Infrared spectra and \textit{ab initio} calculations of matrix isolated dimethyl sulfone and its water complex

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The infrared spectrum of (CH\textsubscript{3})\textsubscript{2}SO\textsubscript{2} (dimethyl sulfone) trapped in several rare gas matrices is reported. Results are compared to previous gas phase and solid state spectra. In water-containing matrices, bands attributed to the (([CH\textsubscript{3}])\textsubscript{2}SO\textsubscript{2})\textsuperscript{n}([H\textsubscript{2}O]) molecular complex are identified. Spectral results are discussed with reference to the bonding scheme suggested by \textit{ab initio} calculations. The similarities to the previously recorded (H\textsubscript{2}SO\textsubscript{4})\textsuperscript{n}([H\textsubscript{2}O]) mode frequencies shed light on the bonding scheme of both. The complex formation between H\textsubscript{2}O and dimethyl sulfone was studied by \textit{ab initio} B3LYP computations using the aug-cc-pVTZ basis sets. The calculations show the existence of a stable 1 : 1 complex of \textit{C\textsubscript{2v}} symmetry, \(\Delta H = -21 \text{ kJ mol}^{-1}\), with a single O - H bond of one water hydrogen bonded to one oxygen of the sulfone.

Introduction

In the Antarctic troposphere, dimethyl sulfide and a variety of its oxidation products including dimethyl sulfoxide, methanethiosulfonic acid and dimethyl sulfone have been detected by Berresheim et al.\textsuperscript{1,2} Laboratory experiments provide different reaction channels and show how tropospheric OH radicals oxidize the dimethyl sulfide.\textsuperscript{3} Dimethyl sulfone is, in addition to methane sulfonic acid, a product of dimethyl sulfide oxidation. The infrared spectrum of (CH\textsubscript{3})\textsubscript{2}SO\textsubscript{2} was previously recorded in the crystalline,\textsuperscript{4} gas phase\textsuperscript{4–6} and liquid\textsuperscript{6} states. No reports of the matrix isolated spectrum were found.

Our interest in the interaction between methyl sulfone and water is twofold. Firstly, dimethyl sulfone, as a trace gas in the troposphere, may interact with ice water and contribute to aerosol formation. Secondly, the geometry and structure of this complex should help in the understanding of similar processes involving sulfuric acid and water. Interest in the water–sulfuric acid complex, (H\textsubscript{2}SO\textsubscript{4})\textsuperscript{n}([H\textsubscript{2}O]), arises mainly from its role in vapor phase nucleation of aerosols. In the troposphere, due to its large affinity to water, sulfuric acid is hydrated to form \((\text{H}_2\text{SO}_4)^n(\text{H}_2\text{O})_n\) \((n = 1–3)\) complexes\textsuperscript{7} or the condensed phase aerosol. In the stratosphere, where the ambient water vapor fraction is only 4–5 ppm, H\textsubscript{2}SO\textsubscript{4} and water exist in the free molecular form. The formation of sulfuric acid aerosols in the stratosphere is thus believed to occur via homogeneous nucleation, with the first step being an interaction between H\textsubscript{2}SO\textsubscript{4} and H\textsubscript{2}O in the vapor phase. For further dissociation of sulfuric acid more water molecules are needed, while some additional trace gases may also be included in the nucleation process.\textsuperscript{8}

Recently we conducted an extensive investigation of molecular H\textsubscript{2}SO\textsubscript{4} and several of its atmospheric molecular complexes. Infrared spectra of pure H\textsubscript{2}SO\textsubscript{4} and D\textsubscript{2}SO\textsubscript{4}\textsuperscript{9} as well as H\textsubscript{2}SO\textsubscript{4} complexes with CO\textsubscript{1,11} N\textsubscript{2}, NO, N\textsubscript{2}O\textsubscript{12}, HCl,\textsuperscript{13} and CO\textsubscript{2}\textsuperscript{14} trapped in solid argon matrices, have been reported. A bonding between the sulfuric acid OH moiety and the respective complexant characterizes all these complexes. This conclusion concerning the nature of the bonding scheme is mainly based on the observation of more significant red shifts of the acid OH bands of the complexes than those found for the relevant SO\textsubscript{2} modes.

While the 1 : 1 (H\textsubscript{2}SO\textsubscript{4})\textsuperscript{n}([H\textsubscript{2}O]) complex is the most important molecular complex of sulfuric acid,\textsuperscript{9} it is an exception to the above. Two \textit{ab initio} calculations\textsuperscript{15,16} indicate that the energetically preferred structure has the water molecule bonded, as expected, to the acidic OH hydrogen. Contrary to these predictions and to the other complexes, no red shifted v(OH) band associated with the 1 : 1 (H\textsubscript{2}SO\textsubscript{4})\textsuperscript{n}([H\textsubscript{2}O]) complex was found. Instead, a band associated with the 1 : 1 (H\textsubscript{2}SO\textsubscript{4})\textsuperscript{n}([H\textsubscript{2}O]) complex formation was recorded slightly blue shifted from the acid v(OH) band of H\textsubscript{2}SO\textsubscript{4}. The alternative attachment of an H\textsubscript{2}O molecule to the oxygens of the SO\textsubscript{2} moiety is significantly less preferred energetically by both calculations (40.6 vs. 11 kJ mol\textsuperscript{−1} and 38 vs. 2 kJ mol\textsuperscript{−1}). On the other hand, free SO\textsubscript{2} species are capable of attaching a water molecule via their central S atom, as suggested for oxygen isolated (SO\textsubscript{2})\textsuperscript{n}([H\textsubscript{2}O]) species\textsuperscript{17,18} and for the (SO\textsubscript{2})\textsuperscript{n}([H\textsubscript{2}O]) complex.\textsuperscript{19–23} Dimethyl sulfone, (CH\textsubscript{3})\textsubscript{2}SO\textsubscript{2} has a similar structure to H\textsubscript{2}SO\textsubscript{4} and a related symmetry (C\textsubscript{2v}) for H\textsubscript{2}SO\textsubscript{4} and C\textsubscript{2v} for (CH\textsubscript{3})\textsubscript{2}SO\textsubscript{2}. It was chosen for this study, as it is capable of attaching water through its SO\textsubscript{2} moiety only. The comparison of the analogous vibrational mode frequencies of (([CH\textsubscript{3}]\textsubscript{2}SO\textsubscript{2})\textsuperscript{n}([H\textsubscript{2}O]) (including the relevant computational results), with those of the (H\textsubscript{2}SO\textsubscript{4})\textsuperscript{n}([H\textsubscript{2}O]) complex may, then, shed light on the structure of both.

Experimental

Dimethyl sulfone (99%) was supplied by Aldrich, argon (99.996%) and nitrogen (99.999%) were provided by the Oxygen and Argon Works (Israel) and the krypton gas (99.995%) was supplied by Matheson. Water vapor was taken from deionised water submitted to several degassing cycles. The experimental details have been given previously.\textsuperscript{9} In short,
the vapors for deposition were taken from a few grains of \((\mathrm{CH}_3)_2\mathrm{SO}_2\) placed in a small glass tube held at room temperature or cooled by ice or solid carbon dioxide (‘dry ice’). Rare matrix gases, either pure or premixed with water, were either passed through the \((\mathrm{CH}_3)_2\mathrm{SO}_2\) vapor or deposited from a separate tube along with the \((\mathrm{CH}_3)_2\mathrm{SO}_2\) vapor beam. These samples (typically of 1:100–1:2000 ratios, as estimated from \(v\)/\(C_0\) dilutions) were condensed on a CsI window cooled to 17 K by an Air Products CSW 202A Heliplex cryostat. Deposition rates were in the range of several mmol h\(^{-1}\) and typical deposition times were of 1–4 h, depending upon sample dilutions. The temperature cycling of the samples was conducted by a slow warming (1 K min\(^{-1}\)) to 33–42 K, as appropriate for the relevant matrix, followed by a quick recooling to 17 K. Infrared spectra were recorded on a Bruker IFS 113v FTIR spectrometer, employing a DTGS detector and coaddung 32–128 scans at resolutions of 2–0.5 cm\(^{-1}\).

**Quantum chemical computations**

DFT computations were carried out with the Gaussian 98W suite of programmes\(^{25}\) employing the B3LYP functional.\(^{26}\) Dunning’s correlation consistent triple-zeta basis sets, aug-cc-pVTZ, which include both diffuse functions and polarization functions, was chosen to obtain a reasonably accurate geometry of the isolated molecules and bonding of complexes.

### Results and discussion

1. **The infrared spectrum of matrix isolated \((\mathrm{CH}_3)_2\mathrm{SO}_2\)**

The infrared spectra of monomeric \((\mathrm{CH}_3)_2\mathrm{SO}_2\) in argon, krypton and nitrogen matrices in the most relevant spectral regions are reproduced in Fig. 1. The monomer band frequencies (designated “M” in Fig. 1) in all three matrices are very similar and the matrix shifts relative to the gas phase values (mostly red) are quite small with a maximum of 1.6% for the antisymmetric \(\mathrm{SO}_2\) stretching mode. Table 1 lists the observed band positions, their description and assignments and the appropriate wavenumber values obtained from the theoretical calculation. The table also includes a comparison to previously published\(^4\) vapor and solid phase values. The full output of calculated vibrational frequencies, both scaled and unscaled, for the monomer along with those for its 1:1 complex with \(\mathrm{H}_2\mathrm{O}\) (discussed below), is listed in Table 2.

<table>
<thead>
<tr>
<th>Wavenumber/cm(^{-1})</th>
<th>((\mathrm{CH}_3)_2\mathrm{SO}_2)</th>
<th>Argon</th>
<th>Krypton</th>
<th>Nitrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>1360</td>
<td>A</td>
<td>F</td>
<td>M</td>
<td>B</td>
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<tr>
<td>1370</td>
<td>C</td>
<td>E</td>
<td>M</td>
<td>P</td>
</tr>
<tr>
<td>1380</td>
<td>F</td>
<td>D</td>
<td>M</td>
<td>P</td>
</tr>
</tbody>
</table>

Table 3 lists the most relevant calculated structural parameters for the monomer and the 1:1 \(((\mathrm{CH}_3)_2\mathrm{SO}_2)\mathrm{H}_2\mathrm{O}\) complex.

In the antisymmetric \(\mathrm{SO}_2\) stretching mode region the sharpest and strongest band was recorded at 1340.1 cm\(^{-1}\) (argon matrix), 1338 cm\(^{-1}\) (krypton) and 1336 cm\(^{-1}\) (nitrogen) and is assigned to the \((\mathrm{CH}_3)_2\mathrm{SO}_2\) species. The isotopically shifted \((\mathrm{CH}_3)_3^{34}\mathrm{SO}_2\) monomer is resolved, at higher resolutions, at 1322 cm\(^{-1}\) on the low frequency side of 1323.4 cm\(^{-1}\) (argon) dimer band. This \(^{34}\mathrm{S}\)–\(^{32}\mathrm{S}\) shift (17.8 cm\(^{-1}\), calculated 18.1 cm\(^{-1}\)) is very similar to that of argon matrix isolated \(\mathrm{SO}_2\) monomers.\(^{27}\) A very weak band (further reducing in intensity with temperature cycling) was found at 1309.3 cm\(^{-1}\) (argon), 1308.5 cm\(^{-1}\) (krypton) and 1310.8 cm\(^{-1}\) (nitrogen). As it does not retain a constant intensity ratio to the monomer band in different experiments it is most probably due to an impurity and need not be further considered.

The next strongest and sharpest band in the spectrum, the symmetric \(\mathrm{SO}_2\) stretching mode is observed at 1157.2 cm\(^{-1}\) (Ar), 1155.7 cm\(^{-1}\) (Kr) and 1159.4 cm\(^{-1}\) (N\(_2\)) for the main \((\mathrm{CH}_3)_2\mathrm{SO}_2\) isotopomer. The \((\mathrm{CH}_3)_2^{34}\mathrm{SO}_2\) isotopomer is calculated to be shifted by ~10.1 cm\(^{-1}\) from the main peak. The weak band at 1147.5 cm\(^{-1}\) is in the appropriate position.

It may be noted (Fig. 1(a) and (b)) that the symmetric and antisymmetric \(\mathrm{SO}_2\) stretches in the two noble gas matrices, shift in a parallel manner and retain an approximately constant wavenumber difference between them. In solid N\(_2\) the shifts result in a smaller frequency gap between the two modes. \(v_{1}(B_{1})\), the antisymmetric \(\mathrm{SO}_2\) stretch, shifts further to the red, as compared to its position in the noble gas matrices, whereas \(v_{2}(A_{1})\), the symmetric \(\mathrm{SO}_2\) stretch shifts to the blue of its position in Ar and Kr matrices. This indicates a stronger interaction of \((\mathrm{CH}_3)_2\mathrm{SO}_2\) with the matrix \(\mathrm{N}_2\) molecules as compared to the other, more inert matrices. It also shows the sensitivity of the S–O bonds to interactions, in line with the tendency of \((\mathrm{CH}_3)_2\mathrm{SO}_2\) to be involved in complexation via its \(\mathrm{SO}_2\) moiety.

In the vicinity of the monomer absorptions, additional bands are discerned and assigned to dimeric or higher polymeric species on the basis of the effects of variations in concentration (Fig. 2) and of temperature cycling (Fig. 3). The relevant bands are marked “D” and “P”, respectively, (in the figures). A summary of their wavenumber values and assignments is given in Table 4. We note the rather complicated pattern found in the \(\mathrm{SO}_2\) antisymmetric stretch region for all three matrices (Table 4, Fig. 1(a)), which is, again, in accord with the higher sensitivity of such modes to their environment.\(^{28}\) The weak \(^{34}\mathrm{S}\) isotopic band at 1147.5 cm\(^{-1}\) in the

![Fig. 1](image-url) Infrared spectra of matrix isolated \((\mathrm{CH}_3)_2\mathrm{SO}_2\) deposited as a 500 : 1 mixture at 17 K. A, Argon matrix; B, Krypton matrix; C, Nitrogen matrix. Band designations: M, monomer; M’, \(^{32}\mathrm{S}\) monomer; D, dimer; P, polymer; x, impurity band. (a) The \(\mathrm{SO}_2\) antisymmetric stretch region. (b) The \(\mathrm{SO}_2\) symmetric stretch region. (c) The \(\mathrm{CH}_3\) deformation region.
Table 1  Infrared band positions and assignments for monomeric (CH₃)₂SO₂ in various matrices (cm⁻¹)

<table>
<thead>
<tr>
<th>Argon</th>
<th>Krypton</th>
<th>Nitrogen</th>
<th>Vapor</th>
<th>Solid (cryst.)</th>
<th>Calculated</th>
<th>Assignment and description</th>
</tr>
</thead>
<tbody>
<tr>
<td>3023</td>
<td>3025</td>
<td>3025</td>
<td>3048</td>
<td>3040 (s)</td>
<td>3030 (2)</td>
<td>v₁₃(B₃) Antisymmetric CH₃ stretch</td>
</tr>
<tr>
<td>3026</td>
<td>3026</td>
<td>3026</td>
<td>3026</td>
<td>3026</td>
<td>3026 (0)</td>
<td>v₀₀(B₃) Symmetric CH₃ stretch</td>
</tr>
<tr>
<td>3024</td>
<td>3024</td>
<td>3024</td>
<td>3024</td>
<td>3024</td>
<td>3024 (1)</td>
<td>v₁₂(B₂) Symmetric CH₂ deformation</td>
</tr>
<tr>
<td>2942</td>
<td>2942</td>
<td>2942</td>
<td>2942</td>
<td>2942</td>
<td>2942 (2)</td>
<td>v₁₂(B₂) Symmetric CH₂ deformation</td>
</tr>
<tr>
<td>1437</td>
<td>1437</td>
<td>1437</td>
<td>1437</td>
<td>1437</td>
<td>1437 (8)</td>
<td>v₀₆(B₆) Antisymmetric CH₄ deformation</td>
</tr>
<tr>
<td>1419</td>
<td>1419</td>
<td>1419</td>
<td>1419</td>
<td>1419</td>
<td>1419 (7)</td>
<td>v₁₂(B₂) Symmetric CH₂ deformation</td>
</tr>
<tr>
<td>1340.1</td>
<td>1340</td>
<td>1340</td>
<td>1340</td>
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</tr>
<tr>
<td>1157.2</td>
<td>1157</td>
<td>1157</td>
<td>1157</td>
<td>1157</td>
<td>1157 (160)</td>
<td>v₁₂(B₂) Symmetric SO₂ stretch</td>
</tr>
<tr>
<td>931.1</td>
<td>931.1</td>
<td>931.1</td>
<td>931.1</td>
<td>931.1</td>
<td>931.1 (s)</td>
<td>CH₃ deformation</td>
</tr>
<tr>
<td>747.2</td>
<td>747.2</td>
<td>747.2</td>
<td>747.2</td>
<td>747.2</td>
<td>747.2 (s)</td>
<td>SO₂ bend</td>
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<tr>
<td>687.8</td>
<td>687.8</td>
<td>687.8</td>
<td>687.8</td>
<td>687.8</td>
<td>687.8 (s)</td>
<td>SO₂ twist</td>
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<td>493.6</td>
<td>493.6</td>
<td>493.6</td>
<td>493.6</td>
<td>493.6</td>
<td>493.6 (s)</td>
<td>SO₂ rock</td>
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<tr>
<td>461.3</td>
<td>461.3</td>
<td>461.3</td>
<td>461.3</td>
<td>461.3</td>
<td>461.3 (s)</td>
<td>C-S-C bend</td>
</tr>
</tbody>
</table>

Data from ref. 4. *'Scaled values from B3LYP/aug-cc-pVTZ calculation, see text. Numbers in parentheses indicate calculated intensities in km mol⁻¹. † Letters in parentheses indicate relative intensities: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; vvw, very very weak.

symmetric S–O₂ stretch region also shows dimeric character (concentration and temperature cycling dependence of its intensity) and is somewhat more intense than expected from isotopic abundance. There is also no alternative dimer band in the region of this mode.

For the ((CH₃)₂SO₂)₂ dimer, we note that both SO₂ stretch modes are red shifted relative to their monomer counterparts, while all other bands (the S–C stretches, SO₂ bend and wag and the CH₃ deformation) are blue shifted. These trends are in accord with the shift in band position from monomer vapor to solid state, as listed in Table 1. In contrast, the SO₂ bands of the polymer demonstrate a different pattern, in that they are discerned at both the blue and the red sides of the monomer absorptions.

The tentative dimer structure most compatible with the number of observed S–O stretching bands is an open configuration, where only a single S–O moiety links to the CH₃ group of the second (CH₃)₂SO₂ molecule. Such a bonding scheme would be characterized by one asymmetric and one symmetric stretch of the free SO₂ moiety and two additional S–O stretches of the bonding SO₂ group. Such a structure would be analogous to the bonding scheme for the complex of (CH₃)₂SO₂ and H₂O, described below. It is also, a structure that can lead to further polymerization and, eventually, to the formation of the solid phase, in contrast to other conceivable closed ring structures.

2. (CH₃)₂SO₂ in water doped rare gas matrices

(a) Spectral results. When a small fraction (~0.5%) of water is mixed into the matrix gas, new spectral features may be discerned, both in the region of the H₂O absorptions and in the vicinity of the main (CH₃)₂SO₂ vibrational modes. These new bands in argon and krypton matrices are summarized in Table 5 and the relevant spectra are shown in Fig. 4 and 5, respectively. In nitrogen matrices the new (weak) bands are probably masked by the polymeric dimethyl sulfone lines.

The complicated spectral pattern in the ν(OH) stretch region of H₂O (Fig. 4(a)) recorded in an argon matrix, comprises previously assigned water bands²⁹–⁴⁵ including the rotating and non-rotating monomers,²⁹–³²,³⁷,³⁸,⁴² dimers,³³,³⁴,³⁵,³⁶,³⁷,³⁸,³⁹,⁴⁰,⁴¹,⁴² and higher polymers.⁴² In addition to these, a new prominent band, irreversibly enhanced by temperature cycling, is recorded at 3568 cm⁻¹. In a krypton matrix, a corresponding, although slightly weaker band is found at 3564 cm⁻¹. Their positions are close to the bands assigned²⁹ to the (H₂SO₄)⁺(H₂O) complex (3572.6 cm⁻¹) and to the ν₁(H₂O) stretch of monomeric H₂SO₄ (3566.7 cm⁻¹) discussed in the Introduction. H₂SO₄ is not involved in the present experiments, nor is it likely to be formed. Obviously, none of the other prominent H₂SO₄ lines were observed (e.g. the strong ν₁(b) antisymmetric SO₂ stretch at 1452.4 cm⁻¹ or the ν₁(a) symmetric S–C stretch at 881.7 cm⁻¹). Furthermore, the bands grow upon temperature cycling of the matrix temperatures, the most obvious characteristic of a complex band. We, therefore, assign the 3568 cm⁻¹ (argon) and 3564 cm⁻¹ (krypton) bands to the bonded ν(OH) stretch of the H₂O moiety in the ((CH₃)₂SO₂)⁺(H₂O) complex, red shifted 70 cm⁻¹ from the ν₁(H₂O) of argon isolated, non-complexed water monomer at 3638 cm⁻¹.⁹ The more appropriate shift to consider, in view of the bonding scheme of the complex suggested by the theoretical computation, is from the “uncoupled” ν(OH) wavenumber value, derived from (v₁(H₂O) + ν₁(H₂O))/2 = (3735.7 + 3638)/2 = 3686.9 cm⁻¹.⁹ Thus the observed value for this shift is −119 cm⁻¹, as compared to the analogous red shift obtained from the calculated band positions of 3520 − (3756 + 3656)/2 = −186 cm⁻¹ (Tables 2 and 5). The corresponding “free” stretching mode of the complexed H₂O moiety cannot be assigned with a sufficient degree of certainty as its intensity is not enhanced by hydrogen bonding and it is expected to fall in the complicated spectral...
Table 2  Calculated band positions (cm\(^{-1}\)) and intensities (km mol\(^{-1}\)) of the modes of vibration of monomeric H\(_2\)O and (CH\(_3\))\(_2\)SO\(_2\) and of the 1 : 1 ((CH\(_3\))\(_2\)SO\(_2\))\(^+\)(H\(_2\)O) complex (cm\(^{-1}\))

\[\text{Table 3} \quad \text{The calculated main structural parameters of monomeric (CH\(_3\))\(_2\)SO\(_2\) (C\(_2v\) symmetry) and of the 1 : 1 ((CH\(_3\))\(_2\)SO\(_2\))\(^+\)(H\(_2\)O) complex (C\(_3v\) symmetry)}\]
region of 3690–3640 cm\(^{-1}\), where the rotating H\(_2\)O monomer and H\(_2\)O multimer bands are active (Fig. 4(a)).

In the \(n(H_2O)\) bending mode region, again an extra band is recorded at 1598 cm\(^{-1}\) with H\(_2\)O-contaminated argon as matrix (Fig. 4(b)). It is similarly assigned to the H\(_2\)O moiety of the \(((CH_3)_2SO_2)^*(H_2O)\) complex. This band is blue shifted by 8 cm\(^{-1}\) (0.5%) relative to the band of the non-complexed water. The calculation predicts only a very slightly larger (0.8%) blue shift, as a result of complexation.

Turning to the dimethyl sulfone spectral absorptions, we find two extra bands in the SO\(_2\) stretch regions at 1326 and 1150 cm\(^{-1}\) (Fig. 4(c) and (d) argon) and 1325 cm\(^{-1}\) and 1153 cm\(^{-1}\) (Fig. 5(a) and (b), krypton). The argon and krypton frequencies are almost identical, in support of their assignment to non-monomeric species, which are less affected by the matrix environment. No other bands assignable to the water–dimethyl sulfone complex were found in the vicinity of the \((CH_3)_2SO_2\) fundamental modes.

Although the theoretical calculation detailed below suggests an interaction scheme of a single O–H bond of H\(_2\)O with a single S=O bond of \((CH_3)_2SO_2\), in \(((CH_3)_2SO_2)^*(H_2O)\) the strength of interaction is still such that the coupling of the two S=O bonds is retained. Both the antisymmetric and symmetric stretches are comparably red shifted from their free molecule positions so that the frequency difference between both modes in \((CH_3)_2SO_2\) and in the \(((CH_3)_2SO_2)^*(H_2O)\) complex are still very similar, 183 and 176 cm\(^{-1}\), respectively. These frequency differences are also very close to those in the theoretically calculated structure (181 and 180 cm\(^{-1}\), respectively).

Further spectroscopic facts support the existence of an \(((CH_3)_2SO_2)^*(H_2O)\) molecular complex of the above configuration. The wavenumber value of the bonded \(\nu(OH)\) stretch (3568 cm\(^{-1}\)) is very close to that of the water dimer (3574 cm\(^{-1}\)), and the \(\nu\) value for the water dimer is proposed to be related to \((\Delta \nu)^{1/2}\), where \(\Delta \nu = \nu_{\text{gas}} - \nu_{\text{complex}}\). The similar spectral shifts thus indicate that the bonding enthalpy per bond, \(\Delta H\), of both complexes is also comparable. Considering the experimental \(\Delta H\) values for single bonded H\(_2\)O...H\(_2\)O dimer and for ice,\(^{16}\) we can estimate the binding energy of a single bond in the \(((CH_3)_2SO_2)^*(H_2O)\) complex to be about \(-22\) kJ mol\(^{-1}\). The \(ab\) initio calculation results in a very similar value of the stabilization energy, \(-21\) kJ mol\(^{-1}\). The calculated interaction scheme, involving one hydrogen of the H\(_2\)O molecule is illustrated in Fig. 6.

Fig. 2  Concentration effects on the infrared spectrum of argon matrix isolated \((CH_3)_2SO_2\) species, as deposited at 17 K. A, 2000 : 1 sample; B, 500 : 1 sample; C, 100 : 1 sample; Band designations: M, monomer; M\(^{0}\), 34S monomer; D, dimer; P, polymer; x, impurity band. (a) The SO\(_2\) antisymmetric stretch region. (b) The SO\(_2\) symmetric stretch region. (c) The CH\(_3\) deformation mode region. (d) The antisymmetric and symmetric S–C stretching mode region. (e) The SO\(_2\) bend and wag mode region. Traces A are not included as the appropriate bands are too weak to be discerned.
molecule and of the water molecule show significant changes as a result of complexation.

The calculated harmonic frequencies of H$_2$O and (CH$_3$)$_2$SO$_2$ deviate slightly from the observed values. A scaling of the harmonic force field, involving 2 and 5 parameters for H$_2$O and (CH$_3$)$_2$SO$_2$, respectively, was therefore launched to obtain an agreement between observed and calculated wavenumbers of the free molecules. The force fields were scaled according to the procedure 

$$ F_{\text{scaled}}^{ij} = F_{\text{calc}}^{ij} \sqrt{\alpha_i \alpha_j} ,$$

where $\alpha_i$ and $\alpha_j$ are scaling parameters for the valence coordinates $i$ and $j$, respectively.

The scaling factors were: S=O (1.101), C–S (1.147), C–H (0.920), OSO= =OSC=CSC (1.110), SCH–HCH (0.967), O–H (0.928), and HOH (0.961). The results for (CH$_3$)$_2$SO$_2$ are shown in Tables 1 and 2.

The calculated fundamental modes of vibration, including their infrared intensities, of free H$_2$O and (CH$_3$)$_2$SO$_2$ are listed in Table 2 and compared there to those of the 1 : 1 complex. The above-mentioned scaling factors were also applied to the calculated harmonic force field of the complex. As can be seen, the calculations predict a number of distinct shifts upon complexation. Naturally, the most noticeable shifts are connected with the OH stretching modes of H$_2$O. According to the calculations the two modes are best described as “bonded” and “free” OH stretching vibrations. Relative to the average of the stretching frequencies in monomeric water, the former is predicted with a red shift of 186 cm$^{-1}$ and a considerable intensity enhancement, the latter with a blue shift of 25 cm$^{-1}$ and no significant intensity change. Further, the calculations predict complex bands of medium infrared intensity around 560 and below 400 cm$^{-1}$. We did not find a suitable band in the spectral region around 550 cm$^{-1}$ and the region below 400 cm$^{-1}$ was not accessible. The two modes are best described as a motion of the H-bonded water hydrogen perpendicular to and in the plane defined by O=S=O. As such, they would give rise to a spectral feature of great width and, hence, of low peak height, which would render it not discernible in a spectral range, rich with polymeric bands (Table 4).

We note that a B3LYP/aug-cc-pVTZ calculation produces a much better fit of vibrational frequencies and intensity ratios than an MP2/cc-pVDZ calculation, indicating the importance of the inclusion diffuse function in calculations of longer range interactions characteristic of molecular or hydrogen bonded complexes. Unfortunately, with current software and hardware limitations, it is not possible to carry out an MP2/aug-cc-pVTZ calculation on the complex.

Fig. 3 Annealing effects on the infrared spectrum of argon matrix isolated (CH$_3$)$_2$SO$_2$, 500 : 1 mixture. A, As deposited at 17 K; B, temperature cycled to 40 K. Band designations: M, monomer; M', 34S monomer; D, dimer; P, polymer; x, impurity band. (a) The SO$_2$ antisymmetric stretch region. (b) The SO$_2$ symmetric stretch region. (c) The CH$_3$ deformation mode region. (d) The S–C antisymmetric and symmetric stretches. (e) The SO$_2$ bend and wag region.

Similarities in the ((CH$_3$)$_2$SO$_2$)*H$_2$O and (H$_2$SO$_4$)*H$_2$O bonding schemes

There is a strong resemblance in the spectral shifts of the bonded ν(OH) frequency of the argon isolated ((CH$_3$)$_2$SO$_2$)*H$_2$O complex (3568 cm$^{-1}$) and the ν(OH) band observed$^a$ at 3572.6 cm$^{-1}$ for the (H$_2$SO$_4$)*H$_2$O complex. Two $ab$ $initio$ calculations$^{15,16}$ suggest that the most stable structure for the latter has the water molecule H-bonded via the acid OH group. According to these computations, the alternative structure involving a bonding of the H$_2$O hydrogens to the SO$_2$ moiety shows an energy minimum, but is
significantly less stable. However, we did not observe the red shift of the bonded acid ν(OH) mode in the predicted regions for the calculated more stable configuration. Instead, a clear band was recorded, on the blue side of the free ν(OH) of the acid at 3572.6 cm⁻¹. A recent isotopic substitution experiment involving H₂¹⁸O red shifted this band by 12 cm⁻¹ (0.33%) to 3560.6 cm⁻¹ showing it to be due to the complexed water molecule rather than to the acid moiety. A very similar isotope shift (13.6 cm⁻¹, 0.37%) was recorded for the O¹⁸O substituted donor moiety in the water dimer.[49] A similar shift was observed for the ν(OH) stretch of complexed H₂O in solid Ar (ref. 9). The infrared spectra of rare gas samples were measured for the calculated more stable configuration. Instead, a clear band was recorded, on the blue side of the free ν(OH) of the acid at 3572.6 cm⁻¹. A recent isotopic substitution experiment involving H₂¹⁸O red shifted this band by 12 cm⁻¹ (0.33%) to 3560.6 cm⁻¹ showing it to be due to the complexed water molecule rather than to the acid moiety. A very similar isotope shift (13.6 cm⁻¹, 0.37%) was recorded for the O¹⁸O substituted donor moiety in the water dimer.[49] A similar shift was observed for the ν(OH) stretch of complexed H₂O in solid Ar (ref. 9).

### Conclusions

The infrared spectra of rare gas/(CH₃)₂SO₂/H₂O samples show clear evidence of a complexing interaction between a water molecule hydrogen and a dimethyl sulfone SO₂ moiety. This bonding scheme is also supported by the ab initio calculations. The frequency similarity between bands assigned to the ((CH₃)₂SO₂)⁺(H₂O) and (H₂SO₄)⁺(H₂O) complexes indicates the possibility that also for the 1 : 1 sulfuric acid-water complex, the water molecule attaches itself to the acid through its SO₂ group and not through the acidic O–H groups, as previously suggested both spectroscopically and theoretically.[5,16]
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References


Fig. 4 Infrared spectrum of Ar/H$_2$O/(CH$_3$)$_2$SO$_2$ samples. A, 1 : 500 (CH$_3$)$_2$SO$_2$ : Ar sample, temperature cycled 17 K → 24 K → 17 K; B, 1 : 2 : 500 (CH$_3$)$_2$SO$_2$ : H$_2$O : Ar sample, temperature cycled 17 K → 24 K → 17 K. Band designations: M, monomer; M', 34S monomer; D, dimer; P, polymer; x, impurity band. (a) H$_2$O stretching modes region. (b) H$_2$O bending mode region. (c) The SO$_2$ antisymmetric stretch region. (d) The SO$_2$ symmetric stretch region.

Fig. 5 Infrared spectrum of Kr/H$_2$O/(CH$_3$)$_2$SO$_2$ samples. A, 1 : 500 (CH$_3$)$_2$SO$_2$ : Kr sample, temperature cycled 17 K → 24 K → 17 K; B, 1 : 2 : 500 (CH$_3$)$_2$SO$_2$ : H$_2$O : Kr sample, temperature cycle 17 K → 24 K → 17 K. Band designations: (*), ((CH$_3$)$_2$SO$_2$)*(H$_2$O) complex band; M, monomer; M', 34S monomer; D, dimer; P, polymer. (a) The SO$_2$ antisymmetric stretch region. (b) The SO$_2$ symmetric stretch region.

Fig. 6 The 1 : 1 ((CH$_3$)$_2$SO$_2$)*(H$_2$O) complex structure. (Numbers in parentheses designate changes from the free molecule values.)