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The ν(OH/OD) band shape of strong hydrogen bonded dimers of phosphinic acids. Phenomenology and formation models

R.E. Asfin *, G.S. Denisov, K.G. Tokhadze

Institute of Physics, St Petersburg State University, Peterhof, St Petersburg 198504, Russia

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Abstract

The infrared spectra of phosphinic acid R_2POOH dimers ($R=CH_3$, CH_2Cl, C_6H_5) have been studied in CCl_4 and CH_2Cl_2 solutions ($T=300$ K). The infrared spectra of deuterated R_2POOD dimers ($R=CH_3$, CH_2Cl) were also studied in the gas phase ($T=400$–550 K) and solid state ($T=100$–300 K). They are compared with previously studied spectra of the light (non-deuterated) dimers in the gas phase, in the solid state and in low-temperature argon matrices ($T=12$–30 K) in the 4000–400 cm^{-1} spectral region. It is found that the strong and broad ν(OH) dimer bands have similar shapes, nearly equal values of bandwidth and low-frequency shift, and possess the Hadzi ABC structure irrespective of the type of acid, significant differences of dimerization enthalpies, influence of solvent, the type of H-bonded complexes (cyclic dimers in the gas phase, in solutions, and in inert matrices, and infinite chains in the solid state), and temperature in the range 12–600 K. Isotopic ratio of the first moments of light and deuterated acid bands has been measured. Analysis of the ν(OH/OD) band of hydrogen bonded dimers of phosphinic acids shows that the interaction between the two intermolecular bonds O–H···O=P in a cyclic complex plays virtually no role in the mechanism of the ν(OH/OD) band formation; the shape of ν(OH/OD) band is controlled mainly by the POOH(D)···O= fragment; and the band shape of strong hydrogen bonded complexes is formed by a number of vibrational transitions from the ground state to different combination levels in the region 3500–1500 cm^{-1}.

Keywords: Infrared spectra; Strong hydrogen bond; Phosphinic acids; Isotopic ratio

1. Introduction

A large number of papers is devoted to interpretation of the unusual width and complicated structure of bands of the ν(OH) stretching vibration of dimers of carboxylic acids, and despite a more than 50-year history of the subject (see discussion of earlier papers in [1,2]), it remains one of the most topical in spectroscopy of hydrogen bond, the publications devoted to experimental and theoretical consideration of the profile nature of this band appear regularly [3–13]. Complexity of the task is determined by several factors, acting simultaneously. To take them into account, one needs to know a great number of parameters. The most general factor is the resonance interaction between the ν(OH) stretching vibration of a dimer and the vibrational modes of a proton donor. An important role also plays the anharmonic interaction of this vibration and low-frequency intermolecular vibrations, leading to strengthening of hot and combination transitions. Additional reasons are the proton tunneling in a symmetric two-well potential with a low barrier, and predissociation. One can think that the significant spectroscopic perturbations—the low frequency shift of 600–800 cm^{-1}, bandwidth of 300–500 cm^{-1}, the increase of integrated intensity by a factor of 40–50 upon dimerization—are caused by the significant strength of cyclic dimers, up to 10–15 kcal/mol. Important additional information is obtained from parallel investigation of the samples with the deuterated hydroxyl group. Since, the ν(OD) frequency is significantly lower, the isotopic substitution leads to a qualitative difference in the interaction of the stretching vibration with the dimer vibrations, whose frequencies change weakly. In addition, the isotope ratio $\chi \equiv \nu_0(OH)/\nu_0(OD)$ depends on the strength of hydrogen bond and can serve as one of the criteria of the potential surface shape [4,14,15].

Previously [16–20], we presented the study of a set of phosphinic acids in the gas phase, solid state and in low-temperature matrices. The characteristic ABC structure of the ν(OH) dimer bands, typical of the spectra of strongly hydrogen-bonded complexes [21–25] is observed in the gas spectra at 400–600 K, in solid state at 90–300 K and in low-temperature

* Corresponding author.
E-mail address: r.asfin@molsp.phys.spbu.ru (R.E. Asfin).

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matrices at 11–20 K. Investigation of the structure and spectra of the phosphorous analogues of carboxylic acids (phosphinic acids R_2POOH), whose dimers are substantially stronger, up to 25–50 kcal/mol, the bandwidth ν(OH) is much broader, and integrated intensity is increased by two orders of magnitude as compared with the monomer [16–21], can provide an insight into the mechanisms of the strong and ultrastrong H-bond band formation. In this paper, we expand our research to solution in organic solvents and also present spectra of deuterated analogues of studied acids to investigate the isotope effects on ν(OD) bands in the gas phase and in the solid state. Based on these results we discuss the possible mechanisms of formation of its structure, using the ideas developed for carboxylic acids.

2. Experimental

The spectra of the $(CH_3)_2POOH$, $(CH_2Cl)_2POOH$, and $(C_6H_5)_2POOH$ in solutions in CCl_4 and CH_2Cl_2 were obtained at 300 K using the standard cells with KRS-5 windows. The path length of the cells was in the range 0.5–3.0 mm. The acid concentrations in solutions are determined mainly by the solubility of the phosphinic acids in solvents (CCl_4, CH_2Cl_2) and were about 10^{-3} mol/l.

The absorption spectra of the phosphinic acids in the gas phase in the temperature range 300–750 K were obtained in special glass cells with MgF_2 windows 1.3 cm in diameter, which were attached to the cells by means of ceramics. The low-frequency transmission limit of these cells was $\nu_M = 1050\ cm^{-1}$. The path length of the cells was in the range from 5 to 8 cm. The acid concentration was $(0.6–3)\times 10^{-3}$ mol/l. In all the experiments, a sample of the substance under study was placed in a cell and then the cell was evacuated to a pressure of $\sim 10^{-2}$ Torr, which was determined by the vapour pressure above the solid substance, and sealed. The cell was placed into a copper heater equipped with KBr windows. The design of the system ensured temperature stability over time and volume within 1–2 K. The spectra of the phosphinic acids $(CH_3)_2POOD$ and $(CH_2Cl)_2POOD$ were obtained in the temperature ranges 370–650 and 400–530 K, respectively. For each acid, the lowest temperature of the measurement range is determined by the vapour pressure of this acid at which its absorption spectrum can be reliably recorded and the highest temperature depends on the thermal stability of the acid. The gas-phase experiments are described in detail in [16,18].

The spectra of polycrystalline films of the acids were measured in the temperature range from 80 to 300 K using the standard cryostat with KBr windows. The vapour of the substance under study heated to ~400 K was condensed onto a CsI window cooled to 80 K. The layer thickness was controlled by spectra recorded during deposition. The crystalline films were annealed by heating to 250–300 K, after annealing, only reversible temperature changes were observed in the spectra in the range 80–300 K. The spectra of the solutions, the gas and crystalline phases were measured with a Bruker IFS 28 Fourier spectrometer with a resolution of 1–2 cm^{-1}.

The dimethylphosphinic acid was obtained from Acros; the bis-(cloromethyl)-phosphinic acid was kindly provided by Prof. Pudovik, Kazan University; the diphenylphosphinic acid

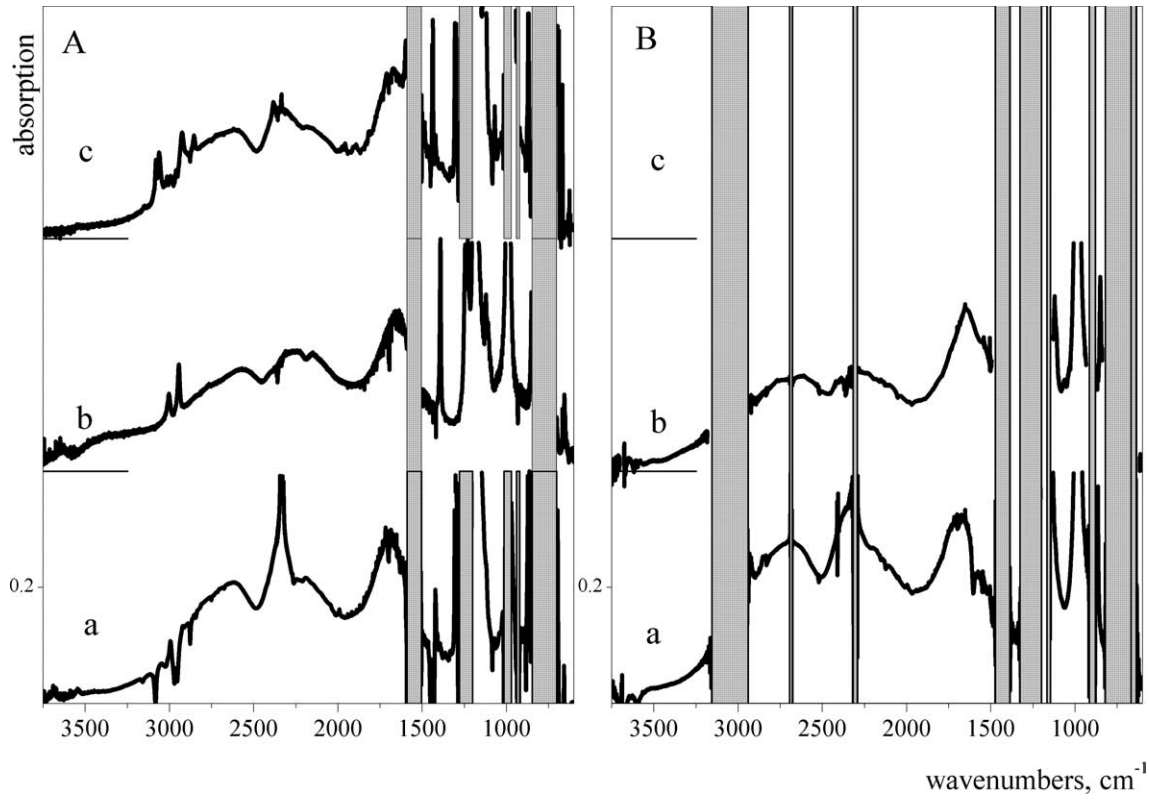

Fig. 1. Absorption spectra of $(CH_3)_2POOH$ (a), $(CH_2Cl)_2POOH$ (b), and $(C_6H_5)_2POOH$ (c) dissolved in CCl_4 (A) and CH_2Cl_2 (B) at room temperature.

was obtained from Aldrich. Deuterated phosphinic acids were prepared by solving R_2POOH in liquid CH_3OD with further alcohol evaporation under vacuum directly in a cell.

3. Results

3.1. The shape of the ν(OH) dimer bands in solution

The spectra of $(CH_3)_2POOH$, $(CH_2Cl)_2POOH$, and $(C_6H_5)_2POOH$ dissolved at 300 K in CCl_4 and CH_2Cl_2 are shown in Fig. 1. The serious experimental problem is the bad solubility of R_2POOH compounds in low-polar solvents. A typical concentration was 10^{-3}–10^{-4} mol/l, the maximum concentration was about 5×10^{-3} mol/l for $(CH_2Cl)_2POOH$ in CH_2Cl_2. The acceptable spectra were obtained with 0.5-mm cell for $(CH_2Cl)_2POOH$ in both solvents and for $(CH_3)_2POOH$ in CH_2Cl_2; with 3-mm cell for $(CH_3)_2POOH$ and $(C_6H_5)_2POOH$ in CCl_4. We failed to obtain the spectrum of $(C_6H_5)_2POOH$ in CH_2Cl_2.

For all phosphinic acids studied in these solvents, the broad ν(OH) dimer bands are located in the range 3500–1000 cm^{-1}. The characteristic ABC structure is similar to that in the gas phase [18]. It is seen from Fig. 1 that the own absorption of the solvents does not allow one to record some parts of the broad dimer spectrum, however, the shape of the bands can be readily estimated. Fig. 2 (curves b) presents the ν(OH) absorption bands of the $(R_2POOH)_2$ dimers in CCl_4.

To describe the characteristics of the broad and complex ν(OH) band of dimers at different temperatures, it is convenient to use the normalized spectral moments: the first spectral moment $M_1^* = M_0^{-1}\int S(\nu)\nu\,d\nu \equiv \nu_0$, i.e. the centre of gravity of the band ν_0, and the second spectral moment $M_2^* = M_0^{-1}\int S(\nu)(\nu-\nu_0)^2\,d\nu$, which characterizes the effective half-width of the band $\Delta\nu_{1/2} = 2\sqrt{M_2^*}$. Here, $S(\nu) = A(\nu)/[\nu(1-\exp(-\nu/T))]$ is the spectral function, where $A(\nu) = 1gI_0/I$ is the absorbance and T is temperature expressed in cm^{-1}, and $M_0 = \int S(\nu)d\nu$. The spectral moments were calculated after separating the ν(OH) bands in the range 3700–750 cm^{-1}. In this case, the weak wings of the dimer band at $\nu > 3250$ cm^{-1} and $\nu < 1100$ cm^{-1} were extrapolated by exponential functions. The values of ν_0 and $\Delta\nu_{1/2}$ obtained in solutions are collected in Table 1. For comparison, these parameters for the ν(OH) bands in the spectra of all systems studied in the gas phase, low-temperature matrices, and solid samples are also presented.

The effective half-widths of the ν(OH) dimer bands (Table 1) are the same, practically, for all these systems. It is necessary to note the large low-frequency shift (about 200 cm^{-1}) of the centre of gravity of the dimer bands on transition from the gas phase to solutions. The frequencies of maxima and minima of the ABC structure in solutions slightly differ from the frequencies in the gas phase. Some redistribution of the ν(OH) band intensity can be noted in favour of the C component of the structure in solution. The same tendency is observed in spectra of solid state and matrices.

3.2. The shape of the ν(OD) dimer bands in the gas phase

The spectra of $(CH_3)_2POOD$ and $(CH_2Cl)_2POOD$ were recorded in the gas phase in the same temperature range 400–550 K, as for the light isotopomers [16–18]. To prevent the loss of deuterium, the samples were deuterated directly in the cells. On an increase in the temperature of the gas cell to 400–450 K, the vapour pressure above the solid sample increases and one can observe the broad absorption due to the ν(OH) and ν(OD) dimer bands. The broad ν(OH) band of the acid dimers with a Hadzi ABC structure lies in region 3500–1000 cm^{-1}, and has effective width $\Delta\nu_{1/2} \sim 1000$ cm^{-1}. The relatively narrow bands associated with fundamental and overtone transitions of

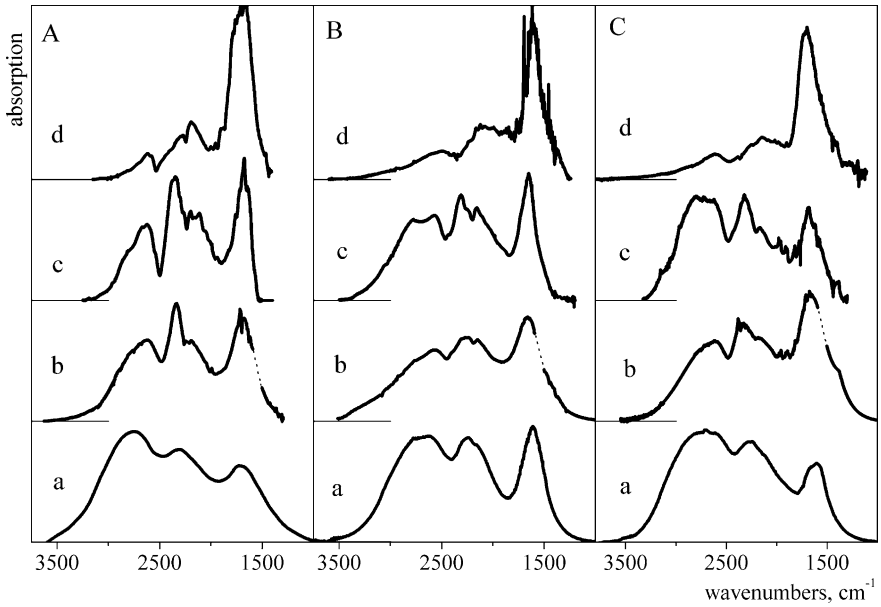

Fig. 2. The separated ν(OH) bands of phosphinic acids. (A) $(CH_3)_2POOH$, (B) $(CH_2Cl)_2POOH$, (C) $(C_6H_5)_2POOH$; (a) in the gas phase (T=530 K for (A); T=450 K for (B); T=540 K for C); (b) in CCl_4 solutions, the dotted region of the bands is presumptive one under the own solvent absorption bands; (c) in Ar matrix (T=12 K); (d) deposited films (T=100 K).

Table 1
The enthalpy of dimerization ΔH and the frequency of center of gravity ν_0 and effective halfwidth $\Delta\nu_{1/2}$ (both in cm^{-1}) of spectral function $S(\nu)$ of the ν(OH) band of the complexes of the phosphinic acids

Sample	$(CH_3)_2POOH$		$(CH_2Cl)_2POOH$		$(C_6H_5)_2POOH$	
$-\Delta H$ (kcal/mol)[a]	24		35		50	
	ν_0	$\Delta\nu_{1/2}$	ν_0	$\Delta\nu_{1/2}$	ν_0	$\Delta\nu_{1/2}$
Solution in CCl_4, $T=300$ K	2150	910	2090	1020	2050	1050
Solution in CH_2Cl_2, $T=300$ K	2080	1100	1970	1120		
Gas phase	2320[b]	1100[b]	2150[c]	1050[c]	2310[d]	1100[d]
Ar matrices, $T=12$ K	2080	800	2200	960	2250	950
Solid, $T=100$ K[e]	1920	750	2050	880	1935	890

[a] From [16].
[b] $T=520$ K.
[c] $T=475$ K.
[d] $T=575$ K.
[e] After annealing at $T=200$ K.

skeletal vibrations of phosphinic acids are also observed in this spectral range. The concentration study allowed us to assign the broad absorption observed in the range 2500–1300 cm^{-1} to the ν(OD) dimer bands of the deuterated phosphinic acids.

The separated ν(OD) dimer bands are presented in Fig. 3(b), the ν(OH) bands are shown in Fig. 3(a) for comparison. At a temperature within the range 470–490 K, for all the acids the ν(OD) band of free molecules appears near 2690 cm^{-1}. The intensity of this band for $(CH_3)_2POOD$ attains a maximum at a temperature of 540–550 K, at which the dimer band practically vanishes.

As shown in Fig. 3, the shape of the dimer band in the gas phase changes significantly upon deuteration. In comparison with ν(OH) bands, the ν(OD) bands in the gas phase are narrower and practically structureless. The ratio of the effective widths $\Delta\nu_{1/2}$(OH)/$\Delta\nu_{1/2}$(OD) is about 2–2.5 for these acids (see Table 2). The isotope effect for the centre of gravity ν_0 is anomalous, namely, the ratio ν_0(OH)/ν_0(OD) was found to be ~1.1 in the gas phase. For comparison, this ratio for the formic and acetic acids in the gas phase is about 1.3 [13]. Note that for monomer bands the ratio ν(OH)/ν(OD) for both acids is close to a value 1.36 typical of a free OH bond.

3.3. The shape of the ν(OD) dimer bands in the solid phase

Fig. 3(d) shows the separated ν(OD) bands of solid films of $(CH_3)_2POOD$ and $(CH_2Cl)_2POOD$ deposited onto a CsI window at 100 K. For comparison, the ν(OH) bands of the light compounds are shown above. As in the gas phase, the dimer bands become narrower upon deuteration. In these systems, the pronounced structure of a band is not observed and it is difficult to speak about the ABC structure. The ratio of the centres of gravity frequencies of the ν(OH) and ν(OD) bands is close to 1.1, as in the gas phase. The same ratio for formic and

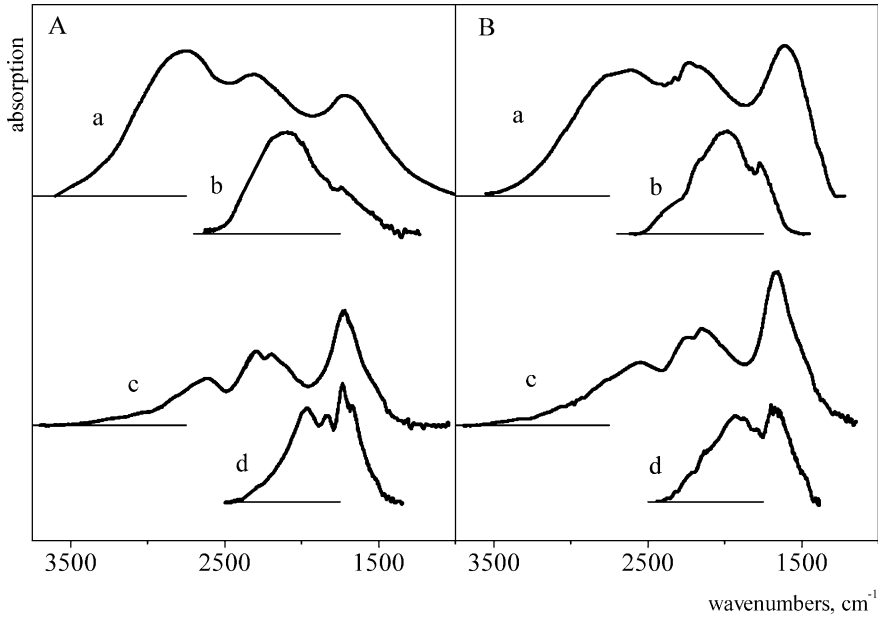

Fig. 3. The separated ν(OH) and ν(OD) band of phosphinic acids dimers. (A) $(CH_3)_2POOH/OD$, (B) $(CH_2Cl)_2POOH/OD$. (a) and (c) light acids, (b) and (d) deuterated acids. (a) and (b) gas phase, (c) and (d) deposited films.

Table 2
The frequency of center of gravity ν_0 and effective halfwidth $\Delta\nu_{1/2}$ (both in cm^{-1}) of spectral functions $S(\nu)$ of the ν(OH) and ν(OD) bands of the complexes of the phosphinic acids and isotope ratio $\chi = \nu_0(OH)/\nu_0(OD)$

	ν_0	$\Delta\nu_{1/2}$	ν_0	$\Delta\nu_{1/2}$	χ
	$(CH_3)_2POOH$		$(CH_3)_2POOD$		
Gas phase, 520 K	2320	1100	2000	480	1.16
Solid state,[a] 100 K	2050	880	1870	450	1.10
	$(CH_2Cl)_2POOH$		$(CH_2Cl)_2POOD$		
Gas phase, 475 K	2150	1050	1980	400	1.08
Solid state,[a] 100 K	2000	950	1810	360	1.10

[a] Without annealing.

acetic acids in crystal [14] is 1.25 and 1.31, respectively. The spectroscopic parameters of the ν(OD) dimer bands are presented in Table 2.

4. Discussion

For all the acids under investigation, the ν(OH) absorption bands of the complexes separated from the experimental spectra of these phosphinic acids in solution at 300 K are shown in Fig. 2. The ν(OH) bands recorded in argon matrices at 12 K, in the gas phase at $T = 460$–520 K, and in crystalline films at 100 K are also presented. The spectral moments of these bands are listed in Table 1. The separated ν(OD) absorption bands in the gas phase at $T = 470$–530 K and in crystalline films at 100 K are shown in Fig. 3, the spectral moments of ν(OD) dimer bands are summarized in Table 2. The comparison of results obtained for light and deuterated complexes with different binding energies in the wide temperature range 12–600 K allows us to formulate some regularities of the formation of the absorption bands of strong hydrogen-bonded systems.

1. Upon formation of the $(R_2POOH)_2$ dimers in all the systems and in the entire temperature range under consideration, the broad ν(OH) absorption bands (one could say anomalously broad: $\Delta\nu_{1/2} \sim 1000\ cm^{-1}$) arise, the centres of gravity of which are shifted from the monomer bands to lower frequencies by 1300–1500 cm^{-1}. It is clear that such considerable shifts of the ν(AH) band are characteristic of very strong hydrogen bonds. This is consistent with the values of the dimerization energies of R_2POOH, which were determined in [16,18] for $(CH_3)_2POOH$ ($-\Delta H = 24$ kcal/mol), $(CH_2Cl)_2POOH$ (35 kcal/mol), and $(C_6H_5)_2POOH$ (50 kcal/mol). In this energy range, the values of the low-frequency shifts virtually do not vary with increasing strength of the dimers.

2. For all the acids under consideration, the broad dimer ν(OH) bands have the so-called ABC structure, which was observed for the first time in the spectra of strong hydrogen bonded crystals [21,23–25]. For the dimers studied, we were able to observe the ABC structure in the gas phase, in inert low-temperature matrices, in organic solutions, and in solid films. Traditionally, the appearance of the holes in the contour of the broad absorption band of complexes is attributed to Fermi resonance between the first excited state of the ν(OH) mode and the doubly excited states of the bending vibrations of the hydroxyl group $2\gamma_{OH}$ and $2\delta_{OH}$ [25]; i.e. the frequencies of the minima observed can be associated with the frequencies of overtones of bending vibrations. Note that, on the whole, the positions of the maxima and minima of the observed ABC structure for these systems depend weakly on the type of the acid and the experimental conditions. The high-frequency minima between the A and B components are associated with the $2\delta_{OH}$ transitions and, in the gas phase, are observed at 2475, 2415, and 2400 cm^{-1} for $(CH_3)_2POOH$, $(CH_2Cl)_2POOH$, and $(C_6H_5)_2POOH$, respectively. The low-frequency minima between the B and C components, related to the $2\gamma_{OH}$ transitions, are located at 1905, 1850, and 1855 cm^{-1}, respectively.

Thereupon, the result of multidimensional quantum-chemical calculations obtained for zeolite–water [26] system is interesting. In this work, the maxima of the ABC structure were assigned to the zeolite ν(OH) vibrations strongly perturbed mainly by $2\gamma_{OH}$ and $2\delta_{OH}$.

3. The ν(OD) bands in the gas phase are narrower ($\Delta\nu_{1/2}(OD) \sim 400\ cm^{-1}$) than the ν(OH) bands and practically structureless. The ratio of the effective widths $\Delta\nu_{1/2}(OH)/\Delta\nu_{1/2}(OD)$ is about 2–2.5 for these acids. Note the study [8] where it was found that the significant decrease in the bandwidth in spectra of acetic acid upon deuteration of hydroxyl group is the result of the disappearance of the conditions for Fermi resonance of $2\gamma_{OH}$ and $2\delta_{OH}$ states after deuteration. Another possible mechanism of ABC structure formation [14,15] can be connected with the splitting of low-lying levels under the low barrier.

It is shown in [20] that after separation of the ν(OH) band into three components, the bandwidth of each component ($\Delta\nu_{1/2} \sim 600\ cm^{-1}$) becomes comparable with the bandwidth of the ν(OD) band of the deuterated compound ($\Delta\nu_{1/2} \sim 400\ cm^{-1}$).

The quantitative analysis of the Fermi resonance in these systems requires the knowledge of the accurate values of transition frequencies for the skeletal vibrations of monomers and dimers of the phosphinic acids under consideration. A reliable interpretation of their spectra in this frequency range should be based on ab initio solution of anharmonic vibrational problems. To date, the vibrational spectra of the monomer and dimer of $(CH_3)_2POOH$ [27] and the spectrum of the monomer of this acid [28] have been calculated in the harmonic approximation and only for light acid. In the first of these two studies, an insufficiently complete set of atomic orbitals was used, and, in the second investigation, the potential surface

was determined semiempirically. This may be the reason for the considerable discrepancies in the interpretation of the vibrational modes and calculated frequencies (see also [19]) even in the case of the monomer.

4. The intensity distribution between the A, B, and C components of the absorption band of a dimer depends primarily on the phase state of a substance. The band shape depends only insignificantly on the type of the phosphinic acid under study. Radical changes are observed on passage from the gas phase to polycrystalline films. As it is seen from Fig. 2 (curves d), the intensity of the A, B, and C components in the spectra of the solid films is redistributed in favour of the C component, whereas the shapes of the ν(OH) absorption bands of the dimers of all the acids are practically identical. The effective half-widths of the bands in the spectra of solid films are smaller than the gas-phase values. It is obvious that the intensity redistribution in favour of the low-frequency component in the spectra of crystals leads to a low-frequency shift of the centre of gravity of the absorption band (Table 1). The spectra of the low-temperature matrices $(CH_2Cl)_2POOH$/Ar and $(C_6H_5)_2POOH$/Ar differ little from the high-temperature spectra in the gas phase; for the $(CH_3)_2POOH$/Ar matrix, as well as the $(CH_3)_2POOH$ and $(CH_2Cl)_2POOH$ solutions, the absorption band of the dimer is located between its positions in the spectra of the gas phase and the solid film.

One can attempt to relate the observed differences in the band shapes of the phosphinic acids in the gas and crystalline phases to different aggregate states of these systems. According to X-ray and neutron diffraction data [29–31], in the crystalline phase, the molecules of phosphoric acids form helical chains stabilized by hydrogen bonds O–H···O=P. The distance between oxygen atoms –O···O–, which characterizes the bond strength, is $R_{O\cdots O}=2.48$ Å for the $(CH_3)_2POOH$ crystal. It has been assumed in [16] that, in the gas phase, these molecules form cyclic dimers with two hydrogen bonds. Experimentally, this assumption was confirmed for dimethylphosphinic acid by the method of gas electron diffraction [19]. It was also found in this study that the distance between the oxygen atoms in the cyclic dimer is equal to $R_{O\cdots O}=2.69$ Å; i.e. it is larger than in the crystal. Therefore, one may think that the hydrogen bonds in the crystal are stronger and that this causes changes in the shape of the absorption band. However, the results of measurements in the gas phase show that the increase in the energy of the cyclic dimers (due to the formation of two hydrogen bonds) from 24 kcal/mol for $(CH_3)_2POOH$ to 50 kcal/mol for $(C_6H_5)_2POOH$ (Table 1) has no significant effect on the position or the shape of the ν(OH) band of the hydrogen bonded molecules. Therefore, we should conclude that the observed changes in the shape of this band are primarily related to changes in the structure of aggregates in polycrystalline films. The similarity between the spectra measured in the gas phase and in the low-temperature matrices follows from the fact that the low-temperature matrices are obtained by condensation of gaseous mixtures R_2POOH/Ar at low-temperatures. Note that the correlation between the length of a hydrogen bridge and the energy of the corresponding hydrogen bond was mainly developed on the basis of measurements of $R_{A\cdots B}$ in crystals, for which the energy cannot be directly measured. We also suppose that in solution the phosphinic acids form the cyclic dimers, like carboxylic acids, at least at room temperature. This assumption was supported by the NMR investigation [32], where complexes containing more than two molecules of phosphinic acid were detected at temperatures below 140 K.

5. It follows from our results that no radical changes in the spectral characteristics of the ν(OH) absorption band of dimers occur in the temperature range 600–12 K. Clearly, the spectral characteristics of the broad band of dimers of these acids do exhibit some weak temperature dependence. However, it takes place only for the given phase state of the substance. For example, in the gas phase, one can note a small decrease in the effective half-width $\Delta\nu_{1/2}$ and an increase in the intensity of the C component, which results in a low frequency shift of the centre of gravity ν_0 with decreasing temperature. In the crystalline state, the intensity of the C component also increases with decreasing temperature and, consequently, the frequency ν_0 decreases [18]. At low temperatures, the band structure becomes more pronounced (see also Fig. 3), while the positions of the absorption minima change little.

Our results allow us to state that, for all the phosphinic acids studied the ν(OH) absorption bands of their dimers observed in the IR spectra are similar in structure and are very broad ($\Delta\nu_{1/2} \sim 1000\ cm^{-1}$). This means that the mechanism of formation of these bands should, first of all, involve the participation of the fragment –POOH, responsible for the formation of the hydrogen bond. Insignificant changes in the shape of the dimer band observed upon passage from cyclic complexes in the gas phase to helical chains stabilized by hydrogen bonds in the crystalline state allow us to believe that the interaction of the two intermolecular bonds O–H···O=P in a cyclic complex does not play a determining role in the formation of the broad absorption band. Finally, the weak temperature dependence of the width of the dimer band and of its ABC structure in the temperature range 12–600 K means that, upon formation of strong hydrogen-bonded complexes, a number of temperature-independent vibrational transitions appears in the range 3500–1500 cm^{-1}, which accounts for the structure and considerable width of this band.

Numerous studies have attempted to explain the observed width and structure of the ν(OH) absorption band of dimers of carboxylic acids [3–12]. Of special interest in this respect are the articles [7,8], in which the frequencies and intensities of the vibrational transitions arising due to resonance interactions between the first excited state of the ν(OH) mode of dimers and doubly excited or combination states of the stretching C=O and C–O and bending OH vibrations were calculated. These calculations made it possible to explain the structure of the absorption band of the $(CH_3COOH)_2$ dimer. By analogy, one can suggest the occurrence of similar interactions in the case of the $(R_2POOH)_2$ dimer; however, a rigorous analysis of the structure of the anomalously broad ν(OH) band of the phosphinic acid dimers requires the solution of an anharmonic vibrational problem. There is little doubt that the interactions between the νOH vibration and the low-frequency

intermolecular vibrations of the dimer should play an important role in the formation of this band. Based on such assumptions we attempted to describe the ν(OH) band of phosphinic acid in experimental temperature range [20]. It was shown that, using a set of reasonable parameters, it is possible to describe the main features (first of all, the effective half-width) of the observed dimer absorption band, which, apart from the fundamental transitions, is formed as a result of superposition of hot and combination transitions.

6. According to [4,14], the isotope ratio χ for hydrogen bonds OH···O depends on the bond strength, it is close to the harmonic value $\sqrt{2} = 1.41$ for weak bonds and decreases with the bond strength reaching minimum near $\chi = 0.9$ for low-barrier bonds. The further increase of the strength results in a significant increase of isotope ratio, which in several cases of especially short bonds even exceeds the value 1.41. The ratio of centers of gravity of ν(OH) band of light and deuterated dimers in gas phase is 1.16 for $(CH_3)_2POOH$ and 1.08 for $(CH_2Cl)_2POOH$ (Table 2), which is noticeably less than the corresponding values for carboxylic acids ($\chi = 1.3$, [13,14]), but is still outside the interval characteristic of low-barrier hydrogen bonds. These data points satisfactorily lie on the correlation dependence χ vs. $\kappa \equiv \nu_0/\nu_M$, where κ is the relative frequency shift on the hydrogen bond formation, ν_M is the frequency of the monomer molecule, this relation was introduced in [4] (see also [14]). It is noteworthy that two points in the interval $\chi = 1.05$–1.20 on the descending branch of this dependence correspond to hydrogen bonds in groups POOH and AsOOH [14].

5. Conclusions

Our investigation of the ν(OH) absorption band of strongly hydrogen-bonded complexes formed by phosphinic acids R_2POOH in the gas phase, solutions, solid films and low-temperature matrices shows that these bands for all the acids, irrespective of their type, phase state, and temperature, are broad ($\Delta\nu_{1/2} \sim 1000\ cm^{-1}$) and similar in shape, exhibiting a characteristic ABC structure. Upon sample deuteration this structure vanishes in the gas phase and is significantly changed in solid films, and the bandwidth essentially decreases. The formation of such an anomalously broad absorption band is primarily associated with the –POOH fragment, involved in the hydrogen bonding; the interaction between the two intermolecular bonds O–H···O=P in a cyclic complex plays practically no role in the mechanism of the ν(OH) band shape formation. In these complexes, a number of vibrational transitions exists in the frequency range 3500–1500 cm^{-1} whose intensity weakly depends on the temperature. All such transitions determine the structure and the half–width of the absorption band.

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