 | 4.900 |
| 3 | r (1,4) | 5.024 | 4.982 | 5.103 | 5.035 | 5.064 | 5.023 |
| 4 | r (1,5) | 5.135 | 5.003 | 4.996 | 4.932 | 4.801 | 4.790 |
| 5 | r (5,6) | 7.834 | 6.691 | 7.869 | 6.579 | 7.797 | 6.491 |
| 6 | φ (2,3,1) | 1.546 | 1.521 | 1.597 | 1.531 | 1.637 | 1.591 |
| 7 | φ (2,4,1) | 1.286 | 1.278 | 1.363 | 1.323 | 1.382 | 1.352 |
| 8 | φ (3,4,1) | 1.286 | 1.278 | 1.337 | 1.309 | 1.412 | 1.383 |
| 9 | φ (2,5,1) | 1.788 | 1.766 | 1.785 | 1.754 | 1.857 | 1.813 |
| 10 | φ (3,5,1) | 1.788 | 1.766 | 1.797 | 1.750 | 1.823 | 1.798 |
| 11 | φ (1,6,5) | 0.760 | 0.800 | 0.753 | 0.782 | 0.838 | 0.829 |
| 12 | τ (4,1,5,6) | 0.037 | 0.036 | 0.061 | 0.042 | 0.105 | 0.088 |
| 13 | r (12,5) | | | 0.237 | 0.283 | 0.314 | 0.314 |
| 14 | φ (12,1,5) | | | 0.157 | 0.082 | 0.328 | 0.282 |
| 15 | τ (12,5,1,2) | | | 0.030 | 0.012 | 0.097 | 0.074 |
| 16 | r (11,12) | | | 7.493 | 7.143 | 7.160 | 6.898 |
| 17 | φ (11,5,12) | | | 0.071 | 0.074 | 0.390 | 0.154 |
| 18 | τ (11,12,5,6) | | | 0.026 | 0.004 | 0.097 | 0.056 |
| 19 | r (7,11) | | | 5.220 | 5.097 | 5.119 | 4.922 |
| 20 | φ (7,12,11) | | | 0.733 | 0.728 | 0.899 | 0.373 |
| 21 | τ (7,11,12,5) | | | 0.024 | 0.005 | 0.102 | 0.076 |
| 22 | r (8,7) | | | 4.668 | 4.692 | 4.793 | 4.807 |
| 23 | φ (8,11,7) | | | 1.069 | 1.063 | 1.065 | 1.058 |
| 24 | τ (8,7,11,12) | | | 0.713 | 0.706 | 0.983 | 0.896 |
| 25 | r (9,7) | | | 4.686 | 4.697 | 4.762 | 4.782 |
| 26 | φ (9,11,7) | | | 1.078 | 1.072 | 1.073 | 1.068 |
| 27 | τ (9,7,11,12) | | | 0.710 | 0.709 | 0.718 | 0.714 |
| 28 | r (10,7) | | | 4.966 | 4.939 | 5.017 | 5.001 |
| 29 | φ (10,11,7) | | | 1.079 | 1.075 | 1.073 | 1.066 |
| 30 | τ (10,7,11,12) | | | 0.747 | 0.738 | 0.747 | 0.739 |
| 31 | r (18,11) | | | | | 0.263 | 0.277 |
| 32 | φ (18,7,11) | | | | | 0.127 | 0.033 |
| 33 | τ (18,11,7,8) | | | | | 0.262 | 0.180 |
| 34 | r (17,18) | | | | | 7.187 | 7.051 |
| 35 | φ (17,11,18) | | | | | 0.113 | 0.074 |
| 36 | τ (17,18,11,7) | | | | | 0.035 | 0.018 |
| 37 | r (13,17) | | | | | 5.206 | 5.067 |
| 38 | φ (13,18,17) | | | | | 0.714 | 0.713 |
| 39 | τ (13,17,18,11) | | | | | 0.023 | 0.012 |
| 40 | r (14,13) | | | | | 4.704 | 4.714 |
| 41 | φ (14,17,13) | | | | | 1.067 | 1.061 |
| 42 | τ (14,13,17,18) | | | | | 0.713 | 0.708 |
| 43 | r (15,13) | | | | | 4.665 | 4.705 |
| 44 | φ (15,17,13) | | | | | 1.076 | 1.071 |
| 45 | τ (15,13,17,18) | | | | | 0.710 | 0.712 |
| 46 | r (16,13) | | | | | 4.962 | 4.952 |
| 47 | φ (16,17,13) | | | | | 1.077 | 1.072 |
| 48 | τ (16,13,17,18) | | | | | 0.748 | 0.740 |

^a For all force constant a consistent scale factor was used. 0.95. ^b For bond stretching force constants in 10^2 N m^{-1} . for deformation ones in Nm^{-18} units. ^c The number of letters "m" indicates the size of the cluster. "a" refers to the isolated cluster. "b" to cluster in solvent. ^d For numbering of the atoms see Fig. 2.

The definition of the applied internal coordinates and the scaled diagonal vibrational force constants are listed in Table 5. The internal coordinates are grouped. The first group belongs to the first molecule (coordinates 1–12, atoms 1–6), the second group contains the coordinates of the second molecule and its interactions with the first molecule (coordinates 13–30), while the third group contains the coordinates of the third molecule and its interactions with the second one (coordinates 31–48). The numbering of the atoms is presented in Fig. 2.

Looking at the first group, and comparing the corresponding diagonal force constants of the isolated molecule (ma) and the same of the largest cluster in solution (mmb), two CH stretch force constants (1–2) became higher, while that of the other CH stretch (coordinate 3) remained practically constant. The last coordinate is positioned in the H6–O5–C1 plane which is the reason for the different behavior. In this comparison the C1–O5 force constant decreases. The largest decreasing effect is observable at the O5–H6 diagonal force constants where the solvent effect dominates.

The diagonal force constant of the H12–O5 hydrogen bond stretch increases under cluster developing and solvent effect. The effect of the H12–O5–C1 deformation constant is different since the larger the isolated cluster, the higher its value of this constant, however, the solvent effect decreases its value. The constants of other coordinates including the hydrogen bond (the O11–H12–O5 in-plane deformation, the O11–H12–O5–H6 and the C7–O11–H12–O5 torsions) show very similar tendencies.

The diagonal force constants of the internal coordinates of the second methanol molecule (atoms 7–12) behave under both effects like the corresponding coordinates of the first molecule.

The value of the force constant of the second hydrogen bond (H18–O11) suggests a weaker bond than the first one. Like in the case of the first one, the solvent effect strengthens the bond. The constants of the deformation coordinates containing H18–O11 (H18–O11–C7 and H18–O11–C7–H) weaken under the solvent effect, like the coordinates including the hydrogen bond H12–O5.

The solvent effect did not cause important changes in the values of the internal diagonal force constants of the third methanol molecule (atoms 13–18). Only two exceptions exist, those of the H18–O17 and the C13–O17 bonds, both show decrease.

For comparison of the corresponding diagonal force constants of three cluster molecules some characteristic stretch constants were chosen in the full cluster under solvent effect (mmb). The constants of the C–O stretch coordinates increase from the first to the third molecule: 479.0 N m^{-1} for C1–O5, 492.2 N m^{-1} for C7–H11 and 506.7 N m^{-1} for C13–H17. A similar effect was found also for the O–H stretchings. Their constants were 649.1 N m^{-1} for O5–H6, 689.8 N m^{-1} for O11–H12 and 705.1 N m^{-1} for O17–H18, respectively. These data series prove that in the applied order the formation of the hydrogen bonds acts less and less on these bonds. Of course, they are influenced by the formation of the hydrogen bonds and the solvent effect, since the corresponding constants for the isolated molecule (ma) are 513.5 N m^{-1} for C1–O5 and 783.4 N m^{-1} for C5–H6.

3.5 Character of the vibrational modes

The calculated fundamental frequencies of the vibrational modes and their characterizations for one isolated methanol molecule (ma) are presented in Table 6a, while those for one methanol molecule in methanol solution (PCM calculations, mb) are listed in Table 6b. The OH and the CH frequencies are characteristic to these molecular groups and also the C–O one that became more characteristic to this group in the solution. The frequencies showed only minimal solvent effect, with only one exception, the OH stretch frequency of the single methanol molecule lowered by more than 280 cm^{-1} , according to its experimental tendency.

The vibrational properties of the isolated cluster of two methanol molecules (mma) are shown in Table 7a, while the same entries for this cluster in methanol solution (mmb) are introduced in Table 7b. It is interesting that the O5–H6 stretch frequency is in the isolated cluster higher than the same for the O11–H12 one, while this order changed as a result of the solvent effect. The O5–H6 bond is close to the hydrogen bond, the solvent environment influences it more strongly. The H12–O5 stretch frequency of the hydrogen bond increases with the solvent effect. Between the C–O stretch frequencies (they are real group frequencies!), the C7–O11 is higher than the C1–O5 one, both show a decrease with the solvent effect and their order does not change. The decrease of the frequency reflect a similar tendency in the diagonal force constants.

The enlargement of the cluster with adding the third methanol molecule brought changes in the interpretation of the spectra

Table 6 Calculated fundamental frequencies of: (a) one isolated methanol molecule; (b) one methanol molecule in methanol solution

| Frequency/ cm^{-1} | PED (type, %) ^a | | | |
|-----------------------------|----------------------------|-----|----|-------------------------------|
| (a) | | | | |
| 3743.0 | ν | OH | 99 | |
| 3024.3 | ν | CH | 99 | |
| 2938.8 | ν | CH | 99 | |
| 2898.3 | ν | CH | 99 | |
| 1469.6 | β | CH | 74 | β HCO 23 |
| 1453.7 | β | CH | 93 | |
| 1451.2 | β | CH | 89 | |
| 1344.2 | β | CH | 11 | β HCO 24 β COH 63 |
| 1138.1 | β | HCO | 94 | |
| 1057.7 | ν | CO | 24 | β HCO 45 β COH 23 |
| 1026.1 | ν | CO | 69 | β HCO 15 |
| 317.9 | τ | COH | 99 | |
| (b) | | | | |
| 3460.5 | ν | OH | 99 | |
| 3012.7 | ν | CH | 99 | |
| 2944.0 | ν | CH | 99 | |
| 2900.3 | ν | CH | 99 | |
| 1465.4 | β | CH | 74 | β HCO 23 |
| 1444.4 | β | CH | 94 | |
| 1444.2 | β | CH | 92 | |
| 1350.2 | β | CH | 18 | β HCO 15 β COH 65 |
| 1136.3 | β | HCO | 94 | |
| 1061.8 | ν | CO | 10 | β HCO 57 β COH 26 |
| 1014.2 | ν | CO | 81 | |
| 311.8 | τ | COH | 99 | |

^a ν : stretching; β : in-plane deformation; τ : torsion; participations not less than 10%.

(see Table 8a and b, respectively). Regarding the OH stretch vibrations, the motions of the O11–H12 and O17–H18 coordinates are coupled already in two vibrational modes of the isolated cluster. The solvent effect drastically lowered the values of all three OH stretch frequencies. Besides, the O5–H6 coordinate also participates in two vibrations. Even the order of these frequencies changed, considering the modes in which one of the coordinates dominates. The order of frequencies for the isolated cluster is O5–H6 > C17–H18 > C11–H12. The solvent effect changed this order as follows: C17–H18 > C5–H6 > C11–H12, *i.e.* the largest effect of the solvent was observed on the O5–H6 coordinate.

Looking at the C–O stretch modes of this cluster, the new phenomenon is the coupling of vibrational motions of the C7–O11 and C13–O17 coordinates in the two higher frequency modes, while the C1–O5 mode is characteristic. All these frequencies decrease in the solvent, but their order remains. The changes in their diagonal force constants are in good accordance with this change.

The largest cluster already contains two hydrogen bonds. The motions of the H12–O5 and H18–O11 hydrogen bond stretch coordinates dominate in two coupled vibrational modes. Formally the solvent effect increased their frequencies. However, the lower frequency mode, in which the H18–O11 coordinate dominates, changes its order in the solvent with the other one. Therefore the frequency of the first one increased by more than 40 cm^{-1} , while the frequency of the second one, in which the vibration of H12–O5 coordinate dominates, was lowered by more than 10 cm^{-1} .

3.6 Vibrational spectra

Based on the scaled frequencies and the calculated integrated infrared intensities, vibrational spectra were simulated, assuming Lorentz type band contours with 15 cm^{-1} FWHH. The spectrum of the cluster in methanol solvent was also simulated with FWHHs fitted to the experimental neat methanol spectrum. The experimental methanol spectra are retrieved from the Nicolet Library.³⁸

These spectra were compared with experimental vapor and neat liquid methanol spectra. Fig. 3 introduces the experimental IR vapor spectrum of methanol together with the simulated spectrum of the isolated methanol. The positions of the bands in the measured and calculated spectra are in good accordance. The deviations in the band structures occur:

(1) partly because the quantum chemical calculations could not consider the rotational structure of the methanol vapor bands,

(2) partly due to the consistent FWHH for the calculated bands.

Fig. 4 contains the FT-IR spectrum of neat methanol and the simulated spectra of the largest cluster in methanol (mmb) in two forms, namely with 15 cm^{-1} FWHH for all vibrational modes, and with fitted FWHHs. The fitted simulated spectra are in good agreement with the experimental ones. Only one difference is striking, the relative intensities of the CH stretch bands. The origin of the deviations is mainly the applied approximation of the intensity calculations in the used quantum chemical model.

Table 7 Calculated fundamental frequencies of: (a) a cluster of two methanol molecules; (b) a cluster of two methanol molecules in methanol solution

| Frequency/cm ⁻¹ | PED (type %) ^{a,b,c} | |
|----------------------------|-------------------------------|-------------------------------|
| (a) | | |
| 3751.3 | ν OH | 99 O5-H6 |
| 3612.8 | ν OH | 99 O11-H12 |
| 3051.6 | ν CH | 99 |
| 3005.7 | ν CH | 99 |
| 2979.1 | ν CH | 99 |
| 2925.9 | ν CH | 99 |
| 2923.9 | ν CH | 99 |
| 2888.4 | ν CH | 99 |
| 1474.4 | β HCO | 40 τ COH 45 |
| 1469.7 | β HCH | 72 β HCO 20 |
| 1462.6 | β HCH | 87 |
| 1452.8 | β HCO | 17 τ COH 80 |
| 1450.3 | β HCH | 12 β HCO 73 τ COH 12 |
| 1444.2 | β HCH | 93 |
| 1402.7 | β COH | 62 τ COH 20 |
| 1331.2 | β HCO | 32 β COH 59 |
| 1143.1 | β HCO | 87 τ COH 10 |
| 1142.0 | β HCO | 90 |
| 1091.7 | β HCO | 61 β COH 14 τ COH 16 |
| 1049.5 | β HCO | 53 β COH 35 |
| 1042.5 | ν CO | 97 C7-O11 |
| 1015.3 | ν CO | 90 C1-O5 |
| 695.2 | τ COH | 17 β hoC 16 β Oho 56 |
| 308.8 | τ COH | 93 |
| 212.5 | ν oh | 83 C5-H12 |
| 128.6 | τ COH | 66 β hoC 22 |
| 106.6 | β COH | 11 τ hoC 43 τ Coh 20 |
| 79.8 | β hoC | 13 τ Oho 58 |
| 78.1 | τ COH | 13 β hoC 16 β Oho 28 τ Oho 30 |
| 52.9 | τ hoC | 24 τ Coh 42 |
| (b) | | |
| 3487.7 | ν OH | 99 O11-H12 |
| 3428.9 | ν OH | 99 O5-H6 |
| 3033.1 | ν CH | 99 |
| 2998.7 | ν CH | 99 |
| 2979.8 | ν CH | 99 |
| 2930.2 | ν CH | 99 |
| 2924.6 | ν CH | 99 |
| 2892.0 | ν CH | 99 |
| 1472.1 | β HCO | 39 β COH 12 τ COH 38 |
| 1466.2 | β HCH | 70 β HCO 20 |
| 1448.2 | β HCH | 24 β HCO 43 τ COH 29 |
| 1446.9 | β HCH | 65 β HCO 10 τ COH 23 |
| 1444.8 | β HCO | 52 τ COH 39 |
| 1440.1 | β HCH | 93 |
| 1420.1 | β COH | 54 τ COH 26 |
| 1339.4 | β HCH | 13 β HCO 21 β COH 63 |
| 1141.9 | β HCO | 83 τ COH 16 |
| 1139.3 | β HCO | 93 |
| 1096.9 | β HCO | 65 β COH 10 τ COH 16 |
| 1056.6 | β HCO | 57 β COH 30 |
| 1030.8 | ν CO | 97 C7-O11 |
| 1007.0 | ν CO | 86 C1-O5 |
| 756.6 | τ COH | 13 β hoC 18 β Oho 44 |
| 298.4 | τ COH | 92 |
| 229.8 | ν oh | 81 C5-H12 |
| 115.1 | τ COH | 67 β hoC 10 |
| 107.2 | β COH | 13 β Oho 14 τ Coh 43 |
| 54.1 | τ hoC | 33 τ Coh 26 |
| 49.9 | β hoC | 14 β Oho 11 τ hoC 10 τ Coh 36 |
| (21.7) ^d | τ Oho | 58 |

^a ν: stretching; β: in-plane deformation; τ: torsion; participations not less than 10%. ^b Lower case letters stand for the head atoms of the hydrogen bonds. ^c For the numbering of the atoms see Fig. 2. ^d Imaginary frequency.

Only a few authors published the vibrational frequencies of methanol clusters. Larsen *et al.* (see also the references therein)³¹ dealt only with the OH stretching vibrations. They presented the calculated OH stretching frequencies of monomer, dimer, trimer, tetramer and pentamer methanol clusters. For the calculations the DFT B3LYP/6-311++G(3df,2p) and the MP2/6-311++G(2df,2p) methods/basis sets were applied, respectively. Besides, they measured the infrared and Raman spectra of CH₃OH, CD₃OH, CH₃OD and CD₃OD of the monomer, the dimer, four different trimers and two tetramers, however only the OH/OD stretching regions of these spectra were introduced.

Mo *et al.*³² calculated the vibrational frequencies of a dimer and three trimer methanol clusters. They used the DFT B3LYP/6-311+G(d,p) level of calculation. They listed all calculated frequencies for all three trimers but gave only an approaching assignment. Namely, they distinguish only four group or frequencies, OH stretches, CH stretches, bending modes, and intermolecular modes.

We tried to compare these results with ours. Difficulties arose:

- due to the different level of the applied calculations,
- due to the different forms of the trimer clusters.

We could not solve the first problem, since the levels of calculations are facts. For the solution of the second problem, we tried to find the trimer methanol clusters which are similar to our trimer cluster. Larsen³¹ measured and calculated the OH stretching frequencies of a “chair-like” trimer, and calculated that of a cyclic one. The chair form is not described in detail but this seems to be closer to our trimer cluster. Under the three trimer forms of Mo *et al.*³² we found nearer to our resulted form the “Y-like” one. Since our calculated frequencies were scaled, while the results in the aforementioned articles were not, for comparison we scaled their results in the same way as ours with $\sqrt{0.95} \approx 0.9747$.

The most sensitive part of methanol clusters are the OH bonds. Therefore the OH stretching vibrations “feel” the best the intermolecular interactions. We collected the measured and calculated OH stretching vibrations published by other scientists together with our results in Table 9. Our results are in good agreement with the calculated results of other authors’ for the monomer and dimer clusters. For the trimers they agree well with Mo’s³² results and for the major part also with those of Larsen. Our calculated OH stretching frequency results for the trimer cluster in methanol solution agree partly with Mo’s measurements.

4. Conclusions

Increasing the size of the methanol cluster acted with the formation of hydrogen bonds essentially on the structure, charge distribution, force field and spectra of the individual methanol molecules (ma, mma and mmma clusters). This effect is monotonic, *i.e.* a property either grew or diminished (or sometimes remained practically constant) with increasing the size of the cluster. This effect is clearly seen on the first molecule of the cluster (atoms 1–6), only a few exceptions exist.

Table 8 Calculated fundamental frequencies of: (a) a cluster of three methanol molecules; (b) a cluster of three methanol molecules in methanol solution

| Frequency/cm ⁻¹ | PED (type %) ^{a,b,c} | | | | | | | | | | | |
|----------------------------|-------------------------------|-----|----|----------------------------------|-----|----|---|-----|----|---|-----|----|
| (a) | | | | | | | | | | | | |
| 3734.1 | ν | OH | 99 | O5-H6 | | | | | | | | |
| 3517.3 | ν | OH | 99 | O11-H12(20)&O17-H18(79) | | | | | | | | |
| 3462.4 | ν | OH | 98 | O11-H12(78)&O17-H18(20) | | | | | | | | |
| 3044.3 | ν | CH | 99 | | | | | | | | | |
| 3024.1 | ν | CH | 99 | | | | | | | | | |
| 3008.9 | ν | CH | 99 | | | | | | | | | |
| 3004.7 | ν | CH | 99 | | | | | | | | | |
| 2960.6 | ν | CH | 99 | | | | | | | | | |
| 2938.1 | ν | CH | 99 | | | | | | | | | |
| 2927.2 | ν | CH | 99 | | | | | | | | | |
| 2913.1 | ν | CH | 99 | | | | | | | | | |
| 2889.3 | ν | CH | 99 | | | | | | | | | |
| 1487.4 | β | HCH | 83 | β | HCO | 11 | | | | | | |
| 1478.1 | β | HCO | 38 | β | COH | 10 | τ | COH | 47 | | | |
| 1474.1 | β | HCO | 36 | τ | COH | 52 | | | | | | |
| 1465.1 | β | HCH | 77 | β | HCO | 19 | | | | | | |
| 1458.0 | β | HCO | 22 | τ | COH | 72 | | | | | | |
| 1453.2 | β | HCO | 19 | τ | COH | 71 | | | | | | |
| 1450.0 | β | HCH | 60 | β | HCO | 17 | τ | COH | 17 | | | |
| 1448.6 | β | HCO | 83 | | | | | | | | | |
| 1444.3 | β | HCH | 27 | β | HCO | 60 | | | | | | |
| 1420.7 | β | COH | 54 | τ | COH | 26 | | | | | | |
| 1416.3 | β | COH | 58 | τ | COH | 20 | | | | | | |
| 1335.0 | β | HCO | 28 | β | COH | 59 | | | | | | |
| 1155.3 | β | HCO | 90 | | | | | | | | | |
| 1144.1 | β | HCO | 83 | τ | COH | 16 | | | | | | |
| 1142.3 | β | HCO | 83 | τ | COH | 15 | | | | | | |
| 1108.9 | β | HCO | 66 | τ | COH | 18 | | | | | | |
| 1098.3 | β | HCO | 64 | β | COH | 10 | τ | COH | 17 | | | |
| 1054.5 | β | HCO | 48 | β | COH | 33 | | | | | | |
| 1044.4 | ν | CO | 97 | C7-O11(20)&C13-O17(77) | | | | | | | | |
| 1036.2 | ν | CO | 96 | C7-O11(77)&C13-O17(19) | | | | | | | | |
| 991.2 | ν | CO | 89 | C1-O5 | | | | | | | | |
| 840.3 | τ | COH | 22 | β | hoC | 16 | β | Oho | 33 | τ | Oho | 15 |
| 717.5 | τ | COH | 11 | β | hoC | 13 | β | Oho | 56 | | | |
| 406.2 | τ | COH | 71 | | | | | | | | | |
| 229.4 | ν | oh | 75 | o5-h12(50)&o11-h18(25) | | | | | | | | |
| 208.9 | ν | oh | 68 | o5-h12(20)&o11-h18(48) | | | | | | | | |
| 184.9 | ν | oh | 15 | τ | hoC | 69 | | | | | | |
| 137.5 | β | hoC | 27 | β | Oho | 16 | τ | Coh | 15 | | | |
| 119.6 | τ | COH | 46 | τ | hoC | 28 | τ | Oho | 11 | | | |
| 112.1 | τ | COH | 18 | τ | hoC | 14 | τ | Oho | 34 | | | |
| 109.3 | τ | COH | 48 | β | Oho | 11 | | | | | | |
| 86.1 | τ | Oho | 49 | | | | | | | | | |
| 66.7 | τ | hoC | 18 | τ | Coh | 38 | | | | | | |
| 55.0 | β | hoC | 31 | τ | Oho | 42 | | | | | | |
| 47.1 | τ | hoC | 10 | τ | Coh | 60 | | | | | | |
| 33.3 | β | hoC | 12 | β | Oho | 17 | τ | Oho | 24 | τ | Coh | 40 |
| (b) | | | | | | | | | | | | |
| 3454.2 | ν | OH | 98 | O11-H12(13)&O17-H18(85) | | | | | | | | |
| 3417.3 | ν | OH | 99 | O5-H6(82)&O11-H12(11)&O17-H18(6) | | | | | | | | |
| 3363.7 | ν | OH | 97 | O5-H6(14)&O11-H12(75)&O17-H18(8) | | | | | | | | |
| 3032.7 | ν | CH | 99 | | | | | | | | | |
| 3021.3 | ν | CH | 99 | | | | | | | | | |
| 3003.9 | ν | CH | 99 | | | | | | | | | |
| 3003.0 | ν | CH | 99 | | | | | | | | | |
| 2967.1 | ν | CH | 99 | | | | | | | | | |
| 2936.7 | ν | CH | 99 | | | | | | | | | |
| 2935.9 | ν | CH | 99 | | | | | | | | | |
| 2915.9 | ν | CH | 99 | | | | | | | | | |
| 2895.4 | ν | CH | 99 | | | | | | | | | |
| 1476.5 | β | HCH | 86 | β | HCO | 10 | | | | | | |
| 1474.7 | β | HCO | 38 | β | COH | 17 | τ | COH | 38 | | | |
| 1472.2 | β | HCO | 35 | β | COH | 15 | τ | COH | 43 | | | |
| 1461.1 | β | HCH | 77 | β | HCO | 19 | | | | | | |
| 1452.0 | β | HCO | 25 | τ | COH | 72 | | | | | | |
| 1449.3 | β | HCO | 25 | τ | COH | 73 | | | | | | |
| 1444.2 | β | HCO | 78 | τ | COH | 17 | | | | | | |
| 1442.1 | β | HCH | 52 | β | HCO | 36 | | | | | | |

Table 8 (continued)

| Frequency/cm ⁻¹ | PED (type %) ^{a,b,c} | | | | | | | | | | | |
|----------------------------|-------------------------------|-----|----|------------------------|-----|----|---|-----|----|---|-----|----|
| 1439.0 | β | HCH | 41 | β | HCO | 39 | τ | COH | 13 | | | |
| 1432.6 | β | COH | 45 | τ | COH | 33 | | | | | | |
| 1423.7 | β | COH | 48 | τ | COH | 27 | | | | | | |
| 1337.8 | β | HCH | 11 | β | HCO | 23 | β | COH | 62 | | | |
| 1153.6 | β | HCO | 89 | | | | | | | | | |
| 1143.0 | β | HCO | 82 | τ | COH | 16 | | | | | | |
| 1141.4 | β | HCO | 83 | τ | COH | 16 | | | | | | |
| 1109.4 | β | HCO | 67 | τ | COH | 18 | | | | | | |
| 1098.9 | β | HCO | 66 | τ | COH | 17 | | | | | | |
| 1059.5 | β | HCO | 56 | β | COH | 31 | | | | | | |
| 1029.6 | ν | CO | 96 | C7-O11(13)&C13-O17(83) | | | | | | | | |
| 1019.8 | ν | CO | 96 | C7-O11(82)&C13-O17(14) | | | | | | | | |
| 985.3 | ν | CO | 89 | C1-O5 | | | | | | | | |
| 885.4 | τ | COH | 21 | β | hoC | 13 | β | Oho | 38 | τ | Coh | 12 |
| 725.6 | β | Oho | 63 | τ | Coh | 10 | | | | | | |
| 425.6 | τ | COH | 75 | τ | Oho | 12 | | | | | | |
| 253.3 | ν | oh | 72 | o5-h12(10)&o11-h18(62) | | | | | | τ | Oho | 11 |
| 216.1 | ν | oh | 71 | o5-h12(60)&o11-h18(11) | | | | | | τ | Oho | 11 |
| 167.2 | τ | COH | 16 | τ | hoC | 65 | | | | | | |
| 137.8 | τ | COH | 14 | β | hoC | 52 | τ | Coh | 12 | | | |
| 123.5 | τ | COH | 45 | β | hoC | 15 | β | Oho | 10 | | | |
| 117.1 | τ | hoC | 58 | τ | Coh | 13 | | | | | | |
| 105.1 | τ | COH | 44 | β | Oho | 12 | | | | | | |
| 83.1 | τ | hoC | 41 | τ | Oho | 21 | | | | | | |
| 72.5 | τ | Coh | 42 | | | | | | | | | |
| 58.5 | τ | Coh | 61 | | | | | | | | | |
| 54.9 | τ | Oho | 62 | | | | | | | | | |
| (134.5) ^d | β | Oho | 10 | τ | Oho | 46 | | | | | | |

^a ν: Stretching; β: in-plane deformation; τ: torsion; participations not less than 10%. ^b Lower case letters stand for the head atoms of the hydrogen bonds. ^c For the numbering of the atoms see Fig. 2.

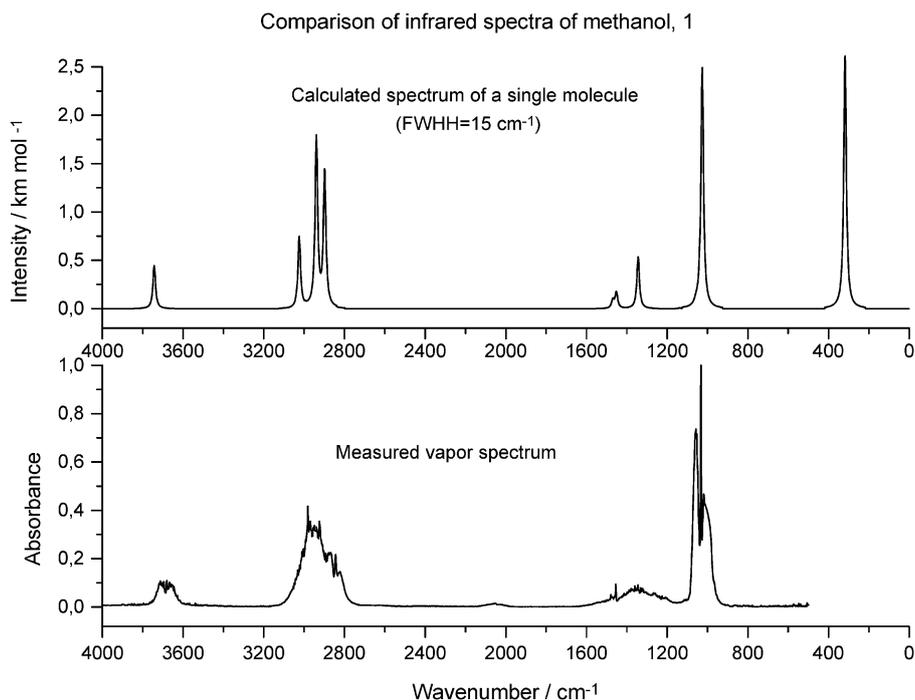


Fig. 3 Measured and simulated infrared spectra of methanol, 1.

The effect of the solvent is striking on the charge distributions, vibrational force constants, and the vibrational frequencies. According to the calculations, the largest changes were

observable in the environment of the hydrogen bonds. The results show clearly that the methanol environment strengthened the hydrogen bonds, the differences in the head atom charges

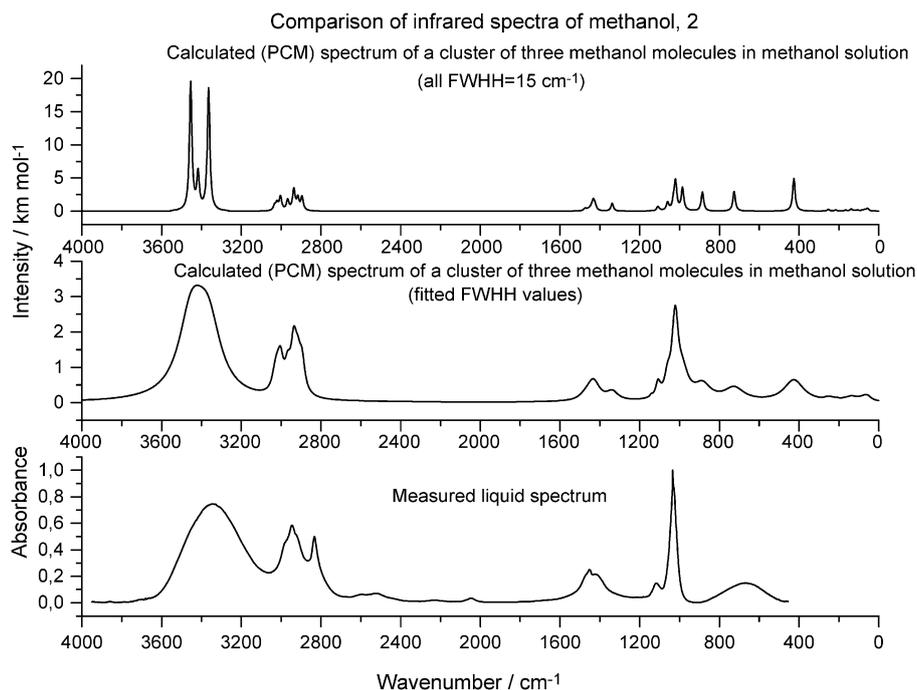


Fig. 4 Measured and simulated infrared spectra of methanol, 2.

Table 9 Comparison of the measured and calculated vibrational frequencies of methanol clusters (cm^{-1})

| Cluster | OH stretching region | | | | | | |
|---------|--|--------------------|-------------------------------------|---|---------------------------------------|--|--|
| | Measured | | Calculated ^d | | | | |
| | Infrared ^a | Raman ^a | B3LYP/ 6-311+G(d,p) ^b | B3LYP/ 6-311++G(3df,2p) ^a | MP2/ 6-311++G(2df,2p) ^a | B3LYP/6-311G** this work ^c | B3LYP/6-311G**, in methanol, this work ^c |
| Monomer | 3686 | 3686, 3683 | 3749 | 3758 | 3793 | 3743 | 3461 |
| Dimer | 3575 | 3575 | 3746, 3013 | 3749, 3599 | 3784, 3646 | 3751, 3613 | 3488, 3429 |
| Trimer | 3505, 3495 3474, 3469 3456, 3434 3412 | 3413 | 3736, 3651, 3630 | 3531, 3520, 3466 | 3562, 3553, 3489 | 3734, 3517, 3462 | 3454, 3417, 3364 |

^a Ref. 31, dimer: linear, trimer: chair-like (cyclic) configuration. ^b Ref. 32, trimer: "Y" like configuration (configuration labelled 3 in the reference). ^c For the configurations see Fig. 1 and 2. ^d Calculated frequencies scaled by 0.9747, square root of 0.95, for approaching the experimental results, in italics.

increased, the diagonal force constants grew or remained unchanged. The calculated frequencies reflect the solvent effect the most. The OH stretch frequencies of the valence bonds showed drastically lowered shifts, while the stretch frequencies of the hydrogen bonds increased.

It was found that the application of the three-molecule cluster and the PCM model for simulation of the infrared spectrum of the neat methanol was a good approximation.

References

- J. A. Morrone and M. E. Tuckermann, *Chem. Phys. Lett.*, 2003, **370**, 406.
- S. L. Boyd and R. J. Boyd, *J. Chem. Theory Comput.*, 2007, **3**, 54.
- M. Matsumoto and K. E. Gubbins, *J. Chem. Phys.*, 1990, **93**(3), 1981.
- T. Kosztolányi, I. Bakó and G. Pálinkás, *J. Chem. Phys.*, 2003, **118**(10), 4546.
- G. Pálinkás, E. Hawlicka and K. Heinzinger, *J. Phys. Chem.*, 1987, **91**, 4334.
- M. Haughney, M. Ferrario and I. R. McDonald, *J. Phys. Chem.*, 1987, **91**, 4934.
- L. Bianchi, A. K. Adya, O. N. Kalugin and C. J. Wormald, *J. Phys.: Condens. Matter*, 1999, **11**, 9151.
- V. V. Zakharov, E. N. Brodskaya and A. Laaksonen, *J. Chem. Phys.*, 1998, **109**(21), 9487.
- R. Sharma, C. Chakravarty and E. Milotti, *J. Phys. Chem. B*, 2008, **112**, 9071.
- I. Bakó, P. Jedlovszky and G. Pálinkás, *J. Mol. Liq.*, 2000, **87**, 243.
- D. Wright and M. S. El-Shall, *J. Chem. Phys.*, 1996, **105**(24), 11199.
- R. Ludwig, M. D. Zeidler and T. C. Farrar, *Z. Phys. Chem.*, 1995, **189**, 19.
- J.-W. Handgraaf, T. S. van Erp and E. J. Meijer, *Chem. Phys.*, 2003, **367**, 617.
- J.-W. Handgraaf, E. J. Meijer and M.-P. Gaigeot, *J. Chem. Phys.*, 2004, **121**(20), 10111.
- I. Yu. Shilov, B. M. Rode and V. A. Durov, *Chem. Phys.*, 1999, **241**, 75.

- 16 V. A. Durov and I. Yu. Shilov, *Russ. J. Phys. Chem. A*, 2007, **81**(2), 196–203.
- 17 M. Tomšič, A. Jamnik, G. Fritz-Popovski, O. Glatter and L. Vlček, *J. Phys. Chem. B*, 2007, **111**, 1738.
- 18 L. Zoranić, F. Sokolić and A. Perera, *J. Chem. Phys.*, 2007, **127**(2), 24502.
- 19 D. Costa, G. Munaó, F. Saija and C. Caccarno, *J. Chem. Phys.*, 2007, **127**, 224501.
- 20 E. Tsuchida, Y. Kanada and M. Tsukada, *Chem. Phys. Lett.*, 1999, **311**, 236.
- 21 M. Pagliai, G. Cardini, R. Righini and V. Schettino, *J. Chem. Phys.*, 2003, **119**(13), 6655.
- 22 J. R. Perchard, F. Romain and Y. Bouteiller, *Chem. Phys.*, 2008, **343**, 35.
- 23 R. Palomar and G. Sesé, *J. Phys. Chem. B*, 2005, **109**, 499.
- 24 W. Sun, Z. Chen and S.-Y. Huang, *Fluid Phase Equilib.*, 2005, **238**, 20.
- 25 V. Pogorelov, L. Bulavin, I. Doroshenko, O. Fesjun and O. Veretennikov, *J. Mol. Struct.*, 2004, **708**, 61.
- 26 H. Torii, *Pure Appl. Chem.*, 2004, **76**(1), 247.
- 27 Y. Takano and K. N. Houk, *J. Chem. Theory Comput.*, 2005, **1**, 70.
- 28 E. Ruckenstein, I. L. Shulgin and J. L. Tilson, *J. Phys. Chem. A*, 2005, **109**, 807.
- 29 I. R. Piletic, K. J. Gaffney and M. D. Fayer, *J. Chem. Phys.*, 2003, **119**(1), 423.
- 30 R. A. Klein, B. Mennucci and J. Tomasi, *J. Phys. Chem. A*, 2004, **108**, 5851.
- 31 R. W. Larsen, P. Zielke and M. A. Suhm, *J. Chem. Phys.*, 2007, **126**, 194307.
- 32 O. Mo, M. Yanez and J. Elguero, *J. Chem. Phys.*, 1997, **107**, 3592.
- 33 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *Gaussian 03, Revision D.01*, Gaussian, Inc., Wallingford CT, 2004.
- 34 A. D. Becke, *Chem. Phys.*, 1993, **98**, 5648.
- 35 R. S. Mulliken, *J. Chem. Phys.*, 1955, **23**, 1833.
- 36 A. E. Reed, R. B. Weinstock and F. J. Weinhold, *J. Chem. Phys.*, 1985, **83**, 735; A. E. Reed, F. J. Weinhold and L. A. Curtiss, *Chem. Rev.*, 1988, **88**, 899.
- 37 M. Cossi, G. Scalmani, N. Rega and V. Barone, *J. Chem. Phys.*, 2002, **117**, 43.
- 38 *Nicolet Library of FT-IR spectra*, Nicolet Magna 75 IR spectrometer.