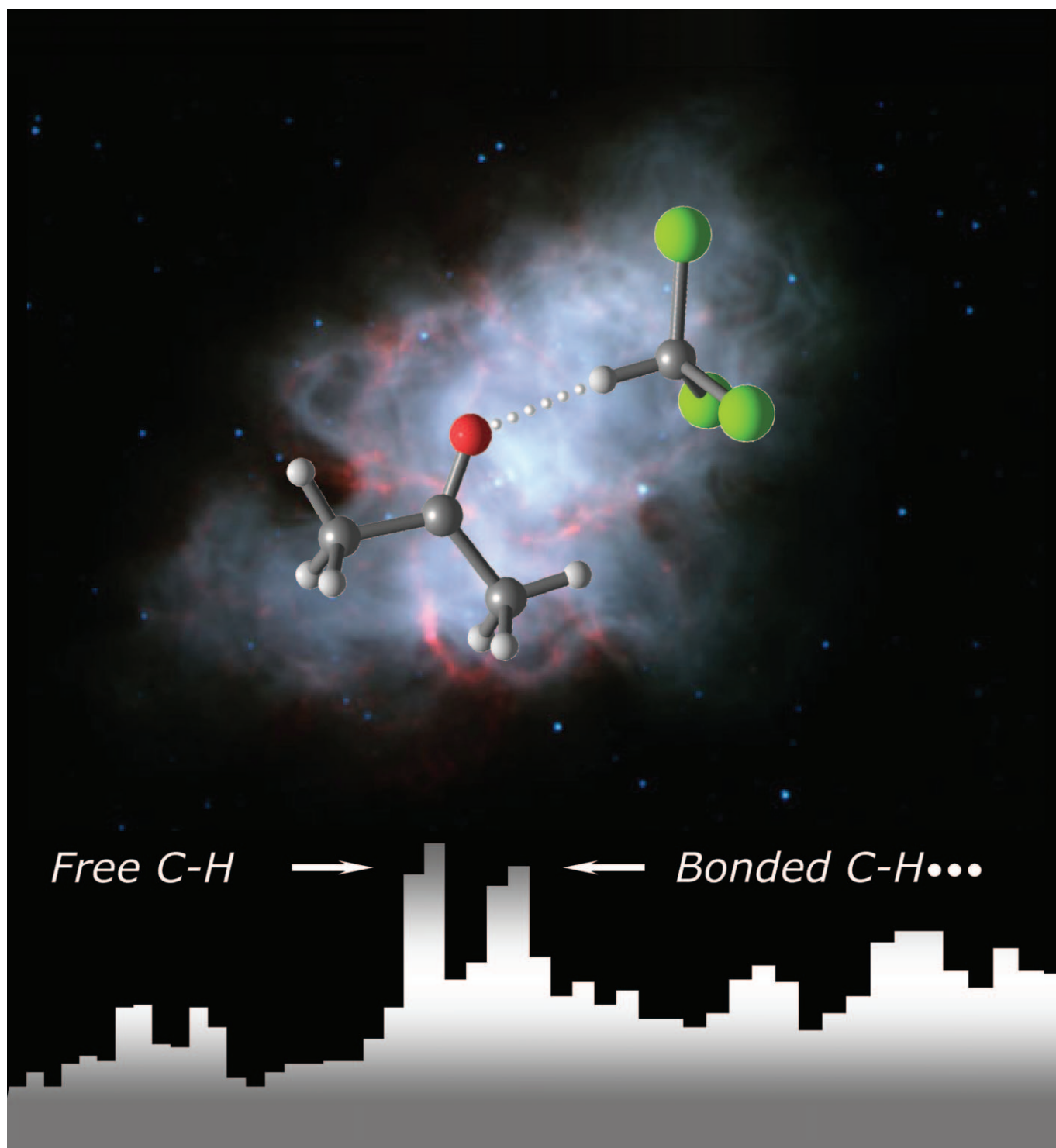


Hydrogen-Bond Dynamics of C–H...O Interactions: The Chloroform...Acetone Case

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Abstract: Spectroscopic evidence for C–H...O hydrogen bonding in chloroform...acetone $[\text{Cl}_3\text{CH}\cdots\text{O}=\text{C}(\text{CH}_3)_2]$ mixtures was obtained from vibrational inelastic neutron scattering (INS) spectra. Comparison between the INS spectra of pure samples and their binary mixtures reveals the presence of new bands at about 82, 130 and 170 cm^{-1} . Assignment of the 82 cm^{-1} band to the $\nu\text{O}\cdots\text{H}$ anti-translational mode is con-

sidered and discussed. In addition, the $\beta\text{C}\text{--}\text{H}$ mode of CHCl_3 at 1242 cm^{-1} is split in the spectra of the mixtures, and the high-wavenumber component is assigned to the hydrogen-bonded com-

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plex. The plot of the integrated intensity of this component shows a maximum for $x=0.5$, in agreement with the 1:1 stoichiometry of the chloroform...acetone complex, with a calculated complexation constant of 0.15 $\text{dm}^3\text{mol}^{-1}$. Results also show that the complex behaves as an independent entity, that is, despite being weak, such interactions play a key role in supramolecular chemistry.

Introduction

Although widely studied, hydrogen bonding still has many aspects that remain unresolved. Hydrogen bonds are important in establishing three-dimensional structures not only in solids but also in liquids.^[1] Such interactions are therefore relevant in supramolecular chemistry ranging from materials to biological systems. Most hydrogen-bonding interactions are described as X–H...Y, where X is an electronegative atom (halogen, N, O) and Y is an available electron pair of an electronegative atom or an excess of electron density (e.g., π electrons). Weaker hydrogen bonds of the C–H...O type have been clearly established in the solid phase,^[2] but experimental evidence of such interactions in the liquid phase is rather more scarce; for example, early experimental work on the interactions between acetone and water portray it in terms of this type of hydrogen bond.^[3,4] This type of C–H...O interaction has been the subject of much discussion, especially concerning the spectral features of systems in which shortening of the C–H bond length is associated with an increase in frequency (or blue-shift) and decrease in intensity of the corresponding stretching vibrational mode ($\nu\text{C}\text{--}\text{H}$) involved in the interaction.^[5,6] Recently, theoretical cal-

culations have shown that the “direction” of the shift (red or blue) is the result of an interplay of hyperconjugation and rehybridisation mechanisms that occur during the interaction.^[7] This has been corroborated and provided with a unified explanation of how red shifts, blue shifts or no shifts are associated with the $\nu\text{C}\text{--}\text{H}$ mode of the hydrogen bonds in the interacting systems.^[8] As opposed to this seemingly random behaviour of the stretch (vibration that entails change in the bond length), the $\beta\text{C}\text{--}\text{H}$ deformation mode (vibration that entails change in the angle between two bonds) responds in a much more understandable way and always shows an increased frequency upon hydrogen-bond formation. To provide an experimental probe for such interactions in the liquid phase some workers have used chloroform as the donor. Chloroform is convenient because it has only a single CH group and thus facilitates experimental work.^[9] The chloroform...acetone system is one of the most studied C–H...O hydrogen-bonded complexes. This system is historically related to the first experimental evidence of C–H...O hydrogen bonding,^[10] and still remains a somewhat challenging problem for vibrational spectroscopic studies. Although compelling evidence for the presence of C–H...O hydrogen bonds in chloroform...acetone mixtures has been found by several techniques,^[10–16] the evidence obtained from vibrational spectroscopy is scarce. Both $\nu\text{C}=\text{O}$ (acetone) and $\nu\text{C}\text{--}\text{H}/\text{D}$ modes (chloroform and [D]chloroform) show very small frequency shifts from the pure liquids to mixtures,^[9,17] in contrast with several C–H...O systems.^[18–26]

Experimental observation of the hydrogen-bond $\nu\text{H}\cdots\text{O}$ mode (the anti-translational mode) in chloroform...acetone mixtures would be clear evidence of C–H...O hydrogen bonds and give indications of its strength. However, due to its weak predicted intensity in both Raman and IR spectra, as well as the experimental difficulties of the low-wavenumber region, direct observation of the $\nu\text{H}\cdots\text{O}$ mode of C–H...O hydrogen bonds remains a challenge.

Inelastic neutron scattering (INS) spectroscopy has unique capabilities to answer this question by overcoming the limitations of far-IR and Raman spectroscopy, since the large cross section of the hydrogen nucleus makes this technique particularly sensitive to the motion involving H atoms, such as the anti-translational $\nu\text{H}\cdots\text{O}$ mode. A signifi-

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cant drawback of this technique is the need to acquire spectra at very low temperature (below 20 K). This makes comparisons with data from IR and Raman spectroscopy, obtained from liquids at room temperature, more difficult and it must be done with caution.

Here we reassess the interaction in the chloroform...acetone system in the light of a vibrational spectroscopy study using the INS technique. The INS spectra of several chloroform...acetone mixtures are reported with the aim of identifying spectroscopic evidence for the presence of C–H...O bonded dimers. Such evidence includes the low frequency ν H...O stretching (anti-translational) mode and the chloroform β C–H mode, which is found to be sensitive to complex formation.

Results and Discussion

Ab initio calculations: Ab initio calculations were performed for the chloroform...acetone complex to predict the spectral features associated with complexation. The calculated structure (C_s symmetry) of the lowest energy minimum is shown in Figure 1. The calculation yielded a dimerisation energy of $-16.4 \text{ kJ mol}^{-1}$ after correction for basis-set superposition error (BSSE), in agreement with previous work,^[7,23] and predicts that the C–H and C=O bond lengths of chloroform and acetone, respectively, increase upon complex formation.

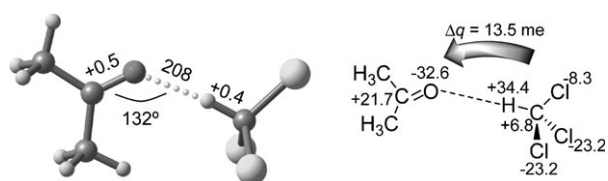


Figure 1. Representation of the chloroform...acetone complex at the B3LYP/6-31G** level in C_s symmetry: optimised structure (left; values in pm) showing the H...O distance; NBO charge transfer (right; values in mlielectrons). All values show variations from the isolated molecules. The value above the arrow is net charge transfer.

An NBO population analysis showed a net charge transfer of 13.5 me from chloroform to acetone, that is, electron-density transfer is predicted to occur from the proton-acceptor to the proton-donor molecule (Figure 1). This represents the characteristic charge transfer from lone pairs (LP) of the carbonyl group (proton acceptor) to the C–H σ^* antibonding orbitals of the proton donor (Table 1). From this calculation, a Wiberg index (bond order) of 0.030 for the C–H...O intermolecular contact is obtained. This value is clearly above the range of values obtained for similar C–H...O hydrogen bonds (ca. 0.005–0.019 at the same level of theory).^[19,18,22]

The existence of an intermolecular interaction is also predicted to induce changes in some vibrational modes. Table 2 summarises the calculated wavenumbers of a few relevant

Table 1. NBO analysis of the chloroform...acetone complex: relevant contributions and respective energies.

Interaction	Energy ^[a] [kJ mol ⁻¹]
$O_{LP1} \cdots \sigma^*_{C-H}$	15.8
$O_{LP2} \cdots \sigma^*_{C-H}$	20.7
$O_{LP2} \cdots Ryd^*_{H^{[b]}}$	0.5

[a] Threshold for printing was 0.5 kJ mol⁻¹. [b] Ryd = Rydberg orbital.

Table 2. Calculated wavenumbers (cm⁻¹) for selected modes of chloroform, acetone and chloroform...acetone complex (values corrected with scale factor of 0.9614).

Mode	Free molecules	Complex	Shift
ν C–H	3065	3030	-35
ν C=O	1751	1734	-17
β C–H	1202	1267	65
ν H...O	–	93 ^[a]	–

[a] Unscaled.

vibrational modes of the free chloroform and acetone molecules and those of their complex.

Here we should mention the possibility of C–H...Cl interactions. Based on the calculated chloroform...acetone complex geometry it was found that the H...Cl distance is 354 pm, which is counter-indicative of any such interaction. This is confirmed by the NBO analysis, which after careful analysis of the Wiberg bond orders and the energy contributions revealed no evidence of such interaction.

Whereas the calculated red-shift of the ν C–H (chloroform) and ν C=O (acetone) modes are consistent with lengthening of both bonds upon complexation, the blue-shift of the β C–H (chloroform) mode is an expected result of the restriction imposed by the hydrogen bond.

Since the number of normal modes in a molecule is $3N-6$, chloroform and acetone are expected to have 9 and 24 modes, respectively (33 in total). The chloroform...acetone complex has 39 vibrational modes, that is, an extra six internal modes that are specific to the complex itself. Results from DFT calculations at the B3LYP/6-31G** level show that these modes are expected at 93, 63, 58, 41, 27 and 23 cm⁻¹. Previous works^[27,28] portrayed the new vibrational modes in a simplified way. For this particular system they can be ascribed as follows: one anti-translational (ν H...O) mode, four intermolecular bending modes and one internal torsion. According to previous results,^[29] the anti-translational mode is expected to be well isolated from the other low-frequency modes. Thus, assuming that the plane of the complex is the same as that of the acetone skeleton (Figure 1), the in-plane intermolecular modes are predicted at 41 and 58 cm⁻¹, and the out-of-plane intermolecular modes at 27 and 63 cm⁻¹. The lowest wavenumber mode at 23 cm⁻¹ is the torsion mode, while that at about 93 cm⁻¹ is the anti-translational mode. The atomic motions of the intermolecular modes (in-plane bending, out-of-plane bending and anti-translational) are shown in a short movie in the Supporting Information.

We stress that the calculated low-wavenumber modes should be handled with care. In fact, since such modes correspond to intermolecular vibrational modes in weakly interacting systems, small forces are involved. This then gives rise to a high degree of anharmonicity, which is ignored by most calculations. As a result, the analysis of such modes is of limited accuracy.

Raman spectroscopy: Raman spectroscopy provides helpful information in the study on this system. The results obtained agree with the calculations above, and the analysis of the region of the $\nu\text{C-H}$ mode shows that consecutive addition of acetone to chloroform shifts the band maximum towards higher wavenumbers.

This behaviour is expected due to the change in the polarizability of the medium (i.e., non-specific interactions) and has already been demonstrated by some of us previously.^[9] Despite this, a broadening towards lower wavenumbers is concomitantly observed due to the specific C–H...O interaction. This red-shifted tail can be assigned to the “hydrogen-bonded” form of the chloroform...acetone complex. In addition, it is possible to obtain information concerning the number of species present in the liquid phase through the presence or absence of a pseudo-isosbestic point, by following the procedure described by Shurvell et al.^[24,25] A pseudo-isosbestic point is observed whenever only two species contribute to the band profile, while its absence indicates the presence of more than two species in equilibrium.^[24,25] Figure 2 shows the room-temperature Raman spectra of solutions of chloroform in $[\text{D}_6]$ acetone (required to observe conveniently the $\beta\text{C-H}$ and $\nu\text{C-H}$ regions) in the $\nu\text{C-H}$ region, with bands normalised to unit intensity and after correction of the band maxima due to the non-specific interactions.

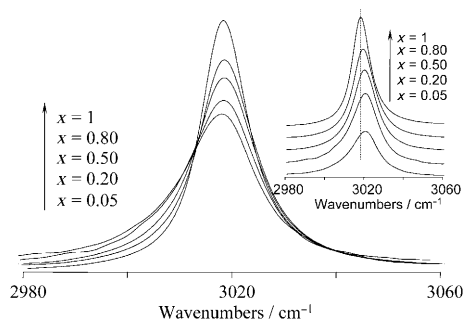


Figure 2. Wavenumber-corrected Raman spectra of chloroform/ $[\text{D}_6]$ acetone solutions in the region of the $\nu\text{C-H}$ mode, normalised to unit area, with molar fractions of chloroform ranging from $x=1.0$ to $x=0.05$; the pseudo-isosbestic point is visible at 3014 cm^{-1} . The inset shows the variation of band maxima due to non-specific interactions (dotted line is only a guide to the eye).

The pseudo-isosbestic point at 3014 cm^{-1} provides further support for assignment of the two observed components to two species in equilibrium, considered to be the “free” and 1:1 “hydrogen-bonded” forms. This feature is also associated

with an increase in the overall band intensity of the $\nu\text{C-H}$ mode. This is not unexpected, given that the lengthening of the C–H bond may result in an increase of its polarizability. Furthermore, a pseudo-isosbestic point can also be analogously identified in the $\nu\text{C=O}$ mode of acetone (not shown) and confirms the contributions of only two species in equilibrium. Such a procedure has already been applied to identify this type of interaction in ketone-like compounds.^[20]

Additional information was also obtained from the Raman spectra of the solid samples in the 173–143 K range. The general profile of the band assigned to the $\nu\text{C-H}$ mode is identical to that observed for the room-temperature liquid solutions (Figure 2). However, in several spectra the chloroform C–H bending mode ($\beta\text{C-H}$) gives rise to two bands, centered at about 1216 and 1254 cm^{-1} , whose intensity ratio is sensitive to sample composition (Figure 3). Thus, whilst

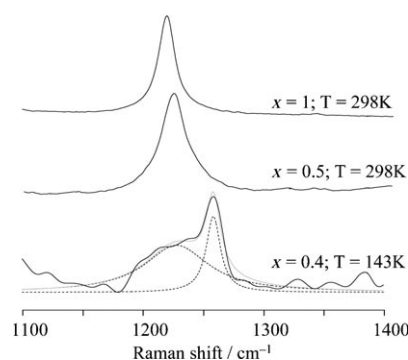


Figure 3. Raman spectra of chloroform/ $[\text{D}_6]$ acetone solutions in the region of the chloroform C–H bending mode ($\beta\text{C-H}$) normalised to unit area, labelled with the chloroform molar fractions and temperatures at which the spectra were acquired. In the low-temperature spectrum a fit of two Lorentzian functions is also shown for the two components discussed in the text (dotted black lines) and the overall fit (solid grey line).

the bending frequency at room temperature for the solution with a molar fraction of 0.5 is blue-shifted (to 1223 cm^{-1} , c.f. 1216 cm^{-1} for neat chloroform), in the low-temperature spectra the blue-shift is greater. This is evidenced by the positions of the bands at 1216 and 1254 cm^{-1} for a chloroform molar fraction of 0.4 at 173 K (not shown). We believe that the sharp feature in Figure 3 ($x=0.4$, 143 K) arises from the ($\beta\text{C-H}$) mode and acts as a probe of those chloroform molecules associated with the preferred geometry of the chloroform...acetone complex. The broad feature in Figure 3 ($x=0.4$, 143 K) represents the response of those chloroform molecules that are uncomplexed or in non-preferred geometries.

Inelastic neutron scattering: Figure 4 shows INS spectra of chloroform...acetone mixtures with different molar fractions, including pure chloroform ($x=1$) and pure acetone ($x=0$), in the region of $40\text{--}3000\text{ cm}^{-1}$.

The spectra of the mixtures are clearly interaction-dependent, as they can not be generated by the weighted sum of the spectra of pure components. Moreover, the quite large differences between the spectra of the mixtures and those of

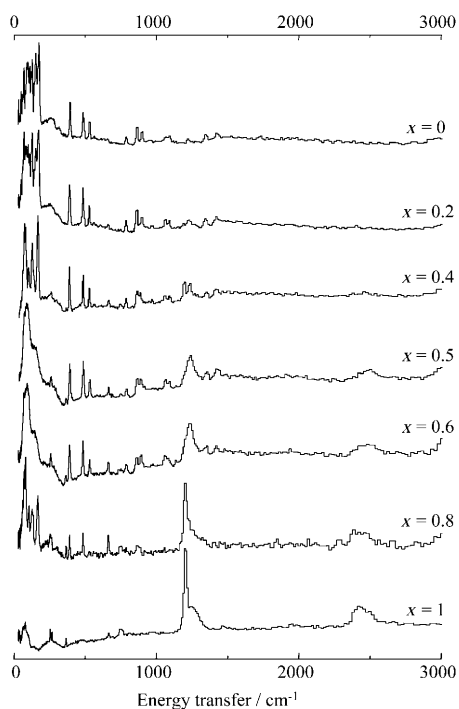


Figure 4. INS spectra of chloroform-acetone mixtures with different mole fractions, including pure chloroform ($x=1$) and pure acetone ($x=0$). See Supporting Information (Figure S1) for data-point version of this figure.

the pure compounds are evidence for a strong interaction between the two components.

The most obvious differences arise in the low-wavenumber region of the $x=0.5$ and $x=0.6$ mixtures, which present a pattern of broad features, in contrast with the sharp features of pure samples and the remaining mixtures. This behaviour, which was found to be consistently reproduced in two different sets of samples (experiments run in different time periods), seems to be related to the maximum interaction between the two components. In fact, the deviation from ideality of chloroform-acetone binary mixtures is known to show a maximum near $x=0.5$, but skewed towards the chloroform-rich region.^[26]

Ab initio calculations reported above point to the occurrence of the anti-translational $\nu_{\text{H}\cdots\text{O}}$ mode at ca. 93 cm^{-1} . Although this value is somewhat higher than expected, it is in agreement with the predicted strength of the C-H \cdots O interaction. The presence of the corresponding band in the spectra of the mixtures can be sought for $x=0.2$ and $x=0.8$.

Figure 5 compares the INS spectra of pure samples and mixtures with $x=0.2$, $x=0.4$ and $x=0.8$ in the region of the low-wavenumber modes. The spectra of the pure samples have been scaled to best fit the intensities observed for the binary mixtures, for easier comparison. The INS spectrum of the $x=0.2$ mixture is generally well described by the sum of the spectra of the pure samples, except for the intensity enhancement observed at about 82 , 130 and about 170 cm^{-1} . In the case of the 82 cm^{-1} band, the new intensity arises on top of a band already present in the INS spectrum of pure

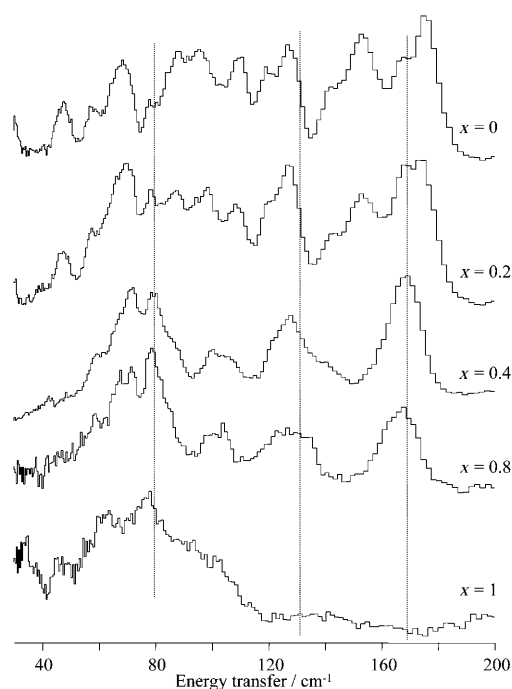


Figure 5. Comparison of the INS spectra of pure components (chloroform: $x=1$, acetone: $x=0$) and with $x=0.2$, $x=0.4$ and $x=0.8$ binary mixtures in the low-wavenumber region (the dotted line is only a guide to the eye). See Supporting Information (Figure S2) for data-point version of this figure.

chloroform, but its presence can not be explained by the sum of the bands of pure samples. The same behaviour is observed for the $x=0.4$ and $x=0.8$ mixtures. The presence of intense bands at about 82 , 130 and 170 cm^{-1} is the main difference between the spectra of the mixture and the sum of the spectra of the pure samples. There are several possible explanations for the presence of these bands in this region. In fact, all of the external modes are expected to be affected by the change in the mixture composition and can contribute to the observed intensity increase.

Comparison with the ab initio results strongly suggests assignment of the band at about 82 cm^{-1} to the anti-translational mode. This assignment is in agreement with the work of Perova et al.,^[29] who associated the increasing strength of a broad band at about 85 cm^{-1} in the far-IR spectra of chloroform-acetone mixtures with the presence of hydrogen-bonded complexes.

On the other hand, the other two possible candidates (bands at ca. 130 and 170 cm^{-1}) are tentatively assigned to the intermolecular deformation modes. As described above, the complex is expected to have low-frequency vibrations related to the moments of inertia of the acetone and chloroform moieties. We may assume a rigid -H- link between the two moieties, about which they deform. Then we note that torsions around this link are unaffected by this assumption and torsional modes should look very similar to external vibrations of the individual moieties. Thus the in-plane and out-of-plane deformation modes can be correlated with the moments of inertia of the individual moieties [Eq. (1)],

$$\frac{\tilde{\nu}_{\text{low}}}{\tilde{\nu}_{\text{high}}} = \frac{I_{\text{AC}} - I_{\text{CLF}}}{I_{\text{AC}} + I_{\text{CLF}}} \quad (1)$$

where $\tilde{\nu}_{\text{low}}$ and $\tilde{\nu}_{\text{high}}$ are the bands at the lowest and at the highest wavenumbers, and I_{AC} and I_{CLF} the moments of inertia of acetone and chloroform, respectively.

The respective moments of inertia for acetone and chloroform are approximately 54 and 350 a.m.u. Å², which yield a $\tilde{\nu}_{\text{low}}/\tilde{\nu}_{\text{high}}$ ratio of about 0.73. This ratio is consistent with the above assignment to the bands at about 130 and 170 cm⁻¹, which have $\tilde{\nu}_{\text{low}}/\tilde{\nu}_{\text{high}} = 0.76$. Taking this to be correct leaves the observed band at about 82 cm⁻¹ as the anti-translational mode.

Further information concerning the C–H...O hydrogen bonding interaction in the chloroform...acetone complex can be obtained from the βC–H mode of CHCl₃ at about 1201 cm⁻¹. Figure 6 shows the dramatic changes experienced by this mode as a function of the different compositions of the binary mixtures. This band is clearly sensitive to the composition of the mixture, and shows a second component for $x=0.4$. The frequency of the new component is 1242 cm⁻¹, about 41 cm⁻¹ higher than the original.

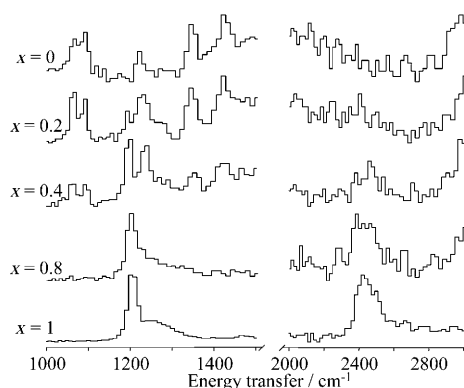


Figure 6. INS spectra of pure components (chloroform: $x=1$, acetone: $x=0$) and binary mixtures in the fundamental (right) and overtone (left) βC–H regions. See Supporting information (Figure S3) for data point version of this figure.

The presence of two bands in this region can be explained in two ways: 1) the higher wavenumber band arises from a combination mode $\tilde{\nu}_i + \tilde{\nu}_j$, with $\tilde{\nu}_j = 41$ cm⁻¹, or 2) both bands correspond to fundamental modes $\tilde{\nu}_i$ and $\tilde{\nu}_j$. The analysis of the overtone bands occurring in the 2400–2500 cm⁻¹ range clarifies the assignment. As shown in Figure 6, this region presents two defined bands in the $x=0.4$ mixture, centred at about 2386 and 2466 cm⁻¹. The separation of about 83 cm⁻¹ between these two bands leads to assignment of the 1201/1242 cm⁻¹ band pair to fundamental modes. In fact, if the 1201/1242 cm⁻¹ band pair is alternatively assumed to result from a combination mode ($\tilde{\nu}_i$ and $\tilde{\nu}_i + \tilde{\nu}_j$), then the most intense bands in the corresponding overtone region would be $2\tilde{\nu}_i$ and $2\tilde{\nu}_i + \tilde{\nu}_j$, with a separation of 41 cm⁻¹ ($2\tilde{\nu}_i + 2\tilde{\nu}_j$ would

have very low intensity). The observed separation of about 83 cm⁻¹ is consistent with the assignments of $2\tilde{\nu}_i$ and $2\tilde{\nu}_j$, that is, the two bands are overtones of two fundamental modes at 1201/1242 cm⁻¹.

The presence of two fundamental modes in the region of the βC–H mode (bending mode) can be most easily ascribed to the coexistence of hydrogen-bonded and non-hydrogen-bonded C–H groups in the mixture, giving rise to the 1201 and 1242 cm⁻¹ components, respectively. If it is the case, then the intensity of the 1201 cm⁻¹ component would be proportional to the concentration of the “free” chloroform molecules, while the intensity of the 1242 cm⁻¹ component would represent the concentration of hydrogen-bonded or “complexed” chloroform molecules. This finding corroborates the results from the low-temperature Raman spectra, as described above. Additionally, both the INS and low-temperature Raman values for the bending mode of chloroform are close to previous values reported for the interaction of chloroform adsorbed on zeolite frameworks,^[30] whereby the strength of the interaction was correlated with the basicity of the zeolite, and the strongest interaction was found for the most basic zeolite (NaX). The present results for the chloroform–acetone system show it to have an interaction as strong as that reported for the chloroform–NaX zeolite system.

The analysis of this region is hampered by the presence of an acetone band at about 1223 cm⁻¹. However, the corresponding intensity contribution can be subtracted from the whole intensity by assuming a constant intensity ratio between the 1223 cm⁻¹ band and another acetone band, such as that about 485 cm⁻¹. The intensity ratio between the 485 and 1223 cm⁻¹ bands was determined from the spectrum of pure acetone and used to treat the spectra of the mixtures. After subtraction, the integrated intensity in the 1160–1320 cm⁻¹ region provides the full chloroform contribution, in both “free” and “complexed” forms. A plot of the intensity of the 1160–1320 cm⁻¹ band versus the molar fraction of chloroform (Figure 7) yields a reasonable linear correlation, and thus supports this procedure.

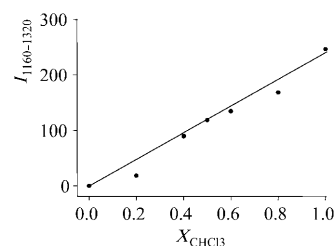


Figure 7. Linear fit of the intensity of the 1160–1320 cm⁻¹ band versus chloroform molar fraction.

In a second step, the chloroform intensity was divided between the “free” and “complexed” forms. To this end, the intensity ratio between the “free” βC–H band and its wing was evaluated from the pure chloroform spectra, and assumed to be constant over the whole mixture range. This

ratio allows subtraction of the “free” $\beta\text{C-H}$ band from the total $\beta\text{C-H}$ intensity, yielding the “complexed” intensity (band+wing). This intensity was plotted against chloroform concentration to produce a Job plot (Figure 8), which shows a maximum for the mixture with $x=0.5$, in agreement with the 1:1 stoichiometry of the chloroform...acetone complex.

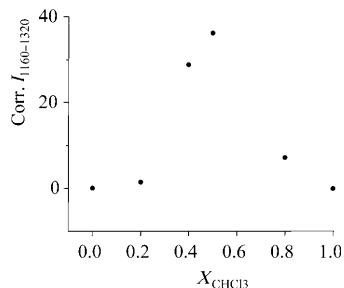


Figure 8. Job plot of the corrected intensity of the 1160–1320 cm^{-1} band versus chloroform molar fraction.

In addition, this procedure made it possible to estimate the equilibrium constant for formation of the chloroform...acetone complex as $0.15 \pm 0.02 \text{ dm}^3 \text{ mol}^{-1}$, in excellent agreement with previous results.^[24,25]

Despite the good results obtained for the Job plot, the procedure is only valid if the intensity of external modes remains proportional to the scattering strength in all solutions. The plot of the external modes area per scattering strength as a function of mole fraction of chloroform is shown in Figure 9. The points closely follow a horizontal straight line,

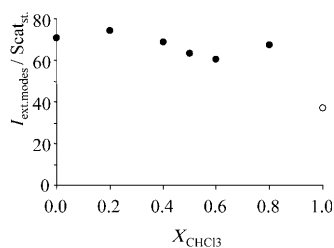


Figure 9. Plot of the external modes area (30–200 cm^{-1}) per scattering strength of each solution (and pure components).

in support of the procedures described above and validation of the results obtained. The point representing the results from pure chloroform is not on the line, probably due to low statistics: in pure chloroform only one H atom contributes to the scattering strength, while significantly more H atoms contribute for all of the remaining solutions and pure acetone.

Conclusion

The INS spectra of acetone...chloroform mixtures show strong evidence for the presence of C–H...O hydrogen-

bonded complexes, in contrast to FTIR and Raman spectra. In particular three bands arise at 82, 130 and 170 cm^{-1} in the low-wavenumber range. The new band arising at about 82 cm^{-1} is tentatively assigned to the $\nu\text{O}\cdots\text{H}$ anti-translational mode, and is in agreement with previous experimental results. The remaining modes are assigned to the out-of-plane and in-plane bending modes of the chloroform...acetone complex due to correlation with the moments of inertia.

The two bands observed in the INS spectra in the region of the $\beta\text{C-H}$ mode have been identified as fundamentals, and the composition-dependent intensity of the higher wavenumber component supports its assignment to the hydrogen-bonded form. Furthermore, the observations are in good agreement with previous reports on the same or related systems, such as the interaction between chloroform and zeolite frameworks.^[7,9,23,30] This is further confirmed by the observation of the overtone of this mode, which shows the same concentration dependence. An equilibrium constant for the association was calculated as $0.15 \pm 0.02 \text{ dm}^3 \text{ mol}^{-1}$, in good agreement with previous results.^[24,25]

Moreover, assuming the above to be true it is now seen that C–H...O hydrogen bonds, despite being longer and weaker than O–H...O,^[31] play a key role in determining supramolecular structures. This is evident from the INS spectra showing that the complex formed behaves as an entity which is independent from the sum of the parts. Although this work has dealt with a simple system, it can be extrapolated to large systems in which these phenomena may occur. This present study has shown that INS is a reliable tool to probe such interactions since it overcomes most of the problems associated with IR and Raman spectroscopy, namely problems dealing with symmetry and low intensity modes.

Experimental Details

Materials: Chloroform and acetone were obtained from Sigma-Aldrich and used as received.

Raman measurements: FT Raman spectra with 2 cm^{-1} resolution were obtained on a Bruker RFS-100 spectrometer with an Nd:YAG laser (Coherent Compass 1064/500N). The samples were sealed in Kimax glass capillary tubes of 0.8 mm i.d, and variable-temperature studies were carried out with a commercial Harney–Miller-type assembly, with temperature monitoring by means of the resistivity of a calibrated thermocouple. Under these circumstances, the error in temperature was estimated to be less than 0.5 K, with fluctuations during each recording of less than 1 K.

Inelastic neutron scattering spectra: Inelastic neutron scattering spectra were recorded on the TOSCA spectrometer at the ISIS pulsed neutron source at the Rutherford Appleton Laboratory, Chilton (UK).^[32] TOSCA is a high-resolution, broad-range, inverse geometry spectrometer well-suited to the spectroscopy of hydrogenous materials. The energy-transfer range is from 16 to 8000 cm^{-1} , and the resolution is $\Delta E/E \approx 1.5\%$. The liquid compounds were placed in thin-walled aluminium cans which filled the beam. Spectra were recorded at about 10 K to reduce thermal effects that degrade the spectra. Fast cooling from 293 to 10 K was used to avoid solubility problems, although the freezing-point diagram of chloroform/acetone mixtures does not indicate phase separation on cooling.^[12] Spectra were converted from time of flight to $S(Q,\omega)$ and corrected for background scattering using standard procedures.

The intensity of the bands assigned to the free and bonded β C–H mode were evaluated by using the following methodology. The whole 1160–1320 cm^{-1} region was integrated for all spectra to yield the total crude intensity. The intensity factor between the bands at 485 and 1223 cm^{-1} was determined for pure acetone. This factor was assumed to be constant for all solutions. For all remaining solutions containing acetone, the 485 cm^{-1} band was integrated and the corresponding intensity of the 1223 cm^{-1} band was calculated by using the factor found previously. The total chloroform intensity was obtained by subtracting the scaled acetone intensity from the total intensity. In the pure chloroform spectrum the band at 1203 cm^{-1} and the corresponding wing were integrated (both truncated due to overlapping) and a factor was found based on their intensity ratio. This factor was assumed to be constant. For all the remaining solutions containing chloroform only the band at 1203 cm^{-1} was integrated and the corresponding wing was calculated by using the factor found previously. To this net chloroform contribution both areas from the chloroform band and corresponding wing were then subtracted, which accounts for the free chloroform contribution. This provides the complexed chloroform contribution (band + wing).

Ab initio calculations: Ab initio calculations were performed with the Gaussian 03 program package, revision C.02.^[33] Molecular structures were fully optimised without constraints at the B3LYP/6-31G** level. Harmonic vibrational wavenumbers were calculated at the same level of theory and scaled by an appropriate factor to provide the best fit with experimental results. NBO analyses were performed with the GENNBO 5.0 algorithm.^[34]

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