

COMPARATIVE INFRARED STUDY OF HYDROGEN-BONDED HETERODIMERS FORMED BY
HCl, DCl, HF AND DF WITH $(\text{CH}_3)_2\text{O}$, CH_3OH AND $(\text{CH}_3)_3\text{COH}$ IN THE GAS PHASE.
ASSIGNMENT OF VIBRATIONAL BAND STRUCTURE IN $(\text{CH}_3)_2\text{O}\cdots\text{HCl}$

D.J. MILLEN

*Christopher Ingold Laboratory, Department of Chemistry, University College London,
20 Gordon Street, London WC1H 0AJ, UK*

and

O. SCHREMS

Department of Chemistry, University of California, Berkeley, California 94720, USA

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Observation of ν_s bands in the infrared spectra of some $\text{O}\cdots\text{H}-\text{Cl}$ and $\text{O}\cdots\text{H}-\text{F}$ dimers and their deuterio derivatives completes the investigation of a series of twelve related dimers. Comparison is made with related spectra, and arguments are advanced in favour of the earlier assignment of the band structure in the spectrum of $(\text{CH}_3)_2\text{O}\cdots\text{H}-\text{Cl}$.

1. Introduction

Of the many gas-phase hydrogen-bonded dimers that have been studied by infrared spectroscopy, the most thoroughly investigated is $(\text{CH}_3)_2\text{O}\cdots\text{HCl}$, the dimer for which band structure for the X-H stretching mode, ν_s , was first reported [1]. Since the original investigation, there have been studies of the temperature dependence [2,3], the Raman spectrum [4] and the

spectrum of the dimer formed by DCl [5], and several theoretical calculations have been made of the band contour [5-11]. While it is generally accepted that the band structure has its origin in combination bands, conveniently described as $\nu_s \pm n\nu_\sigma$ where ν_σ refers to the hydrogen-bond stretching mode, two assignments of the sub-bands in the structure have been made as shown in table 1.

Assignment (1) [1,12] was made on the basis of as-

Table 1
Assignments of the ν_s sub-band structure for $(\text{CH}_3)_2\text{O}\cdots\text{HCl}$

Transition $[\nu'_s, \nu'_\sigma] \leftarrow [\nu''_s, \nu''_\sigma]$	Label $\nu_s \pm n\nu_\sigma$	Assignment (1) ^{a)}	Assignment (2) ^{b)}
[1,2] \leftarrow [0,0]	$\nu_s + 2\nu_\sigma$	—	2660
[1,1] \leftarrow [0,0]	$\nu_s + \nu_\sigma$	2660	2570
[1,0] \leftarrow [0,0]	ν_s	2570	2480
[1,0] \leftarrow [0,1]	$\nu_s - \nu_\sigma$	2480	2360
[1,0] \leftarrow [0,2]	$\nu_s - 2\nu_\sigma$	2360	—

a) Refs. [1,12]. b) Refs. [2,3].

signing the strongest sub-band to ν_s , while assignment (2) has been supported by the observed temperature dependence [2,3] and by theoretical calculations [6–10], although one theoretical calculation [11] has supported assignment (1). The second assignment appears to be widely accepted, but Trudeau et al. [13] have nevertheless emphasised the need for caution about this.

We now report comparative studies, first for a series of O...H–A dimers and secondly for a range of B...H–A and B...D–A dimers. A re-examination of earlier evidence in the light of these comparisons has also been made and new arguments are advanced in favour of the original assignment (1) of the band structure in the spectrum of $(\text{CH}_3)_2\text{O}\cdots\text{HCl}$. In order to make these comparisons among a series of related dimers, we have obtained the spectra of dimers formed by HCl with $(\text{CH}_3)_3\text{COH}$, by DCl with CD_3OD and $(\text{CH}_3)_3\text{COD}$, and by DF with $(\text{CH}_3)_3\text{COD}$, which completes the investigation of a series of twelve dimers formed by HCl, DCl, HF and DF with methanol, tert-butanol and dimethyl ether.

2. Experimental

Samples involving HCl and DCl were prepared in a glass manifold previously pumped down to 10^{-6} Torr. A cylindrical gas cell made of glass and fitted with KBr windows and of 260 mm pathlength has been used for recording the spectra. Temperature variation was achieved either by wrapping heating tape around the cell or by use of a cooling jacket. The temperature was measured with a thermometer which was placed inside the cell. After mixing, the samples were equilibrated before observation of the spectra. In the case of tert-butanol it was necessary to record the spectra immediately after mixing because HCl reacts rapidly with tert-butanol. HCl (Matheson, 99%), $(\text{CH}_3)_2\text{O}$ (Liquid Carbonic), methanol and tert-butanol (Mallinckrodt) were used without further purification. DF was produced by mixing equimolar amounts of F_2 and D_2 at a low pressure in a stainless-steel cylinder. The spectrum of the mixture containing DF was observed using a stainless-steel cell of similar design to that described previously [14]. The infrared spectra were recorded with a Nicolet 7199 Fourier transform spectrometer equipped with a globar source and a liquid-nitrogen-cooled

HgCdTe photon detector. The spectral resolution was either 0.24 or 1 cm^{-1} and the frequency accuracy of the instrument is better than 0.1 cm^{-1} .

3. Results and discussion

Spectra recorded for the ν_s band of the dimers formed between CH_3OH , $(\text{CH}_3)_3\text{COH}$, $(\text{CH}_3)_2\text{O}$ and HCl are compared in fig. 1. As anticipated, $\Delta\nu$ for the dimer formed by $(\text{CH}_3)_3\text{COH}$ is very similar to that for $(\text{CH}_3)_2\text{O}\cdots\text{HCl}$. Indeed, the spectrum has similarities to the spectra of both $(\text{CH}_3)_2\text{O}\cdots\text{HCl}$ and $(\text{CH}_3)_2\text{O}\cdots\text{DCl}$. There is a central band with a weak shoulder to low frequencies and indications of another at higher frequencies. The relative intensities are low, reminiscent of $(\text{CH}_3)_2\text{O}\cdots\text{DCl}$, as is the doubling of the central peak with a spacing of $\approx 40\text{ cm}^{-1}$ which may arise from a combination involving ν_β as suggested [2] for $(\text{CH}_3)_2\text{O}\cdots\text{DCl}$, where the spacing has a value of $\approx 50\text{ cm}^{-1}$.

It is now possible to compare values of ν_s and $\Delta\nu$

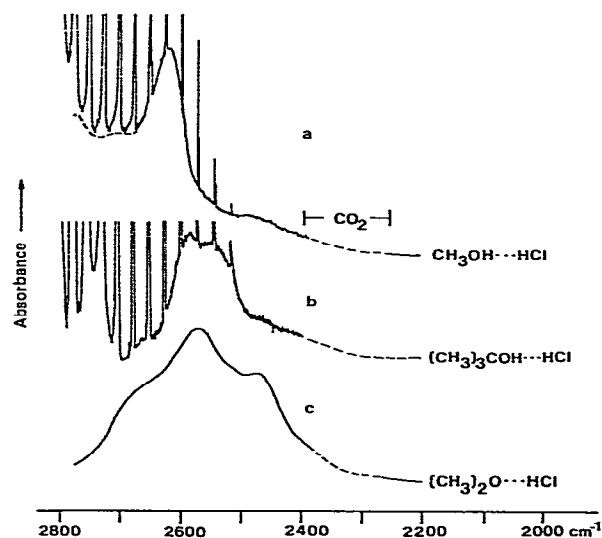


Fig. 1. Comparison of infrared absorption spectra of O...HCl dimers formed by methanol, tert-butanol and dimethyl ether (26 cm pathlength). (a) mixture of CH_3OH (50 Torr) and HCl (300 Torr) at $+35^\circ\text{C}$. (b) mixture of $(\text{CH}_3)_3\text{COH}$ (10 Torr) and HCl (140 Torr) at $+25^\circ\text{C}$. (c) mixture of $(\text{CH}_3)_2\text{O}$ (25 Torr) and HCl (100 Torr) at 25°C (spectra of unmixed samples of HCl and $(\text{CH}_3)_2\text{O}$ have been computer subtracted).

Table 2

Comparison of wavenumber displacements $\Delta\nu$ for dimers formed by methanol, tert-butanol and dimethyl ether with a series of proton donors ^{a)}

HX	CH ₃ OH...HX $\Delta\nu$	(CH ₃) ₃ COH...HX $\Delta\nu$	(CH ₃) ₂ O...XH $\Delta\nu$	$\frac{\Delta\nu(\text{CH}_3\text{OCH}_3)}{\Delta\nu(\text{CH}_3\text{OH})}$
HF	428 ^{b)}	498 ^{b)}	498 ± 10 ^{c)}	1.16 ± 0.04
HCl	264 ^{d)}	309 ⁱ⁾	316 ^{e)} (1)	1.19 ± 0.04 (1)
		(344)	416 ^{f)} (2)	1.57 ± 0.04 (2)
CF ₃ CH ₂ OH	173 ^{g)}	205 ^{g)}	205 ^{g)}	1.18 ± 0.06
(CF ₃) ₃ CHOH	264 ^{h)}	290 ^{h)}	313 ^{h)}	1.19 ± 0.04
	(245)	(300)	(305)	(1.24)

^{a)} Wavenumbers in parentheses refer to shoulders. Entries (1) and (2) refer to alternative assignments.

^{b)} Ref. [14]. ^{c)} Refs. [15-17]. ^{d)} Ref. [18]. ^{e)} Refs. [1,12]. ^{f)} Refs. [2,3].

^{g)} Ref. [19]. ^{h)} Ref. [20]. ⁱ⁾ This work.

Table 3

Comparison of wavenumbers of ν_s (cm⁻¹) for dimers formed by protium and deuterium donors

Protium species	ν_s^H	Deuterium species	ν_s^D	ν_s^H/ν_s^D	$\frac{\nu_s^H(d)/\nu_s^D(d)^{a)}}{\nu_s^H(m)/\nu_s^D(m)}$
HF monomer	3958.5	DF monomer	2906.9	1.362	—
(CH ₃) ₂ O...HF ^{b)}	3470 ^{e)}	(CH ₃) ₂ O...DF	2550 ^{e)}	1.361 ± 0.010	0.999 ± 0.01
CH ₃ OH...HF ^{m)}	3530 ^{m)}	CH ₃ OD...DF	2601 ^{m)}	1.357 ± 0.01 ^{d)}	0.996 ± 0.01
(CH ₃) ₃ COH...HF ^{m)}	3460 ^{m)}	(CH ₃) ₃ COD...DF	2559 ^{l)}	1.352 ± 0.01 ^{d)}	0.993 ± 0.01
CH ₃ CN...HF ^{e)}	3626.5 ^{f)}	CH ₃ CN...DF ^{e)}	2667.0 ^{f)}	1.360	0.999
HCN...HF ^{c)}	3710.5 ^{f)}	DCN...DF ^{c)}	2720.2 ^{f)}	1.364	1.002
HCl monomer	2886.0	DCl monomer	2090.8	1.380	—
(CH ₃) ₂ O...HCl	2570 ^{g)} (1)	(CH ₃) ₂ O...DCl	1850 ^{g)} (1)	1.389 ± 0.012	1.007 ± 0.01
	2470 ^{h)} (2)		1850 ^{h)} (2)	1.335 ± 0.012	0.967 ± 0.01
CH ₃ OH...HCl	2622 ^{k)}	CH ₃ OD...DCl	1912 ^{l)}	1.371 ± 0.01 ^{d)}	0.993 ± 0.01
(CH ₃) ₃ COH...HCl	2577 ^{l)}	(CH ₃) ₃ COD...DCl	1872 ^{l)}	1.376 ± 0.01 ^{d)}	0.997 ± 0.01
CH ₃ CN...HCl	2730 ⁱ⁾	CH ₃ CN...DCl	1980 ⁱ⁾	1.379 ± 0.012	0.999 ± 0.01
CH ₃ OH monomer	3682	CH ₃ OD monomer	2720	1.354	—
(CH ₃) ₃ N...HOCH ₃	3350 ^{j)}	(CH ₃) ₃ N...DOCH ₃	2500 ^{j)}	1.340 ± 0.012	0.990 ± 0.10
(CH ₃) ₂ HN...HOCH ₃	3380 ^{j)}	(CH ₃) ₂ HN...DOCH ₃	2510 ^{j)}	1.347 ± 0.012	0.995 ± 0.10

^{a)} $\nu_s(m)$ refers to monomer and $\nu_s(d)$ to dimer.

^{b)} Bevan et al. [21] have reported ν_s^H/ν_s^D for three ethers with values in the range 1.363 ± 0.017.

^{c)} For dimers of HCN and CH₃CN with HF and DF, ν_s refers to the origin of the ν_β sequence; all other values refer to the intensity maximum of the sub-band.

^{d)} In calculating these ratios it is assumed that the wavenumbers for spectra of ROH...DA and ROD...DA are not significantly different.

^{e)} Ref. [15]. ^{f)} Ref. [22]. ^{g)} Refs. [1,12]. ^{h)} Refs. [2,3]. ⁱ⁾ Ref. [23]. ^{j)} Ref. [19]. ^{k)} Ref. [18]. ^{l)} This work.

^{m)} Ref. [14].

for dimers formed by each of CH_3OH , $(\text{CH}_3)_3\text{COH}$ and $(\text{CH}_3)_2\text{O}$ with four different proton donors, as shown in table 2. For each of the four proton donors it is seen that values of $\Delta\nu$ for dimers formed with $(\text{CH}_3)_3\text{COH}$ or $(\text{CH}_3)_2\text{O}$ are the same within experimental error. The last column shows the corresponding ratio for dimers formed by $(\text{CH}_3)_2\text{O}$ and CH_3OH with each of the same four protons. For $(\text{CH}_3)_2\text{O}\dots\text{HCl}$, ratios are given for both assignments (1) and (2). It is seen that assignment (1) is in accord with the ratios found for the other dimers while that for assignment (2) is quite different. It would be possible to maintain assignment (2) and avoid the discrepancy in the ratios by the possible but improbable assumption that ν_s is the strongest band in the spectra of all the dimers considered except those formed by HCl , for which the strongest band in the spectrum would be assigned to $\nu_s + \nu_\sigma$ in each case, making the supposition that ν_s is a weaker band for $(\text{CH}_3)_2\text{O}\dots\text{HCl}$, is even weaker for $(\text{CH}_3)_3\text{COH}\dots\text{HCl}$ and is either very weak or absent for $\text{CH}_3\text{OH}\dots\text{HCl}$.

Fortunately, there is other evidence at hand, from observations of the effect of deuterium substitution in hydrogen-bonded dimers, which removes the need to rely on improbability to discount this hypothesis. Table 3 collects ν_s values for three series of gaseous protium- and deuterium-bonded dimers $\text{B}\dots\text{H}-\text{A}$ and $\text{B}\dots\text{D}-\text{A}$. For the dimer $(\text{CH}_3)_2\text{O}\dots\text{HCl}$, entries have been made for both assignments (1) and (2). An important conclusion, evident from the comparison, is that $\nu_s^{\text{H}}/\nu_s^{\text{D}}$ remains unchanged within experimental error in passing from monomer to dimer for all three classes of dimer for which information is available. Thus, the ratios in the last column of table 3 are all unity within experimental error. This generalisation includes $(\text{CH}_3)_2\text{O}\dots\text{HCl}$ for assignment (1), while for assignment (2) it becomes the single exception.

While the evidence derived from tables 2 and 3 points clearly to assignment (1), the arguments from temperature-dependence studies of ν_s band profiles and theoretical calculations of band profiles have led to general acceptance of assignment (2), so there is need now to re-examine those arguments.

The temperature dependence of the band profile has been clearly illustrated by Bertie and Falk through a comparison of band profiles for $(\text{CD}_3)_2\text{O}\dots\text{HCl}$ at $+34^\circ\text{C}$ and -30°C as shown in fig. 2. The changes on moving to a lower temperature were summarised as:

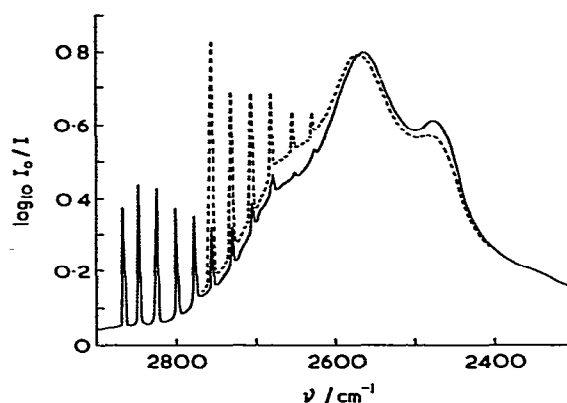


Fig. 2. Infrared absorption in 10 cm pathlength by 250 Torr of $(\text{CD}_3)_2\text{O}$ mixed with 250 Torr of HCl at $+34^\circ\text{C}$ (dashed line) and by 100 Torr of $(\text{CD}_3)_2\text{O}$ mixed with 100 Torr of HCl at -30°C (solid line). In each case the reference beam contained 250 or 100 Torr, as appropriate, of $(\text{CD}_3)_2\text{O}$ in a 10 cm cell at $+34^\circ\text{C}$. Reproduced with permission from ref. [2].

(i) a shift of the main peak by 8 cm^{-1} to lower wavenumber, (ii) the feature at 2475 cm^{-1} is resolved as a peak and is more intense relative to the maximum, and (iii) the entire high-frequency side of the band has lower intensity relative to the maximum [2]. Lassègues and Huong [3] have obtained similar results, though for a wider temperature range. The original assignment (1) attributed the band at 2475 cm^{-1} to a hot band, $\nu_s - \nu_\sigma$, but the temperature-dependence studies did not show an increase in intensity of this band with increase in temperature. At that time, the origin of the breadth of the individual sub-bands was not understood. Understandably, the temperature dependence was interpreted to conclude that the band at 2475 cm^{-1} could not be attributed to the hot band, $\nu_s - \nu_\sigma$, and assignment (2) was put forward. The origin of the breadth of the individual bands in the band profile for $(\text{CH}_3)_2\text{O}\dots\text{HCl}$ is still not established, but fine structure of analogous bands in the spectra of $\text{CH}_3\text{CN}\dots\text{HCl}$, $\text{HCN}\dots\text{HCl}$, $\text{HCN}\dots\text{HF}$ and $\text{CH}_3\text{CN}\dots\text{HF}$ and their deuterio derivatives has been observed and interpreted by Thompson and Thomas [22,23]. The observed fine structure is attributed to a series of hot bands, based on the low-frequency bending mode, which give rise to a sequence of nearly equally spaced transitions ($\nu_s + \nu_\beta\nu_\beta \leftarrow \nu_\beta\nu_\beta$), where ν_β has values 0, 1, 2, 3... to quite high values, the intensity of any member of the series being related to $(\nu_\beta + 1) \exp(-h\nu_\beta\nu_\beta/kT)$. An analo-

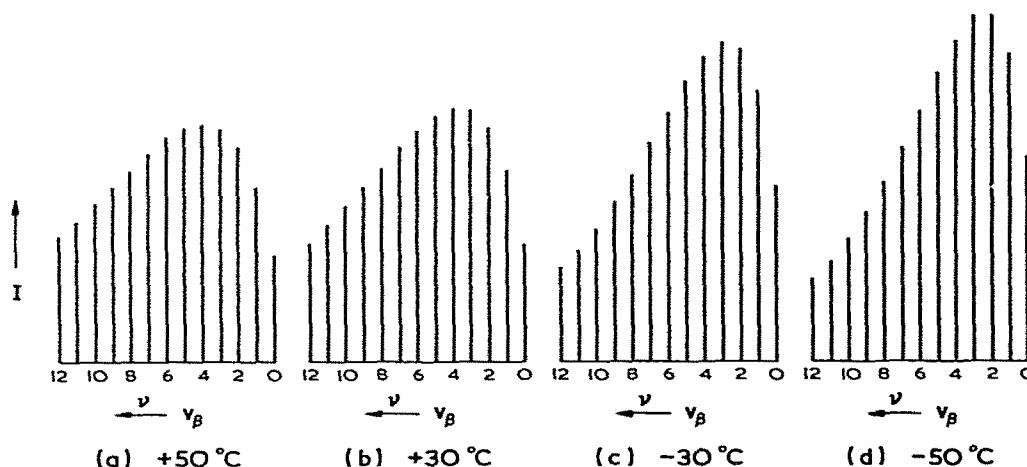


Fig. 3. Stick diagram showing relative intensities of hot bands based on ν_β for $\nu_\beta = 0-12$ at (a) $+50^\circ\text{C}$, (b) $+30^\circ\text{C}$, (c) -30°C and (d) -50°C . The total intensity under the complete band is taken to be the same in all four cases.

gous series arises for the band $\nu_s - \nu_\sigma$. The band contour arising from such a series of lines is quite strongly temperature dependent, and calculations have been made to illustrate this for $\nu_\beta = 45\text{ cm}^{-1}$, the value appropriate for $\text{CH}_3\text{CN}\cdots\text{HF}$. The corresponding stick diagrams for $\nu_\beta = 0-12$ are shown for -50°C , -30°C , $+30^\circ\text{C}$ and $+50^\circ\text{C}$ in fig. 3, where, for simplicity, the spacing between the lines has been taken to be uniform. In this interpretation, each sub-band contributing to the ν_s band profile has a hot-band fine structure extending to high frequencies with a temperature dependence as shown. It is seen that the overall effect of lowering the temperature is: (i) sub-band peak frequencies move to lower values (the peak occurs at $\nu_\beta(\text{max}) = kT/hc\nu_\beta\nu_\beta - 1$), (ii) the peaks become sharper and more rapidly resolved, and (iii) the entire high-frequency side of the band profile loses intensity relative to the low-frequency side. These are just the experimental observations so succinctly summarised by Bertie and Falk [2]. The sharpening of the peaks as the temperature is lowered is shown very clearly in the spectra of Lassègues and Huong [3], who investigated a wide temperature range (226–360 K). Finally, it must be noted that, for the sub-band $\nu_s - \nu_\sigma$, the increase in peak height with fall in temperature will be counteracted as a result of an overall decrease in the population of the $\nu_\sigma = 1$ level, while at the same time the peak of sub-band ν_s may lose some intensity if the $\nu_s - \nu_\sigma$ band profile overlaps it. The actual temperature de-

pendence of the relative *peak* heights of ν_s and $\nu_s - \nu_\sigma$ may be zero, positive or negative depending on the balance of these factors.

The form of the ν_β hot-band structure for $(\text{CH}_3)_2\text{O}\cdots\text{HCl}$ is not known, but the ability of the model to account for a number of the main features of the band profile suggests that ν_β hot bands may be important in determining the band contour. A comparable low-frequency bending mode of 50 cm^{-1} has in fact been suggested [2] for $(\text{CH}_3)_2\text{O}\cdots\text{HCl}$. The double degeneracy of the bending mode will be removed, but if the two bending modes have similar frequencies and a similar dependence of rotational constant on vibrational state, which appears to be largely determined by the effective shortening of the hydrogen bond on excitation of ν_s , then a qualitatively similar hot-band structure may result, allowing the main experimental observations on the band profile to be understood.

Finally, although theoretical calculations have supported assignment (2), it must be noted, first, that these calculations have used the temperature dependence of the peak heights in the band profile to obtain parameters to be used in the calculation whereas integrated intensities would be required if ν_β hot-band sequences are important, and secondly, that in the reconstruction of the spectrum the effect on band profiles of the ν_β hot band has not been taken into account. In any case, it may be that combinations $\nu_s \pm \nu_\beta$ are also important [2] in determining the intensity distribution in the band profile.

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