

IR $\nu(\text{OH})$ Band and Dimerization of Phosphorus Acids in the Gas Phase and Solid State*

by R.E. Asfin, G.S. Denisov, D.N. Poplevchenkov,
K.G. Tokhadze and T.V. Velikanova

*Institute of Physics, St. Petersburg State University, Peterhof, St. Petersburg, 198504, Russia
E-mail: rus@mosp.phys.spbu.ru (R.E. Asfin)*

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The infrared absorption spectra of phosphorus acids R_2POOH ($\text{R} \equiv \text{H}, \text{CH}_3, \text{CH}_2\text{Cl}, \text{CH}_2\text{I}, \text{C}_6\text{H}_5, \text{C}_3\text{F}_7, \text{CH}_3\text{O}, \text{C}_4\text{H}_9\text{O}$) have been recorded in the gas phase and in the solid state in the range $4000\text{--}1000\text{ cm}^{-1}$. The equilibrium between monomers and dimers of R_2POOH was studied in the gas phase between $400\text{--}650\text{ K}$. The broad absorption band of the $\nu(\text{OH})$ stretching vibration of the cyclic dimer in the region $3600\text{--}900\text{ cm}^{-1}$ is registered in the gas phase spectra at $400\text{--}600\text{ K}$ and in thin films spectra at $90\text{--}300\text{ K}$. In all cases the band has the characteristic ABC structure, typical for spectra of complexes with strong hydrogen bond in the crystal phase and solution. The intensity and the first and second spectral moments of this band were determined. It was found that, on passing from thin films at low temperature to the gas phase at high temperature, the redistribution of intensity from the low frequency wing to the high frequency wing takes place. Despite significant differences of dimerization enthalpies ($20\text{--}60\text{ kcal/mole}$), the spectra of all acids have similar structure and close values of spectral moments, although the values of intensities are different.

Key words: phosphorus acids, dimerization, gas phase and solid state, IR spectra

The phosphorus acids R_2POOH form the strongest hydrogen bonded associates among neutral molecules. In the crystalline phase, these molecules form infinite chains or, more rarely, cyclic dimers due to $\text{OH}\dots\text{O}=\text{P}$ bonds, in which the $\text{O}\dots\text{O}$ distance in the POHOP fragment lies, according to the data of X-ray and neutron scattering analysis, in the interval $2.40\text{--}2.55\text{ \AA}$ [1–7]. In conformity with the classification [8], such distances are characteristic for the strongest bonds of the OHO type in homoconjugated ions. These bonds are the most typical examples of a three-centre four-electron bond $\text{A-H}\dots\text{B}$; *i.e.*, their nature is essentially covalent [8,9]. The investigation of such bonds is of fundamental importance both for the theory of chemical bonding and intermolecular interactions and understanding of biological processes with participation of phosphate group [10–12]. Unfortunately, the energetics, dynamics, spectral manifestations of this hydrogen bond have not been adequately explored. The monomer-dimer equilibrium of the dimethylphosphinic acid $(\text{CH}_3)_2\text{POOH}$ in the gas phase has been studied by IR spectra using the technique, which permits the

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measurements up to 700 K [13]. The obtained enthalpy and spectral characteristics of dimers are in satisfactory agreement with the results of high-level quantum-mechanical calculations [14].

The aim of our paper is to record the IR spectra of the following phosphorus acids: phosphinic acid H_2POOH , dimethylphosphinic acid $(\text{CH}_3)_2\text{POOH}$, bis-(chloromethyl)-phosphinic acid $(\text{CH}_2\text{Cl})_2\text{POOH}$, bis-(iodomethyl)-phosphinic acid $(\text{CH}_2\text{I})_2\text{POOH}$, diphenylphosphinic acid $(\text{C}_6\text{H}_5)_2\text{POOH}$, bis-(heptafluoropropyl)-phosphinic acid $(\text{C}_3\text{F}_7)_2\text{POOH}$, dimethylphosphate $(\text{CH}_3\text{O})_2\text{POOH}$ and dibutylphosphate $(\text{C}_4\text{H}_9\text{O})_2\text{POOH}$, to determine the enthalpy of their dimerization in the gas phase, to compare the spectra of dimers in the gas and condensed phase at low temperatures, to examine the correlation between the spectral and energy characteristics of dimers.

EXPERIMENTAL

The technique of experiment was described in [15]. IR spectra were recorded between 300–650 K in the gas cells of two types. The glass cells with welded sapphire windows (I) with low-frequency transmission limit at $\nu_{\text{lf}} \approx 1500 \text{ cm}^{-1}$ and glass cells with MgF_2 windows (II) fixed on ceramic ring with $\nu_{\text{lf}} \approx 1000 \text{ cm}^{-1}$ were used. Most experiments were performed with cells I, in which the loss of substance during experiments, within the studied temperature interval, was minimal. Unfortunately, by help of these cells only high frequency part of the dimer $\nu(\text{OH})$ band could be registered. Cells II allowed us to register the whole band, but the studied temperature range was narrower, due to sample decomposition on ceramic.

In all experiments, certain amount of substance was placed in a cell, the cell was pumped out down to about 10^{-2} torr (defined by vapour pressure above the sample at 300 K) and sealed. The optimal measurements were carried out at concentrations of $(0.6\text{--}3.0) \cdot 10^{-3} \text{ mol/l}$, which correspond to a solid sample mass of 3–15 mg. After this, the cell was placed in a heater. The temperature interval of measurements is governed, on the one hand, by the vapour pressure of acids, at which the spectra are reliably recorded and, on the other hand, by the chemical stability of the sample.

The solid film spectra of R_2POOH at 80–300 K were recorded in the standard cryostat with external KBr windows. The films were deposited on CsI window maintained at 80 K by liquid nitrogen. An ampoule with the sample was placed in the cryostat and heated up to 440–480 K for sample deposition. The films were annealed at 250–300 K, the spectra of annealed films are totally reversible on temperature variation within 80–300 K.

The spectra were recorded with the Fourier spectrometer Bruker IFS-28 with the resolution of 2–5 cm^{-1} for the gas-phase spectra and 1 cm^{-1} for the solid-phase spectra.

RESULTS AND DISCUSSION

In Fig. 1 the experimental spectra of $(\text{CH}_3)_2\text{POOH}$ in the gas phase at different temperatures are presented. The spectra of other studied phosphorus acids have similar shape and exhibit similar temperature behaviour. For all acids, at relatively low temperatures, the intense broad absorption bands are present in the 3600–1000 cm^{-1} range (Fig. 1, spectrum 1). These bands are assigned to the $\nu(\text{OH})$ stretching vibration of the cyclic dimers with very strong hydrogen bonds. In all cases, except H_2POOH , on the broad $\nu(\text{OH})$ band the relatively narrow bands of stretching (near 3000 cm^{-1}) and bending (near 1500 cm^{-1}) vibration modes of CH groups are superimposed. In the

spectra of H_2POOH the band of PH stretching vibration at 2405 cm^{-1} is present. With increasing the temperature, the $\nu(\text{OH})$ band of monomers grows in the $3630\text{--}3670\text{ cm}^{-1}$ range (Fig. 1, spectra 1, 2, 3). Only in the case of H_2POOH , the monomer $\nu(\text{OH})$ band could not be registered, due to thermal instability. The width at half-height of monomer bands lies in the range $40\text{--}25\text{ cm}^{-1}$. The intensity of the band monotonously increases with temperature, due to rising of the monomer content. The intensity of the $\nu(\text{OH})$ bands of dimers increases until a certain temperature, depending on the initial quantity of a sample in the cell. This is connected with rising of the substance concentration in the gas phase. With subsequent heating, the intensity of the dimer bands decreases, due to the shift of the monomer-dimer equilibrium to the monomers (Fig. 1, spectrum 3). The intensity of $\nu(\text{CH})$ band does not depend on temperature and dimer-monomer ratio, and it can be used for estimation of the compound quantity in the gas phase.

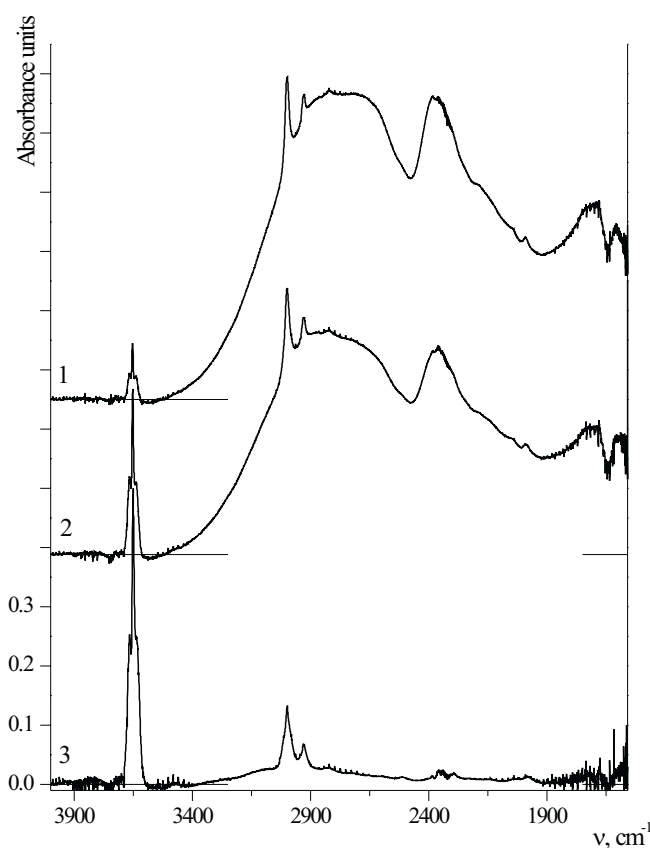


Figure 1. Experimental spectra of dimethylphosphinic acid in the gas phase at temperature: 1 – 475 K; 2 – 525 K; 3 – 625 K. $C_0 = 1 \cdot 10^{-3}$ mol/l, path length $l = 5$ cm.

In Fig. 2 the monomer and dimer $\nu(\text{OH})$ bands of all studied acids separated from experimental spectra are presented. The dimer bands have a characteristic ABC structure, well known in spectra of systems with strong hydrogen bonding in solutions and crystals [16]. This structure is accounted for by Fermi resonance between the $\nu(\text{OH})$ mode and the overtones of low-frequency vibrations of the hydroxyl group ($2\delta(\text{OH})$ and $2\gamma(\text{OH})$) of a dimer. One can see that the shape of dimer bands of all R_2POOH is rather similar.

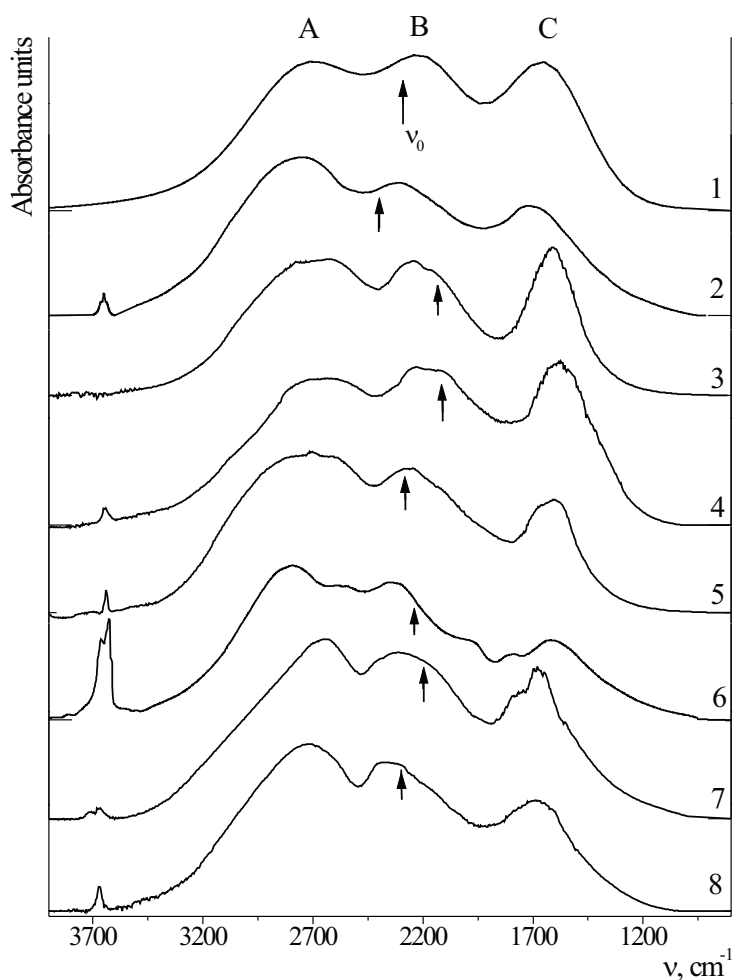


Figure 2. The $\nu(\text{OH})$ bands of R_2POOH dimers in the gas phase: 1 – H_2POOH ($T = 345 \text{ K}$); 2 – $(\text{CH}_3)_2\text{POOH}$ (530 K); 3 – $(\text{CH}_2\text{Cl})_2\text{POOH}$ (450 K); 4 – $(\text{CH}_2\text{I})_2\text{POOH}$ (465 K); 5 – $(\text{C}_6\text{H}_5)_2\text{POOH}$ (540 K); 6 – $(\text{C}_3\text{F}_7)_2\text{POOH}$ (500 K); 7 – $(\text{CH}_3\text{O})_2\text{POOH}$ (435 K); 8 – $(\text{C}_4\text{H}_9\text{O})_2\text{POOH}$ (425 K). The arrows denote the centre of gravity ν_0 of the dimer band. A, B, C denote the components of ABC structure.

The spectra of $(\text{CH}_3)_2\text{POOH}$, $(\text{CH}_2\text{Cl})_2\text{POOH}$, $(\text{CH}_2)_2\text{POOH}$, $(\text{C}_6\text{H}_5)_2\text{POOH}$ and $(\text{C}_4\text{H}_9\text{O})_2\text{POOH}$ were recorded also in the solid state for comparison with the gas phase. It follows from Fig. 3, where the spectra of $(\text{C}_6\text{H}_5)_2\text{POOH}$ in the solid and the gas phases are presented, that the $\nu(\text{OH})$ band shapes of dimers do not differ significantly in the spectra of the solid and gas phases. One can observe only intensity redistribution between the A, B, and C components, which makes the C component the most intense one in the solid state spectrum. A relative decrease in the intensity of C component also takes place with increasing temperature in all phases. A similar situation is observed for all acids studied.

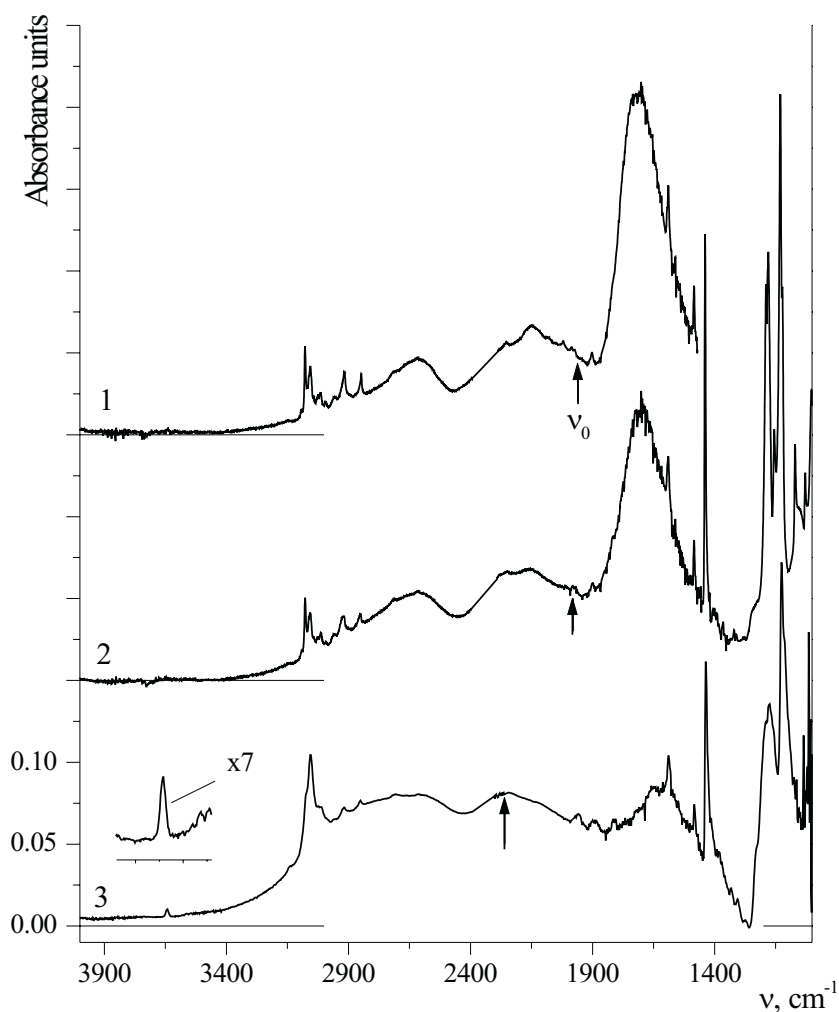


Figure 3. Experimental spectra of diphenylphosphinic acid at: 1 – 80 K (solid state), 2 – 300 K (solid state), 3 – 515 K (gas phase). The arrows denote the centre of gravity ν_0 of the dimer band. The monomer band at 515 K scaled by factor 7 is presented also.

For description of broad and complicated bands we used the set of first spectral moments: namely, the zero spectral moment $M_0 = \int S(\nu) d\nu$ (the integral intensity of a band), the first spectral moment $M_1^* = M_0^{-1} \int S(\nu) \cdot \nu d\nu \equiv \nu_0$ (the centre of gravity of the band related to the fundamental transition $\nu(\text{OH})$ of a dimer), and the second central spectral moment $M_2^* = M_0^{-1} \int S(\nu) (\nu - \nu_0)^2 d\nu$, the effective half width $\nu_{1/2}$ of a complicated band is $\nu_{1/2} = 2\sqrt{M_2^*}$. Here, $S(\nu) = D(\nu) / [\nu(1 - \exp(-\nu/T))]$ is the spectral function, $D(\nu)$ – absorbance, and T – temperature in cm^{-1} . ν_0 and $\nu_{1/2}$ of the dimer bands of phosphorus acids are presented in Table 1. The spectral moments were evaluated over the range $4000\text{--}900 \text{ cm}^{-1}$, with the band wings at $\nu < 1100 \text{ cm}^{-1}$ and $\nu > 3500 \text{ cm}^{-1}$ approximated by exponential functions. It follows from Table 1, that all dimers are characterized by an extremely large low-frequency shift of the centre of gravity with respect to monomer frequencies ($\Delta\nu = \nu_m - \nu_0 \sim 1250\text{--}1500 \text{ cm}^{-1}$, where ν_m – the $\nu(\text{OH})$ monomer band frequency) and a significant half width of a band ($\nu_{1/2} \sim 1000\text{--}1300 \text{ cm}^{-1}$). The position of the centre of gravity and the half width of the band change only insignificantly with temperature.

Table 1. The gravity center ν_0 and the effective half width $\nu_{1/2}$, in cm^{-1} , of the $\nu(\text{OH})$ band of the phosphorus acids dimers in the different states.

	State	T, K	ν_0, cm^{-1}	$\nu_{1/2}, \text{cm}^{-1}$
H₂POOH	gas	350	2290	1080
(CH₃)₂POOH	gas	460	2350	1060
	gas	525	2400	1050
(CH₂Cl)₂POOH	film	290	2090	1040
	gas	475	2140	1050
(CH₂I)₂POOH	film	80	1960	1020
	gas	505	2110	1120
(C₆H₅)₂POOH	film	80	2150	930
	gas	575	2320	1120
(C₃F₇)₂POOH	film	80	1960	1000
	gas	500	2240	1150
(CH₃O)₂POOH	gas	435	2200	1050
	film	80	2050	840
(C₄H₉O)₂POOH	gas	450	2330	1280

The integral absorption coefficients of $\nu(\text{OH})$ band of monomers ξ_M and dimers ξ_D were obtained from the integral intensities of corresponding bands $B_i = C_i \cdot l \cdot \xi_i$, where l is the path length and C_i is the concentration ($i = M$ or D). In system containing monomers and dimers the total concentration of an acid is $C_0 = C_M + 2C_D$, and the following relationship

$$\frac{B_M}{\xi_M C_0 l} + 2 \frac{B_D}{\xi_D C_0 l} = 1 \quad (1)$$

represents a straight line, if C_0 and ξ_i do not change during experiments with temperature variation. In this way the integral absorption coefficients ξ_M and ξ_D can be obtained. We found that for $(\text{CH}_3)_2\text{POOH}$, $(\text{CH}_2\text{Cl})_2\text{POOH}$, $(\text{C}_6\text{H}_5)_2\text{POOH}$, and $(\text{CH}_2\text{I})_2\text{POOH}$ the experimental points at different C_0 satisfactorily lie on a straight

line, described by (1). This indicates both the absence of more complicated, than dimer, complexes in the gas and the absence of a significant dependence of ξ_D and ξ_M on temperature. The magnitude of C_0 , which can be obtained from weight of a sample in the known cell volume, varied within the interval $(0.6\text{--}3.0)\cdot 10^{-3}$ mol/l for all acids studied. The integral absorption coefficients are presented in Table 2.

Table 2. The H-bond enthalpy ($-\Delta H$), in kcal/mol, and integral absorptivities of monomers (ξ_M) and dimers (ξ_D), in $10^4\cdot\text{l}/(\text{mol}\cdot\text{cm}^2)$, of the phosphorus acids.

	$-\Delta H$	ξ_M	ξ_D
$(\text{CH}_3)_2\text{POOH}$	24±6	0.3±0.1	35±9
$(\text{C}_3\text{F}_7)_2\text{POOH}$	24±6		
$(\text{CH}_2\text{Cl})_2\text{POOH}$	35±5	0.19±0.05	20±7
$(\text{C}_6\text{H}_5)_2\text{POOH}$	50±8	0.16±0.05	16±4
$(\text{CH}_2\text{I})_2\text{POOH}$	60±10	0.2±1	10±6
$(\text{CH}_3\text{O})_2\text{POOH}$	21±6		
$(\text{C}_4\text{H}_9\text{O})_2\text{POOH}$	29±7		

The dimerization enthalpy ΔH of phosphorus acids can be evaluated from the temperature dependence of the equilibrium constant $K_D = C_D/C_M^2 = K_0\cdot\exp(-\Delta H/kT)$ of the dimer formation $2\text{ROH} \rightleftharpoons (\text{ROH})_2$

$$\ln(K_D(T)) = -\Delta H/kT + \ln K_0 = \ln\left(\frac{B_D(T)}{B_M^2(T)}\right) + \ln\left(\frac{l\cdot\xi_M^2}{\xi_D}\right) \quad (2)$$

Assuming that ξ_D and ξ_M are independent on temperature, we obtain

$$\ln\left(\frac{B_D(T)}{B_M^2(T)}\right) = -\Delta H/kT + \text{const} \quad (3)$$

It is important that (3) does not depend on C_0 , *i.e.*, to determine the dimerization enthalpy ΔH , it is possible to use the experimental intensities of the monomer and dimer bands, measured during the evaporation process when $C_0 \neq \text{const}$. Since the measurements of ΔH were carried out in a cell with sapphire windows I, only a part of the dimer band, limited by the low-frequency transmittance boundary ($\sim 1600\text{ cm}^{-1}$), could be recorded in experiments at different temperatures. To determine the dimer band intensity, it is possible to use the relation $B_D = \kappa B_D^*$, where B_D^* is the integral intensity of a part of the dimer absorption band, lying within the frequency interval $4000\text{--}1700\text{ cm}^{-1}$, of a spectrum recorded in cell I. κ can be obtained from the experiments carried out using cell II with MgF_2 windows. Additional experiments showed that κ could be assumed to be constant within 10% over a wide temperature range.

Fig. 4 displays the dependencies of $\ln(B_D/B_M^2)$ on $1/T$ for some of the acids studied. One can see that the deviation of experimental points from the straight lines ob-

tained by the least-squares method is small. The enthalpies of dimerization of some phosphorus acids derived from (3) are presented in Table 2.

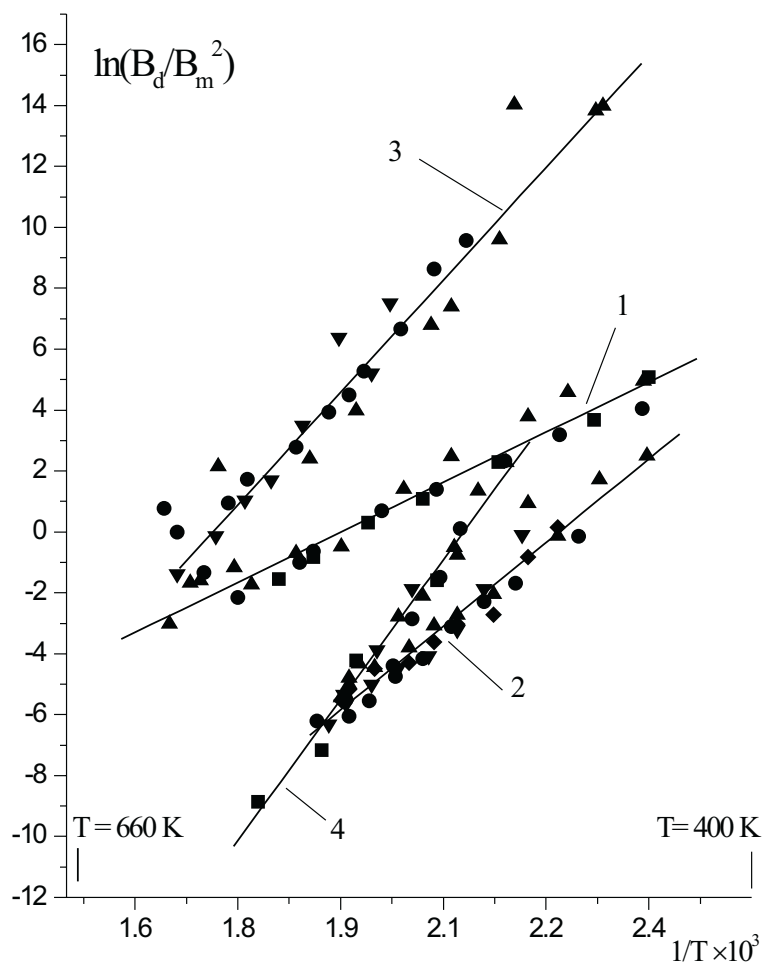


Figure 4. The dependence of $\ln(B_d/B_m^2)$ on $1/T$ for R_2POOH in the gas phase. 1 – $(C_3F_7)_2POOH$; 2 – $(CH_2Cl)_2POOH$; 3 – $(C_6H_5)_2POOH$; 4 – $(CH_2I)_2POOH$. The data obtained in experiments with the same C_0 are denoted by the same marks.

CONCLUSIONS

An extremely broad and intense $\nu(OH)$ band with the structure typical for strong $OH...O$ bond is characteristic for the dimers of the phosphorus acids studied in the gas phase and solid state. Despite the differences in dimerization enthalpies of the acids,

the shape of this band is virtually the same for all compounds studied. The shape of $\nu(\text{OH})$ band generally does not change on transition from the gas to solid state, except intensity redistribution between its components. The halfwidth of these bands is also practically unchanged. The individual specific features of the band are determined by interaction of $\nu(\text{OH})$ and low-frequency modes of the dimer.

The close values of the first moment of different acids and a decrease of integral intensity of the $\nu(\text{OH})$ band with an increase of dimerization enthalpy are surprising. This is in contradiction with the well known regularities, which connect the spectral characteristics of complexes with moderately strong hydrogen bonds – the augmentation of intensity, of low-frequency shift and of width of $\nu(\text{OH})$ band with the hydrogen bond energy [17,18]. However, these relationships were obtained for complexes in solutions, whose energies do not exceed 12–15 kcal·mol⁻¹; therefore, it can be assumed that the mechanism of interaction in the case of a strong hydrogen bond is changed and, considerably, the covalent contribution to the energy of a hydrogen bond is increased. It should be mentioned here that the deviation from such correlation regularities in the gas phase was observed earlier for weaker bonds, for example for the OH...N system in a mixture of fluorinated alcohols and tertiary amines [19].

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