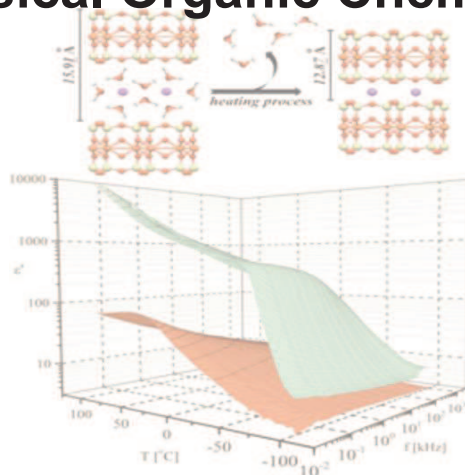


Structure and Reactivity

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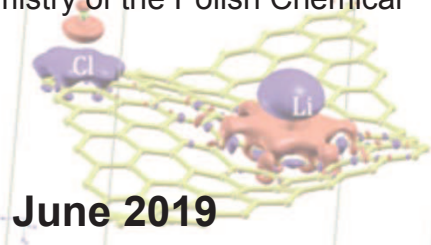
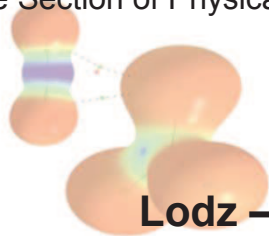
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Spectroscopic and X-ray diffraction study of bis-chloromethyl-phosphinic acid crystal

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Bis-chloromethyl-phosphinic acid $(\text{CH}_2\text{Cl})_2\text{POOH}$ is the member of the class of phosphinic acids. In the gas phase they form cyclic dimers with two hydrogen bonds. These H-bonds are one of the strongest bonds among those observed in neutral molecular complexes. The measured energy of dimerization of $(\text{CH}_2\text{Cl})_2\text{POOH}$ is 35 kcal/mol per dimer [1,2]. The strong bonding leads strong manifestations in IR spectra. The intense broad $\nu(\text{OH})$ band covering $3500 - 1000 \text{ cm}^{-1}$ is observed in IR absorption spectra of phosphinic acids recorded in the gas phase, in solutions, and in low temperature matrices [1-4].

Recently [5] $(\text{CH}_2\text{Cl})_2\text{POOH}$ crystals were studied using attenuated total reflection (ATR) and Raman spectroscopy. It was shown that corrected ATR spectra of bis-chloromethyl-phosphinic acid crystals almost coincide with the absorption spectra of thin film obtained by deposition of acid on the cold window from the gas phase. The shifts of bands in the Raman spectra match the wavenumber of corresponded bands in the absorption spectra of the crystals. The exception is the broad $\nu(\text{OH})$ band, which is visually absent in the Raman spectra.

The structure of bis-chloromethyl-phosphinic acid crystals was obtained by X-ray diffraction study [5]. The $(\text{CH}_2\text{Cl})_2\text{POOH}$ molecules form infinite chains connected by $\text{O}-\text{H}\cdots\text{O}$ H-bonds. Such a structure is typical for most phosphinic acids. The distance between oxygen atoms in the bridge is equal to 2.507 \AA that corresponds to a strong hydrogen bond.

In this report the spectra of $(\text{CH}_2\text{Cl})_2\text{POOH}$ crystals recorded by different technique is compared with spectra obtained in different phases. The difference in absorption and Raman spectra of the crystals is discussed. The correlation of structural and spectral parameters is considered.

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