

First example of the ABC $\nu(\text{OH})$ absorption structure for both gaseous and crystalline phase: infrared studies of dimethylphosphinic acid

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Abstract

Infrared spectra for both gaseous (4000–1000 cm^{-1}) and polycrystalline (4000–400 cm^{-1}) samples of dimethylphosphinic acid ($\text{CH}_3)_2\text{POOH}$ (DMPA) at various temperatures are reported and discussed. The main attention is focused on the hydrogen bond vibrations. For the first time, the characteristic ABC structure of the $\nu(\text{OH})$ band, occurring in the spectra of solid samples of strongly hydrogen bonded complexes was observed in the gas phase spectra of DMPA dimers. In spite of different types of aggregates present in the solid state a similar shape of the $\nu(\text{OH})$ absorption was found in the crystalline sample spectra. However, an inverse intensity distribution of the ABC subbands was observed. The presented results fully confirm the explanation of the ABC structure as being due to the Fermi resonances between $\nu(\text{OH})$ and overtones of the deformation modes $2\delta(\text{OH})$ and $2\gamma(\text{OH})$. © 1997 Elsevier Science B.V. All rights reserved.

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1. Introduction

According to the data available so far on phosphinic acids, R_2POOH , these compounds show association through strong hydrogen bonds both in solution and in the solid phase [1–5]. In the crystalline state they often exist as spiral polymers or less usual as discrete cyclic dimers. The $R(\text{O}\cdots\text{O})$ distance in phosphinic acid crystals as found by X-ray diffraction analysis is in the 2.48–2.53 Å range which is characteristic for very strong hydrogen bonds [6,7]. Very recently a first attempt to obtain the gas phase infrared spectrum of dimethylphosphinic acid (DMPA) was undertaken in

our laboratory [8]. The equilibrium between monomers and cyclic dimers of DMPA was studied in the temperature range 450–750 K. The obtained values of the equilibrium constants and enthalpy of dimerization were found to be equal to

$$K_d = 55 \text{ l mol}^{-1} \text{ at } 633 \text{ K,}$$

$$K_d = 3600 \text{ l mol}^{-1} \text{ at } 523 \text{ K,}$$

and

$$-\Delta H = 100 \pm 25 \text{ kJ mol}^{-1}.$$

The above value of the enthalpy is the highest one obtained so far for a homodimer in the gas phase. In this paper the FT infrared (between 300–14 K) and

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room temperature FT Raman spectra of a crystalline sample of DMPA and its deuterated analogue DMPD are presented. Spectroscopic results obtained for both gaseous and solid phases are compared and discussed. The attention is focused on the shape of the $\nu(\text{OH})$ absorption in both phases. A tentative assignment of other internal vibrations is proposed.

2. Experimental

Dimethylphosphinic acid (DMPA) was obtained from Aldrich and used without further purification. The deuterated analogue was obtained by threefold recrystallization of the compound from a D_2O solution. The infrared spectra of the powdered crystals were recorded as a suspension in nujol and poly(chlorotrifluoroethylene) in the temperature range 300–14 K. Low temperature was obtained by means of a closed-cycle helium cryostat (APD Cryogenics). FT infrared and Raman spectra were recorded on a Bruker IFS 88 spectrometer with a resolution of 0.5 and 2 cm^{-1} , respectively. A detailed description of the gas phase measurements is given elsewhere [9]. A gas cell of a special construction (path length 6 cm, diameter 2 cm) with sapphire, MgF_2 or BaF_2 windows was used.

3. Results and discussion

3.1. The $\nu(\text{OH})$ hydrogen bond stretching vibration

3.1.1. The gas phase results

The $\nu(\text{OH})$ region in the infrared spectrum of gaseous DMPA at 525 K is presented in Fig. 1. The hydroxyl group stretching vibration of the acid monomer gives rise to the band at 3650 cm^{-1} with two shoulders due to the P and R rotational branches. The half width of this absorption is $\sim 35\text{ cm}^{-1}$.

The intense and broad absorption extending over the region $3600\text{--}1000\text{ cm}^{-1}$ is assigned to the $\nu(\text{OH})$ vibration of the hydrogen bonded DMPA dimers. This absorption consists of three relatively broad components which are situated approximately at 2800 (A), 2400 (B) and $1700\text{ (C)}\text{ cm}^{-1}$ with the A band being the most intense one. The corresponding minima between the three subbands are situated at 2450 and 1925 cm^{-1} .

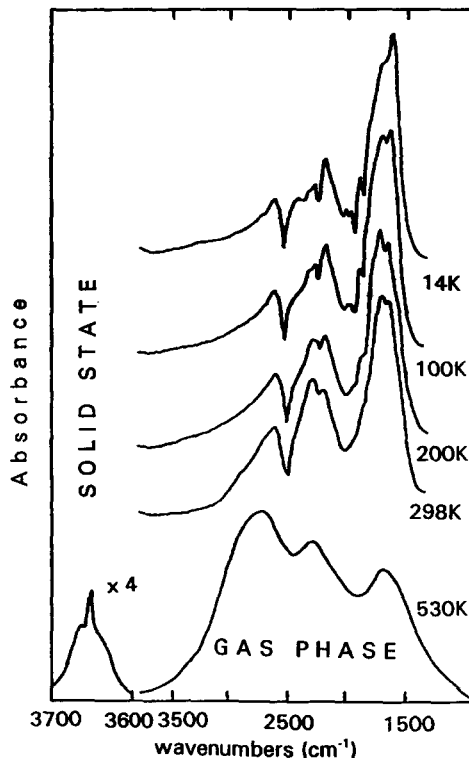


Fig. 1. The $\nu(\text{OH})$ stretching region of the infrared spectra obtained for dimethylphosphinic acid in the gas phase at 525 K and in the crystalline phase (Fluorolube emulsion) at 298, 200, 100 and 14 K. The presented gas phase spectrum was obtained by subtracting the overlapping bands arising from other internal vibrations.

The M_1^* and M_2^* normalized spectral moments ($M_1^* = \nu_0 = M_0^{-1} \int D(\nu) d\nu$, $M_2^* = M_0^{-1} \int (\nu - \nu_0)^2 / \nu d\nu$, where $M_0 = \int D(\nu) / \nu d\nu$ and $D(\nu)$ is the optical density) of the $\nu(\text{OH})$ band were calculated and are presented in Table 1 for DMPA dimers at three different temperatures. The presented results indicate that both the centre of the gravity of the $\nu(\text{OH})$ absorption and its effective half width (equal to $\sim 1050\text{ cm}^{-1}$) calculated by means of second spectral moment M_2^* are only slightly changed when the temperature is increased.

The relative intensities of the three submaxima do not depend essentially on temperature. Their positions are slightly changed when the temperature is increased, namely: the A band shifts to higher wavenumbers, the C band to lower wavenumbers while the B maximum remains unchanged.

Table 1
Spectral parameters of the $\nu(\text{OH})$ band of the DMPA dimers in the gas phase

T (K)	M_1^* (cm^{-1})	$2\sqrt{M_2^*}$ (cm^{-1})	$\Delta\nu$ (cm^{-1})
460	2350	1060	1300
490	2370	1050	1280
525	2400	1050	1250

The shape of the $\nu(\text{OH})$ absorption with the characteristic ABC structure is a well known feature for strong hydrogen bonded systems in the solid state [6,7]. To our knowledge the presented results for the DMPA dimers are the first example of such a trio detected in the gas phase.

3.1.2. Crystalline sample spectra

The results obtained for solid DMPA in the $\nu(\text{OH})$ region at four different temperatures are presented in Fig. 1. The whole range Fourier transform infrared spectra of the crystalline DMPA and its deuterated analogue for 298 and 14 K are shown in Fig. 2 and

Fig. 3. The wavenumbers of the bands and their assignments are listed in Table 2. The positions of the FT Raman bands for DMPA and DMPD observed at room temperature are also included.

According to the X-ray data [2] the DMPA crystals are built up from infinite chains of molecules held together by strong hydrogen bonds with a $\text{O}\cdots\text{O}$ distance of 2.48 Å. In spite of different types of hydrogen bonded aggregates present in gas and crystalline phases a similar shape of the $\nu(\text{OH})$ absorption is observed in the spectra of both phases. The corresponding submaxima are situated at 2626 (A), ~ 2250 (B) and ~ 1680 (cm^{-1}) (C) in the DMPA spectrum taken at room temperature. In comparison with the gas phase data the reversed relative intensities are observed for the ABC structure with the C component being the most intense in the trio. As can be seen in Fig. 1 both B and C components consist of doublets situated at 2302.5 and 2200.0 cm^{-1} and at 1714.9 and 1665.4 cm^{-1} in the room temperature spectrum. Corresponding transmission windows between A, B, C sub-bands are situated at 2517.4 and 2024.0 cm^{-1} .

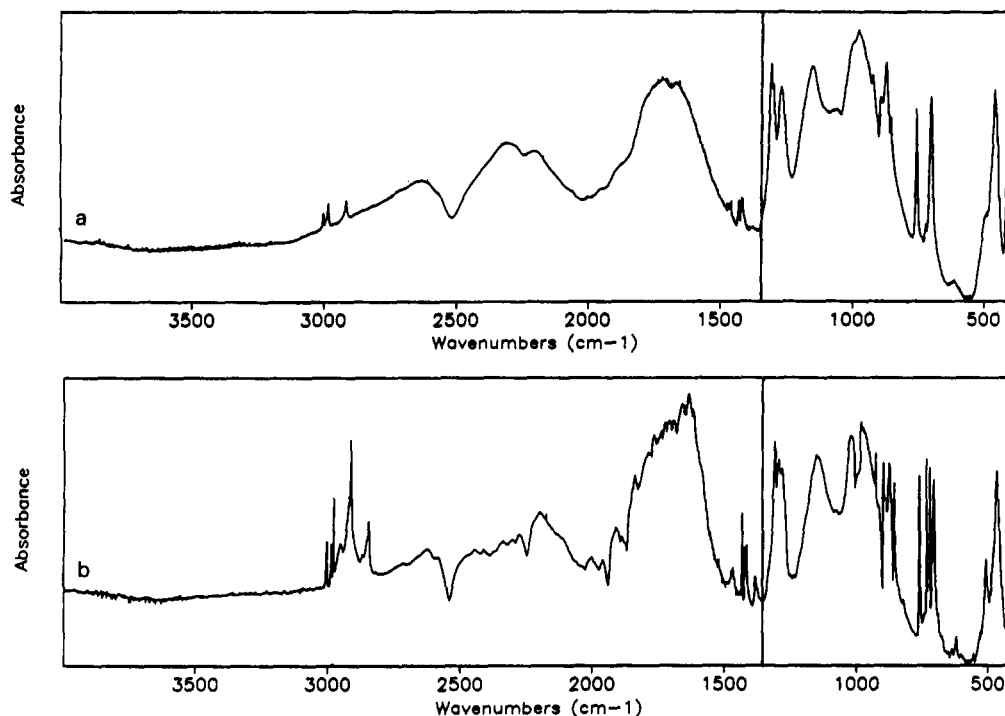


Fig. 2. The infrared spectra of crystalline dimethylphosphinic acid DMPA at 298 K (a) and 14 K (b) measured in Nujol and Fluorolube emulsion.

Table 2

Infrared and Raman frequencies (cm^{-1}), relative intensities and assignment for dimethylphosphinic acid (DMPA) and deuterated dimethylphosphinic acid (DMPD)

Infrared spectra				Raman spectra		Assignment
DMPA 298 K	DMPA 14 K	DMPD 298 K	DMPD 14 K	DMPA	DMPD	
2983.0 vw	2986.5 w 2978.0 w 2951.0 w			2999 w 2984 m	3000 w 2985 m	$\nu_{\text{as}}(\text{CH}_3)_2$
2915.0 vw	2920.0 w 2912.0 m 2868.0 w 2845.5 w			2916 vs 2811 vw	2916 vs 2813 vw	$\nu_{\text{s}}(\text{CH}_3)_2$
2626.0 m, b	2712.5 m, sh 2623.0 m, b 2580.0 m, b	2595.0 m	2605.0 m 2573.0 m, sh	2583 vw	2589 vw	$\nu(\text{OH})$ (A)
2302.5 s, b 2200.0 s, b	2275.5 s, b, sh 2194.0 s, b	2292.0 m, sh	2316.0 s, sh			$\nu(\text{OH})$ (B)
		2221.0 s, sh 2055.5 s, sh 1977.0 s 1851.0 s, sh	2221.0 s, 2058.0 s, sh 1974.0 s 1874.0 vs, sh 1842.5 vs 1784.0 vs	2109 vw		$\nu(\text{OD})$
1715.0 vs 1665.5 vs	1697.0 vs 1633.0 vs	1740.0 vs 1686.0 vs, sh	1737.0 vs, b 1688.5 vs, sh 1624.5 s, sh			$\nu(\text{OD})$ $\nu(\text{OH})$ (C)
1430.5 vw	1466.0 vw 1432.8 w 1426.5 vw 1422.0 w	1430.0 m	1431.0 s	1433 vw	1433 vw	
1416.0 vw	1416.0 w 1405.0 vw 1382.5 vw 1364.0 vw sh	1416.5 m	1417.0 s 1401.5 s	1411 vw	1412 vw	$\delta_{\text{as}}(\text{CH}_3)_2$
1306.0 vs 1298.0 vs	1307.0 vs 1294.0 vs 1282.0 vs	1377.0 m 1309.5 vs 1305.0 vs sh	1354.0 vs 1311.0 vs 1304.0 vs	1298 vw		$\delta_{\text{s}}(\text{CH}_3)_2$
1267.0 vs	1270.0 vs sh					$\delta(\text{OH})$
1149.5 vs 1058.5 s sh	1153.5 vs	1264.5 s 1187.0 vs sh 1119.0 vs	1276.5 vs 1189.0 vs sh 1106.0 vs	1272 vw 1029 vw	1072 vw	$\delta_{\text{s}}(\text{CH}_3)_2$ $\nu(\text{OD})$ C? $\nu(\text{P}=\text{O})$
996.5 vs sh 977.0 vs	1019.5 vs ca. 1005 vs 982.0 vs	1019.0 vs sh	1011.5 vs sh			$\gamma(\text{OH})$ $\nu(\text{P}-\text{O})$
922.0 vs	927.5 vs 916.0 m sh	952.0 vs sh 924.0 vs	958.0 vs 928.0 vs 916.0 m sh	924 vw	983 vw 924 vw	$\delta(\text{OD})$ $\rho_{\text{s}}(\text{CH}_3)_2$
891.0 vs	898.5 vs 888.0 s sh	894.0 s	897.5 vs	893 vw	894 vw	
873.0 vs	875.5 vs	876.0 vs	879.0 vs 869.5 s sh	870 vw	867 vw	

Table 2 Continued

Infrared spectra				Raman spectra		Assignment
DMPA 298 K	DMPA 14 K	DMPD 298 K	DMPD 14 K	DMPA	DMPD	
		865.0 s	866.0 s 861.0 m			$\rho_r(\text{CH}_3)_2$
856.0 s	860.0 s 856.0 s			857 vw		
758.0 vs	761.5 vs 755.5 m 733.0 vs 721.0 vs	847.5 s 758.5 s	847.5 s 760.5 vs 755.5 w sh 733.5 w 710.5 vs sh	758 w	845 vw 759 vw	$\nu_{as}(\text{PC}_2)$
702.0 vs	704.5 vs	702.0 vs 695.0 m sh	706.0 vs 710.0 m sh	707 s	706 s	$\nu_s(\text{PC}_2)$ $\gamma(\text{OD})$
612.0 vw 493.0 m sh 458.7 vs 412.2 s	620.0 w 504.5 s 462.9 vs 411.7 s	480.5 m 452.7 vs 412.7 m	480.0 m sh 455.5 vs 412.4 m	504 vw 460 vw 410 vw	482 vw 456 vw	$\delta_{as}(\text{CPO})$ $\delta_s(\text{CPO})$

The positions of these minima correspond well to the frequencies of two overtones: an overtone of the in-plane-bending mode, $2\delta(\text{OH})$ ($2 \times 1267.6 = 2535.2 \text{ cm}^{-1}$) and an overtone of the out-of-plane-bending mode, $2\gamma(\text{OH})$ ($2 \times 996.4 = 1992.8 \text{ cm}^{-1}$), respectively.

When the temperature of the sample is gradually reduced down to 14 K the following changes are observed on the $\nu(\text{OH})$ absorption profile.

1. The gravity centre of the absorption shifts to lower wavenumbers. This can be recognized by changes in the relative intensities within the B and C doublets. In the spectrum recorded at 14 K the lower wavenumber components of both doublets (2200.0 and 1665.4 cm^{-1}) become apparently more intense than those at higher wavenumbers (2302.5 and 1714.9 cm^{-1}).
2. Both minima (transmission windows) shift when the temperature is changed. The minimum observed at 2517.4 cm^{-1} at room temperature changes its position gradually up to $\sim 2540.5 \text{ cm}^{-1}$ at 14 K. A similar trend is observed for the second minimum.

3.2. Deuteration effect on the hydrogen bond stretching absorption

As can be noticed from Figs. 2 and 3 there is no straightforward correlation between $\nu(\text{OH})$ and $\nu(\text{OD})$

absorptions in the spectra of nondeuterated, DMPA, and deuterated, DMPD samples. The ABC structure which is well defined in the DMPA spectra is not observed for the DMPD sample. One intense and broad feature with numerous submaxima is observed extending from $\sim 3100 \text{ cm}^{-1}$ up to at least 1300 cm^{-1} . A precise value of the low wavenumber limit of the absorption is difficult to estimate due to its overlapping with other strong bands appearing in the $1300\text{--}1000 \text{ cm}^{-1}$ region. The positions of the submaxima are listed in Table 2. Some of them are situated at the wavenumbers close to those observed for the $\nu(\text{OH})$ maxima. They must be due to the residual $\nu(\text{OH})$ absorption. Two of the subbands which are new in the DMPD spectrum (298 K) situated at 1977 and 1740 cm^{-1} may correspond to the A and B components in the DMPA spectrum giving isotopic shift ratios $2626/1977 = 1.33$ and $2302/1740 = 1.32$, respectively. The location of the C component of the $\nu(\text{OD})$ absorption is not obvious. An apparent intense shoulder at $\sim 1190 \text{ cm}^{-1}$ which is observed on the $\nu(\text{P}=\text{O})$ band (situated at 1119 cm^{-1} at 298 K) in the DMPD spectra may be very tentatively assigned to the C component of the $\nu(\text{OD})$ absorption giving an isotope shift ratio equal to $1715/1190 = 1.44$. Difficulties in localizing the C band have been already pointed out for other phosphinic acids [1]. The apparent weakening of the C component by deuterium substitution was reported also for $(\text{CH}_3)_2\text{AsOOH}$ by Joannidou and Fillaux [10].

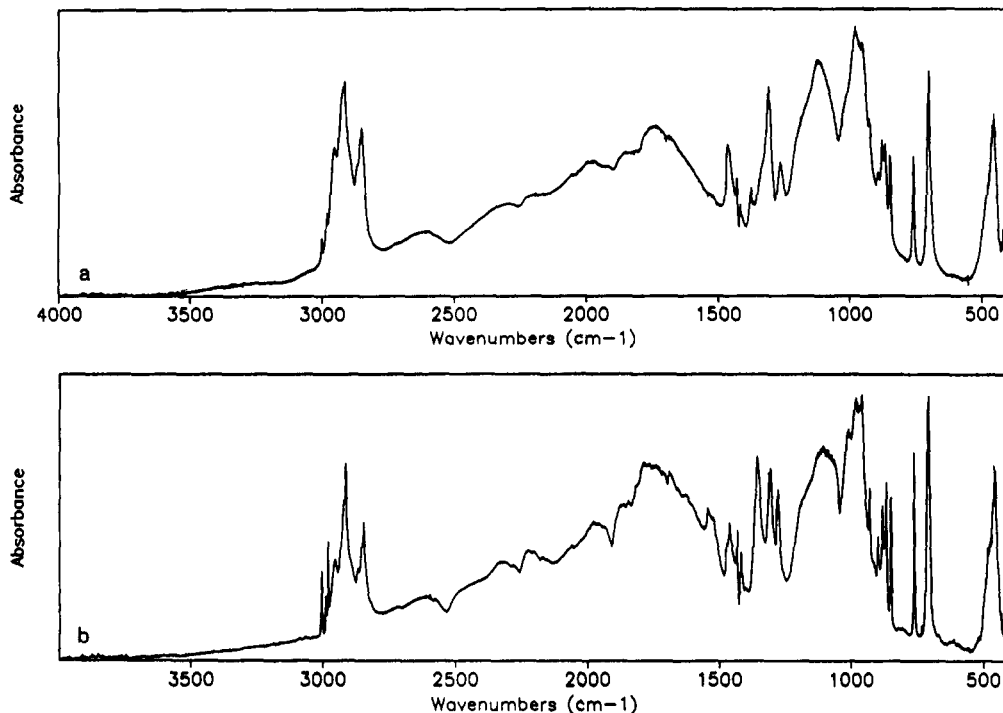


Fig. 3. The infrared spectra of crystalline deuterated dimethylphosphinic acid DMPD at 298 K (a) and 14 K (b) measured in Nujol emulsion.

At low temperature the shape of the $\nu(\text{OD})$ band does not change markedly, however, the components of the absorption are better resolved and some transmission windows are narrowed.

3.3. The hydrogen bond deformation modes

According to the data published for similar hydrogen bonded systems the in-plane-bending mode $\delta(\text{OH})$ is expected to occur in the 1300–1200 cm^{-1} region [10,11]. There is one band in this range in the DMPA spectrum at 300 K at 1267.2 cm^{-1} which is strongly sensitive to deuteration. This feature does not disappear completely. However, its relative intensity diminishes apparently in the spectrum of the deuterated sample. In the low temperature spectrum the band at 1267.2 cm^{-1} shifts toward higher wavenumbers and is situated at 1282.1 cm^{-1} with a broad shoulder at $\sim 1270 \text{ cm}^{-1}$. Upon deuteration this shoulder disappears and a relatively narrow band at 1276.7 cm^{-1} remains. On the basis of these observations the bands at 1267.2 cm^{-1} (298 K) and at

$\sim 1270 \text{ cm}^{-1}$ (14 K) are attributed to the in-plane-deformation mode $\delta(\text{OH})$.

When the sample is deuterated a new feature develops due to the $\delta(\text{OD})$ mode at 952 cm^{-1} (298 K) and at 958 cm^{-1} (14 K) which gives isotopic shift ratios equal to 1.33. A small shift to higher wavenumbers of the in-plane-deformation mode in both DMPA and DMPD spectra upon lowering the temperature points to the slightly stronger interaction at 14 K. The out-of-plane-deformation $\gamma(\text{OH})$ appears in the spectrum measured at 298 K at $\sim 1000 \text{ cm}^{-1}$ as a broad shoulder on the $\nu(\text{P}-\text{O})$ absorption situated at 977 cm^{-1} . When the temperature of the sample is lowered a broad transmission window appears at 1005 cm^{-1} indicating the Evans hole interaction [12,13] between $\nu(\text{P}-\text{O})$ and $\gamma(\text{OH})$ modes. The $\gamma(\text{OD})$ occurs as a strong shoulder at ~ 695 and $\sim 710 \text{ cm}^{-1}$ for 298 and 14 K, respectively.

3.4. Other internal vibrations

According to the crystal structure [2] the two P–O

bonds have lengths 1.50 and 1.56 Å and the positions of the stretching vibrations found for the POOH groups indicate that the two P–O oscillators are rather different [14–16]. Two very intense bands situated at 1149.6 cm^{-1} (1153.4 at 14 K) and 977.3 cm^{-1} (981.9 at 14 K) are attributed to the $\nu(\text{P}=\text{O})$ and $\nu(\text{P}-\text{O})$ stretching vibrations, respectively. Their deuterated counterparts appear in the DMPD spectra at 1119.1 cm^{-1} (1106.1 at 14 K) and 980.3 cm^{-1} (981.1 at 14 K).

Fundamentals assigned to the P–C stretching vibrations occur in the region $820\text{--}570\text{ cm}^{-1}$ for a variety of organophosphorous compounds [16]. Therefore a pattern of bands between $770\text{--}700\text{ cm}^{-1}$ insensitive to isotopic substitution is assigned to the asymmetric and symmetric stretching modes of the PC_2 groups.

The methyl group vibrations give rise to three patterns of bands, namely in the regions: $3000\text{--}2800\text{ cm}^{-1}$ (seen only in the DMPA spectra taken in Fluorolube emulsion), $1440\text{--}1300\text{ cm}^{-1}$ and $930\text{--}850\text{ cm}^{-1}$. These features are assigned to the stretching, bending and rocking modes of the CH_3 groups, respectively. It is worth noting that in these regions some pronounced changes are observed when the temperature of the sample is reduced, namely several new bands gradually appear in each of these regions. The CH_3 groups are expected to rotate at room temperature [17]. When the sample is cooled down several different orientations may be frozen giving rise to the additional bands. Similar behaviour as in the CH_3 regions was also observed for the stretching modes of the PC_2 fragments where two medium intensity bands develop for both DMPA and DMPD at ~ 756 and $\sim 733\text{ cm}^{-1}$ when the temperature is lowered.

4. Conclusions

The results presented in this paper for gaseous and crystalline dimethylphosphinic acid allow for the following observations and conclusions.

1. For the first time, the ABC structure of the $\nu(\text{OH})$ absorption characteristic for the spectra of solid samples of strongly hydrogen bonded complexes was observed in the gas phase spectra for the DMPA dimers.
2. In spite of different types of aggregates present in the solid state (infinite chains) a similar shape of the $\nu(\text{OH})$ absorption was found in the spectra of the crystalline sample however an inverse intensity distribution within the ABC structure was observed.
3. The presented data indicate that the ABC trio of the $\nu(\text{OH})$ absorption is related to the intrinsic properties of the hydrogen bond.
4. The half width of the $\nu(\text{OH})$ absorption for gaseous and crystalline samples is of the same order of magnitude and is extremely large, namely: 1050 cm^{-1} (525 K, gas phase) and $\sim 1100\text{ cm}^{-1}$ (298 K, solid phase).
5. The results fully confirm the interpretation accepted for the solid phase explaining the ABC trio in terms of Fermi resonances between $\nu(\text{OH})$ and overtones of the deformation modes, $2\delta(\text{OH})$ and $2\gamma(\text{OH})$ [7,18].
6. Transition from the gas to solid sample leads to the strengthening of the hydrogen bond. A similar effect is observed for the crystalline phase when the temperature of the sample is lowered. The maximum of the $\nu(\text{OH})$ band moved to lower wavenumbers whereas both deformations to higher wavenumbers.
7. Relatively small changes in the crystalline spectra are observed for other internal vibrations when the temperature is reduced. However worth noting are new features arising from the CH_3 groups modes appearing at lower temperatures. Rotation of the CH_3 groups which occurs at 298 K is hindered at low temperatures and several different orientations of the methyl groups are frozen giving rise to the additional bands.

Acknowledgements

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