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Hydrogen bonding in amylose/DMSO complexes studied by vibrational spectroscopy and density functional theory calculations

Alberto Milani,^{a*} Nur Aiman Fadel,^a Luigi Brambilla,^a Mirella Del Zoppo,^a Chiara Castiglioni,^a Giuseppe Zerbi^a and Riccardo Stradi^b

The intermolecular interactions in amylose/dimethyl sulfoxide (DMSO) complexes are discussed both experimentally and theoretically by means of Raman and infrared spectroscopies.

The study is based on a preliminary analysis of well known systems such as pure liquid DMSO or DMSO in mixture with water: for such systems, an analysis of the CS stretching region is carried out both by means of Raman and infrared spectra.

In particular, Raman spectra reveal a high sensitivity to the strength and to the type of interaction involving the DMSO molecules.

These results, applied to the investigation of amylose-DMSO complexes, show the presence of different hydrogen-bonded complexes which coexist in this compound. In particular, DMSO molecules are identified both on the external surface of the V-amylose helix, where they can interact via one hydrogen bond and in the inner channel of the helix where they can interact via two hydrogen bonds.

The present findings open the possibility of applying vibrational spectroscopy to the characterization of inclusion compounds of amylose which are currently being involved in many fields of nanosciences. Copyright © 2009 John Wiley & Sons, Ltd.

Keywords: hydrogen bonding; first-principles calculations; host-guest compounds; intermolecular interactions

Introduction

Amylose and amylose complexes have attracted the interest of scientists in many different fields. Their importance is not restricted only to research in biology, food sciences or macromolecular structure,^[1–18] but recently proved to be interesting systems in many other fields, such as nanotechnology^[19–25] and pharmaceutical science.^[26–29]

Amylose complexes are host-guest systems where many different kinds of molecules can be included in the helical structure of V-amylose, thus affecting their environmental properties.^[5–11]

In the field of organic nanotechnology, complexes of amylose and conjugated oligomers have been recently prepared for possible applications as optical devices,^[19–23] or complexed with carbon nanotubes^[24,25]; furthermore, complexes of amylose and drugs are currently investigated for applications in drug delivery.^[26–29]

A reliable chemical and physical characterization is required in order to understand the morphology and the molecular structure of these systems, first of all as proof of the existence of the inclusion complexes.

The peculiar properties of amylose, either in the solid state or in solution with different solvents, have been already investigated.^[5–18] In particular, the properties of amylose dissolved in dimethyl sulfoxide (DMSO) or in water/DMSO mixtures have seeded much interest. This solvent interacts strongly with amylose, significantly affecting its molecular and supramolecular organization, and possibly promoting the formation of inclusion complexes. Indeed, amylose/DMSO solutions are used in the preparation of many complexes which have been carefully analyzed in the past.^[12–18]

From the point of view of vibrational spectroscopy, the intermolecular properties of DMSO in different environments have been analyzed in many works, both by infrared and Raman spectroscopies.^[30–41] The vibrational dynamics of these molecules were found to be sensitive to intermolecular interactions, and the related spectroscopic features were identified.

In this paper, the Raman spectra of amylose/DMSO complexes are investigated on the basis of the spectroscopic markers identified by the analysis of the spectra of simpler systems such as pure DMSO and mixtures of DMSO with water or benzene.

The study of the spectra in the CS stretching region has allowed to find evidence of the existence of different kinds of intermolecular interactions, thus offering a spectroscopic marker which has been almost completely overlooked in previous studies.^[30–32]

The reliability of our interpretation, and the validity of the markers identified, are further supported by the infrared spectra.

The comparison of DMSO-H₂O, DMSO-benzene solutions and DMSO-amylose complexes indicates that it is possible to identify different types of complexation.

In previous papers by Winter and Sarko,^[12,13] on the basis of X-ray diffraction data, it was found that DMSO molecules inside the

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channel created by V-amylose would form two hydrogen bonds with the host macromolecule.

In this work we will show that spectroscopic markers in the Raman spectra allow to discriminate between DMSO molecules interacting via one, two or no hydrogen bonds.

Once these markers have been identified they can be used for the interpretation of the vibrational spectra of other amylose complexes involving DMSO.

The study is based both on experimental and theoretical results; experimental Raman and IR spectra have been interpreted with the help of Density Functional Theory (DFT) calculations on related model systems.

Experimental

Samples and experimental setup

DMSO (99.9% purity and H₂O content lower than 0.1% weight/weight) was purchased from Aldrich and used without any purification. DMSO-amylose complexes were prepared according to the procedure reported in the papers by Winter and Sarko.^[12,13]

Samples of amylose-DMSO complexes in the solid state were prepared in glass capillary tubes for the Raman analysis. Liquid pure DMSO, DMSO-H₂O (with molar ratio ranging from 5:1 to 1:100) and DMSO-benzene (1:10 molar ratio) were prepared in NMR glass tubes for FT-Raman analysis; drops of the liquid were sandwiched between two ZnSe windows for FT-IR analysis.

Solid DMSO samples were obtained keeping a NMR tube filled with DMSO at -30°C . In order to prevent sample melting (m.p. 18°C) the Raman spectrum was recorded in 40 s (32 scans).

FT-Raman spectra, with 1064 nm exciting line of a Nd:YVO₄ laser were recorded with a Nicolet NXR9650 FT-Raman spectrometer in back-scattering geometry. Depending on the sample analyzed, we used laser power ranging from 400 to 800 mW, and scan number ranging from 256 to 2048 with a 2 cm^{-1} resolution. Infrared spectra were recorded with a Nicolet Nexus FT-IR Spectrometer with a 1 cm^{-1} resolution.

OriginPro7 software has been used to perform a multippeak curve fitting on the DMSO-amylose spectrum.

DFT calculations

DFT calculations have been carried out by means of the Gaussian03 code.^[42] The exchange-correlation functional chosen for all the calculations is the B3LYP functional^[43,44] with 6-311++G** basis set.

Basis set superposition error (BSSE) has been corrected both in the geometry optimization and wavenumber calculations using the Counterpoise (CP) correction^[45,46] as implemented in Gaussian03 code.

Raman spectra were calculated on the basis of completely optimized molecular structures of the model systems.

The model systems are shown in Fig. 1:

- DMSO as isolated molecule;
- a DMSO dipole-dipole dimer;
- a dimer with a DMSO molecule interacting via hydrogen bond with one H₂O molecule;
- a trimer with a DMSO molecule interacting via hydrogen bond with two H₂O molecules;
- a trimer where two DMSO molecules are bridged by one water molecule;

- DMSO molecule interacting with a glucose molecule via one hydrogen bond;
- DMSO molecule interacting with a glucose molecule via two hydrogen bonds.

Model d) is used to simulate the 1:100 DMSO-H₂O complexes; indeed, also previous molecular dynamics simulations^[47–49] suggested that in a dilute mixture of DMSO and H₂O the most stable clusters involve DMSO molecules hydrogen-bonded to two water molecules in different configurations.

At high dilution of DMSO in water (i.e. large water content), we can expect that for each DMSO molecule, more than two water molecules are available for hydrogen bonding; model d) describes this situation.

When the water content in DMSO/H₂O complexes decreases, the relative number of H₂O molecules available for forming hydrogen bonds with DMSO decreases too. Under this condition, different H-bonded complexes are expected.

In particular, it seems reasonable that in a 1:1 solution, complexes with only one H bond between DMSO and water are dominant. This situation is described by model c).

In Section III.2 (Infrared Spectra) it is shown how the above assumptions can be justified on the basis of the IR spectra by analyzing both the OH stretching and the SO stretching wavenumber ranges. For the analysis of OH stretching bands, model e) is introduced and is discussed below only.

The last two cases should mimic the effect of hydrogen bonding in amylose/DMSO complexes. The local character of the hydrogen bond and the lack of significant long-range vibrational interactions in the amylose chain allow the use of such simple systems as models for the complex.

In Fig. 2, the Raman spectra, not corrected for BSSE, are reported. Indeed, we found that CP correction has no significant effect on the computed wavenumbers. This is consistent with the results of a previous work where the BSSE effect on the vibrational wavenumbers was found to be negligible even if poor basis sets are used.^[50]

Interaction energies for the different models have been calculated introducing both BSSE corrections and Zero-Point Vibrational energy corrections^[51] (see Table 1).

Results and Discussion

Several Raman spectroscopic studies of intermolecular interactions of DMSO in various environments have appeared in the

Table 1. Calculated (B3LYP/6-311++G**) interaction energies (corrected for BSSE and zero-point vibrational energy corrections) and wavenumber for the CS stretching modes and the S=O stretching mode for the models of Fig. 1

	E^{int} (KJ/mol)	$\nu^{\text{CS}}_{\text{symm}}$ (cm^{-1})	$\nu^{\text{CS}}_{\text{asymm}}$ (cm^{-1})	ν^{SO} (cm^{-1})
Isolated DMSO (<i>model a</i>)	//	623	653	1051
DMSO dimer (<i>model b</i>)	24.142	631	666	1038–1031
DMSO + 1H ₂ O (<i>model c</i>)	26.108	631	661	1030
DMSO + 2H ₂ O (<i>model d</i>)	50.334	635	679	1023
DMSO + glucose, 1 H bond (<i>model f</i>)	36.401	633	667	1035
DMSO + glucose, 2 Hbond (<i>model g</i>)	37.279	635	676	1027

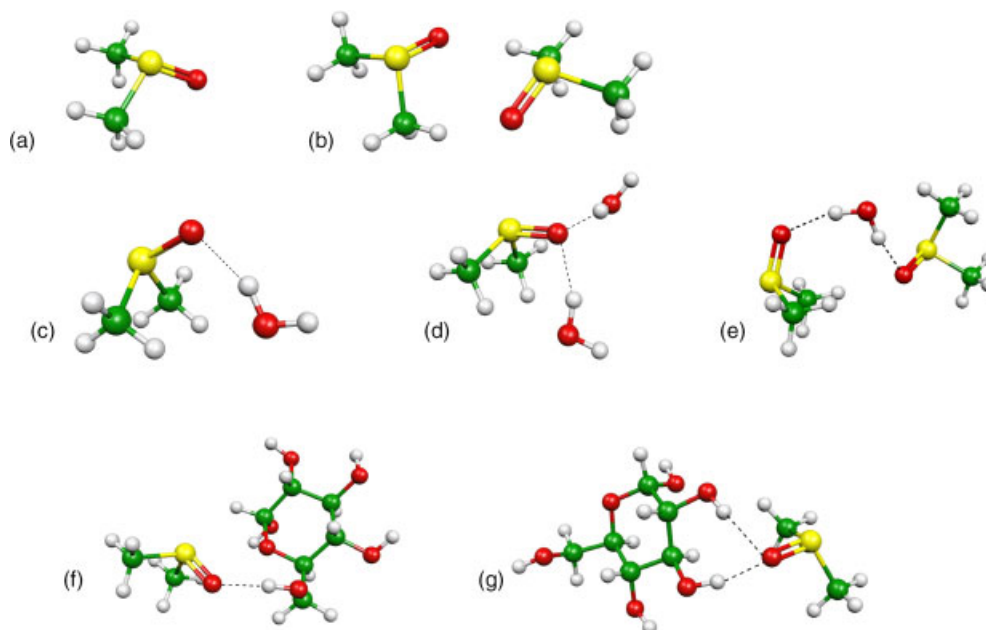


Figure 1. Sketch of the structures of DMSO and of the different molecular complexes studied by means of DFT calculations: a) isolated molecules; b) DMSO dimer; c) DMSO-H₂O with one H bond; d) DMSO-H₂O with two H bonds; e) two DMSO bridged by one H₂O; f) DMSO-glucose complex (one H bond); g) DMSO-glucose complex (two H bonds). This figure is available in colour online at www.interscience.wiley.com/journal/jrs.

literature in the past.^[30–41] In most of them, the attention was focused on the S=O stretching band in the wavenumber range 1000–1060 cm^{−1}. This band is broad and structured, showing different components already in the pure liquid.^[33–41] Intermolecular interactions (dipole–dipole or hydrogen bonding) were found to cause a red shift of the S=O stretching wavenumber, thus allowing a qualitative interpretation of aggregation phenomena in DMSO solutions.^[30–41]

In this work, we look for spectroscopic markers which may suggest where and how DMSO molecules are interacting in DMSO/amylose complexes.

From this point of view, the S=O stretching band is of little help since it is broad, thus making it very difficult to extract the information we are looking for. This problem is made even worse since in the region around 1000 cm^{−1} many bands relative to amylose or the inclusion compounds can be found both in the Raman and infrared spectra.

In the past, only very few papers have briefly analyzed the effect of intermolecular interactions on the CS stretching bands of DMSO in the region 600–800 cm^{−1}.^[30–32] A blue shift was detected for interactions of increasing strength, opposite to the red shift observed for the S=O stretching lines^[33–41]; CS stretching bands are thus alternative spectroscopic markers for these systems. However, since in this wavenumber range (600–800 cm^{−1}) bands assigned to amylose are observed in the IR spectra, only Raman spectroscopy becomes useful for our present purposes.

Analysis of Raman spectra

In Fig. 2, the experimental Raman spectra in the CS stretching region (from 500 to 800 cm^{−1}) of pure DMSO (liquid and solid), DMSO-H₂O (1:1 and 1:100 complexes) and DMSO-benzene solutions are reported in panel a).

DFT-computed Raman spectra for the models sketched in Fig. 1 are reported in panel b). Consistently with previous works,^[30–32] from the calculations, we predict a blue shift of the two

Table 2. Experimental Raman wavenumber of the lines assigned to CS stretchings

	$\nu_{\text{sym}}^{\text{CS}}$ (cm ^{−1})	$\nu_{\text{asym}}^{\text{CS}}$ (cm ^{−1})
DMSO + benzene	664	693
Liquid DMSO	669	699
Solid DMSO	672	704
DMSO + H ₂ O 1 : 1 solution	673	705
DMSO + H ₂ O 1 : 100 solution	678	713
DMSO + Amylose (Component 1)	675	709
DMSO + Amylose (Component 2)	681	716

CS stretching lines with increasing strength of intermolecular interactions, as reported in Tables 1 and 2. Furthermore, the blue shift is larger for the higher wavenumber line (antisymmetric CS stretching).

From the experimental spectra shown in Fig. 2, it can be seen that the lowest wavenumbers are found for DMSO-benzene solution where only weak intermolecular dispersion interactions can take place. Dipole–dipole intermolecular interactions are already non-negligible in pure liquid DMSO, and further increase in solid DMSO giving rise to a systematic blue shift of the CS stretching lines in the experimental Raman spectra.

The DMSO-H₂O 1 : 1 complex shows a spectral behavior very similar to that of solid DMSO: pure DMSO is indeed characterized by strong dipole–dipole interactions which are very effective in the solid state where the effects due to the dynamical disorder of the liquid are absent.

Finally, the DMSO-H₂O 1 : 100 complex shows the highest wavenumbers, suggesting the existence of more strongly bonded complexes.

In the case of the DFT-calculated spectra, an analogous trend is obtained (Fig. 2). In particular, the DMSO dimer (model b) should

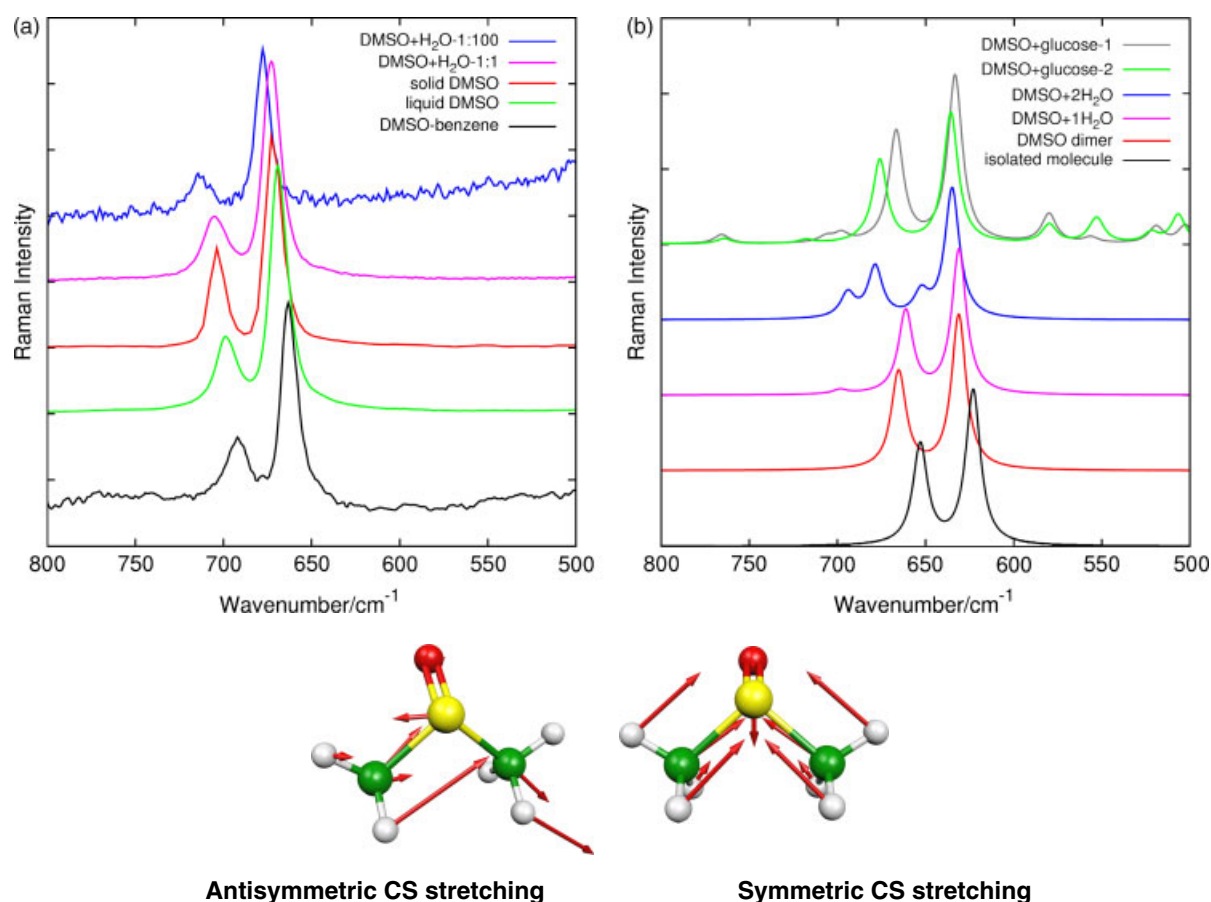


Figure 2. Comparison between experimental Raman spectra a) and DFT-computed (B3LYP/6-311++G**) spectra b) for the DMSO complexes (reported in Fig. 1) in the wavenumber range 500–800 cm^{-1} . The high wavenumber line is assigned to the antisymmetric CS stretching while the low wavenumber line is assigned to symmetric CS stretching. The computed vibrational displacements are shown below the spectra. Only BSSE uncorrected spectra are reported in the left panel. As discussed in the text, thanks to the rather extended basis set used (6-311++G**), no significant differences are found for the vibrational wavenumber when applying CP corrections. All the ratios reported refer to molar ratios (see text). This figure is available in colour online at www.interscience.wiley.com/journal/jrs.

be compared to the solid DMSO where DMSO dimers take up a well defined stable structure. According to the calculations, the DMSO-water dimer (with one only hydrogen bond, model c) has CS stretching wavenumbers very close to those of the DMSO dimer. This observation suggests that in a 1:1 solution, singly hydrogen-bonded DMSO dominate. The largest blue shift of CS stretchings observed at high DMSO dilution compares favorably with the results of our calculations for model d).

An analysis of the computed geometries shows that these effects are directly related to a change in the electronic structure as a consequence of intermolecular interactions. Also in the case of hydrogen bonding, these geometrical changes are not limited to the S=O bond, but extend to the remaining part of the molecule, accounting for the trends observed in the vibrational spectra. From the calculations it clearly appears that the formation of H bond is not limited to a sort of localized coulomb interaction between the acidic hydrogen and an electron-donating oxygen: the formation of the hydrogen bond induces an overall intramolecular charge rearrangement.

The top calculated spectra of Fig. 2 correspond to models f) and g). It can be seen that the Raman spectra behave in the same way as models c) and d). In other words, DMSO-glucose, where only one hydrogen bond is present, shows CS stretching lines very similar to those of model c), as expected. On the same ground,

DMSO-glucose with two hydrogen bonds is strictly related to model d).

On this basis, the analysis of the Raman spectra of amylose-DMSO complexes allows to distinguish the occurrence of one, two or no hydrogen bonds as revealed by the Raman spectra in the 600–800 cm^{-1} region.

In Table 1, the calculated S=O wavenumbers are reported for the different models. A red shift is found for increasing interaction strength, in very good agreement with the results of previous papers,^[30–41] thus supporting our present analysis.

Infrared spectra

In the previous section, we have shown that CS stretching lines are significantly sensitive to the strength of intermolecular interactions.

The interpretation of such spectroscopic features is based on the hypothesis that in water mixtures at different DMSO concentrations several species occur, namely complexes with one or two hydrogen bonds, and DMSO molecules with no hydrogen bonds, and suitable Raman markers in the CS stretching region have been proposed. The agreement between experimental and DFT-computed spectra turned out to be very good, thus supporting our interpretation.

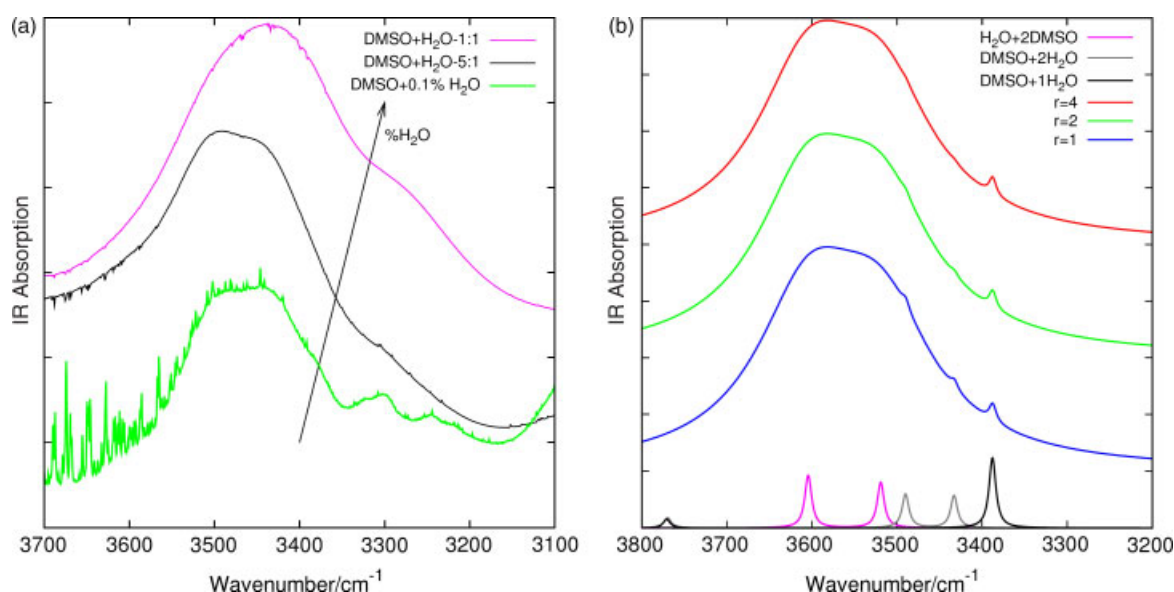


Figure 3. a) Experimental IR spectra in the OH stretching wavenumber range of mixtures of DMSO and H₂O at different relative molar ratios. b) Theoretical IR spectra built as a weighted sum of the contributions due to models c), d) and e). Different bandwidths were imposed to simulate the experimental spectra. Different spectra are reported for varying ratio ($r = C_c/C_d$) of the coefficients associated in the spectrum to models c) (C_c) and d) (C_d). For comparison, intensities have been normalized with respect to the number of the H₂O molecules which are present in each model. The spectra of each individual model are also reported at the bottom of the figure. All the ratios reported refer to molar ratios (see text). This figure is available in colour online at www.interscience.wiley.com/journal/jrs.

In order to find further support, the infrared spectra of DMSO/H₂O complexes have been analyzed both in the OH stretching and S=O regions for samples with very small or very large water content.

In Fig. 3 a) the experimental spectra in the OH stretching region of DMSO containing a very small fraction of water is shown and compared with the spectra of DMSO–H₂O 1 : 1 complex. As shown, in addition to the broad feature ascribed to doubly H-bonded water molecules, two minor features are found at lower wavenumbers.

In Fig. 3 b) the DFT-computed spectra are reported: a theoretical spectrum is built as the sum of the contributions from models c), d) and e) (see above). In the theoretical spectra, different coefficients have been introduced to describe the relative amount of the different species (see the caption of Fig. 3 for more details).

Since the water content is very low it is very likely that each DMSO is bonded to only one water molecule (models c) and e)).

Indeed, the comparison between the experimental and the theoretical spectra makes it possible to assign the broad band to DMSO molecules bridged by one water molecule (model e)) and the minor bands to DMSO–H₂O dimers (model c)). This model contributes to the simulated spectra with a larger weight than model d), as expected, due to the very low concentration of water in the sample.

If this conclusion is correct we should find further evidence also in the CS stretching region. Looking at the spectra reported in Fig. 4 we find that in the presence of a relatively small amount of water (DMSO–H₂O 5 : 1 complex) a broadening of the CS antisymmetric stretching band is observed. This is due to the occurrence of DMSO–H₂O complexes whose contribution can be extracted by subtracting the spectrum of pure liquid DMSO (red spectrum). The band obtained almost coincides with that of DMSO–H₂O 1 : 1 complex.

Therefore, according to the results obtained by the analysis of the OH stretching bands, we can conclude that the CS stretching

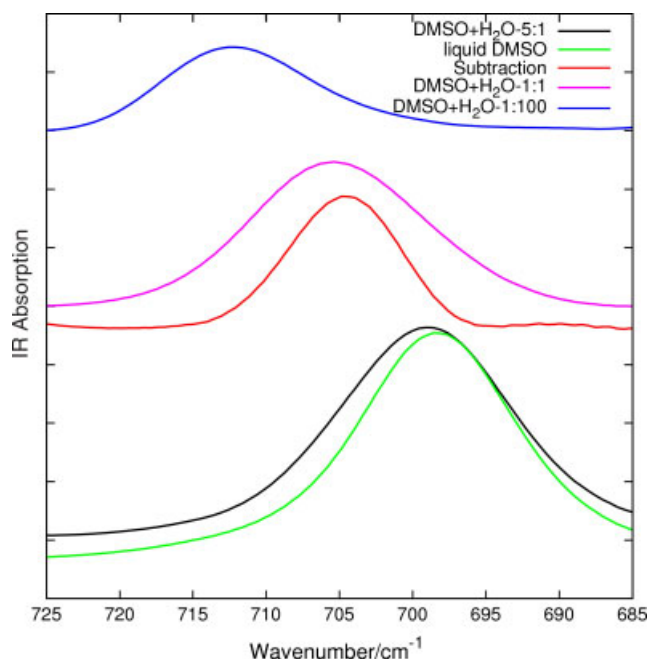


Figure 4. Experimental IR spectra in the antisymmetric CS stretching wavenumber range for the different samples analyzed (see text). All the ratios reported refer to molar ratios. This figure is available in colour online at www.interscience.wiley.com/journal/jrs.

band of 1 : 1 complex is a marker of DMSO–H₂O complexes with mostly only one hydrogen bond (models c) and e)).

As further support to the conclusions drawn above, in Fig. 5, the experimental IR spectra in the S=O stretching region are presented for samples where a large amount of water is present, that is the case of DMSO–H₂O 1 : 100 complex. If the assumptions discussed above are correct we should expect in this case that

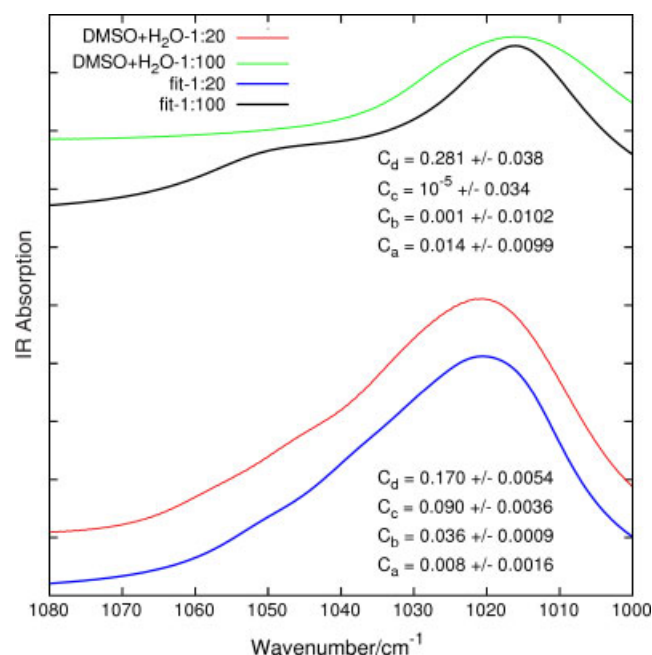


Figure 5. Experimental IR spectra in the SO stretching wavenumber range for the 1 : 100 and 1 : 20 DMSO-H₂O complexes (molar ratios). Experimental spectra are fitted by theoretical spectra built as a weighted sum of the contributions due to models a), b), c) and d). This figure is available in colour online at www.interscience.wiley.com/journal/jrs.

each DMSO molecule interacts via hydrogen bonds with two water molecules (model d)).

The experimental spectra are fitted with a theoretical spectrum built by summing the contributions of model a), b), c) and d). The coefficients of each contribution are determined by the fitting procedure. As illustrated in Fig. 5 the fit is satisfactory; moreover the largest coefficient (for both spectra analyzed) is that related to model d), that is, DMSO bonded to two water molecules.

Accordingly, in the case of DMSO-H₂O 1 : 100 complex, in the IR spectrum, a further upward wavenumber shift is found for the antisymmetric CS stretching (see Fig. 4).

This finding confirms that in the Raman spectra of the DMSO-H₂O 1 : 100 complex, the shifts observed in the CS stretching lines can be related to the occurrence of complexes characterized by two hydrogen bonds for each DMSO molecule.

In summary, by looking at the IR spectra of samples obtained in totally different and 'extreme' conditions (i.e. a very small or a very large amount of water in DMSO-H₂O solutions) and analyzing, respectively, the OH stretching and S=O stretching regions, we confirmed the assignments proposed in Section III.1 (Analysis of Raman Spectra) for the CS stretching lines.

Experimental Raman spectra of the amylose-DMSO complex

On the basis of the analysis reported in the previous sections, we now have all the elements for the interpretation of the spectra of amylose-DMSO complexes.

In Fig. 6, we report the experimental Raman spectrum of the amylose-DMSO complex in the solid state.

Both bands, and in particular, the antisymmetric CS stretching mode in the 700–720 cm⁻¹ range, reveal a broad feature where different components can be distinguished.

Spectral curve fitting has been applied by using two components (Fig. 6). The fitting procedure gives for the wavenumbers of

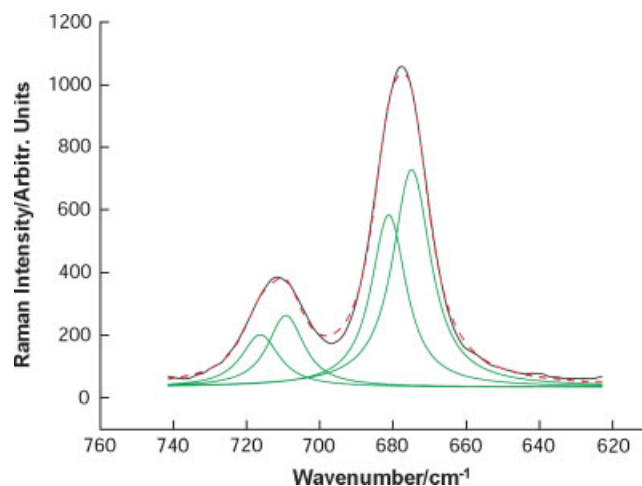


Figure 6. Experimental Raman spectra in the region 600–780 cm⁻¹ for the amylose-DMSO complex and resolution by curve fitting of the CS stretching lines into the two components related to DMSO interacting via two hydrogen bonds and one hydrogen bond (green). This figure is available in colour online at www.interscience.wiley.com/journal/jrs.

the two components the values 709–716 cm⁻¹ (antisymmetric CS stretching) and 675–681 cm⁻¹ (symmetric CS stretching) which match those of DMSO-H₂O 1 : 100 complex and DMSO-H₂O 1 : 1 complex.

In this way, we demonstrate that in amylose-DMSO solid state complexes, different kinds of complexes coexist and can be distinguished, namely DMSO interacting via one hydrogen bond, and DMSO interacting via two hydrogen bonds.

The first case can be ascribed to the presence of DMSO interacting on the external surface of the V-amylose helix where one only hydrogen bond is possible for one DMSO molecule; the last case can be interpreted as DMSO molecules trapped inside the amylose channel. This interpretation is consistent with the structure proposed by Winter and Sarko,^[12,13] based on x-ray diffraction experiments, where the DMSO molecules inside the helix are involved in two hydrogen bonds.

These results show that normal modes of DMSO (as revealed by Raman spectroscopy) are sensitive to different kinds of intermolecular interactions and can be used to characterize the structure and the properties of large amylose complexes. This allows Raman spectroscopy to be used in the characterization of new kinds of complexes which are currently investigated both in nanosciences and pharmaceutical research.

Conclusions

In this paper, the Raman spectra of several DMSO complexes have been analyzed both experimentally and theoretically. The effect of intermolecular interactions in the region of the CS stretchings shows systematic trends of the wavenumbers which have been rationalized with the occurrence of different complexes, characterized by different kinds of hydrogen bonds.

The analysis is applied to amylose-DMSO complexes and related theoretical models. On the basis of the results obtained for pure DMSO and its mixtures with water or benzene, markers are identified which demonstrate that different kinds of complexes are present. On this basis, it is possible to state that DMSO molecules are present both on the external surface and in the channel created by the helical V-amylose.

The high sensitivity of Raman spectroscopy to the structure of these DMSO-amylose complexes opens new ways for the application of this technique in the investigation of the different properties of such systems.

The wavenumber of the CS stretching lines can be used to obtain indications on the structure of V-amylose and their use can be generalized to the study of amylose complexes from DMSO solutions where different types of organic molecules (drugs, conjugated molecules, etc) are included.

Acknowledgment

This work has been supported by Project CARIPLO 2006: Self-assembled nanostructured materials for biological applications.

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