GAS PHASE VIBRATIONAL SPECTROSCOPY OF ALKYL PHOSPHATES AND ALKYL PHOSPHONATES: SPECIFICITIES OF THE FAR INFRARED DOMAIN

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A new study has currently underway aiming at recording and assigning the gas phase rovibrational spectra of several organophosphorus compounds. Most of these molecules are non-toxic chemical agents and exhibit many of the group frequencies associated with common chemical-warfare agents. Preliminary experiments have been completed in the spectroscopic station of the AILES beamline of the SOLEIL synchrotron with the internal sources of the FTIR Bruker IFS125 interferometer combined with a multipass cell allowing an optical path of 20 m. The sensitivity of the spectrometer was sufficient to obtain the spectra of three compounds: DiMethylMethylPhosphonate (DMMP), TriMethylPhophate (TMP) and TriEthylPhosphate (TEP) at room temperature. All the spectra were recorded in the 50 - 5000 cm^{-1} frequency range with a resolution of 0.5 cm^{-1}. For a molecule such as TriButyl Phosphate (TBP), the vapour pressure of the compound at ambient temperature (P=0.14 Pa) is too weak for a detection in these experimental conditions. For DMMP, TMP and TEP, the complete set of the infrared active vibrational modes have been observed and allows an unambiguous discrimination between the three molecules. The vibrational analysis of the spectra was performed by comparison with MP2 and B3LYP harmonic and anharmonic ab initio calculations. For DMMP and TMP, two lowest energy conformers were taken into account in the vibrational assignment of the spectra. The far-infrared part of the vibrational spectra associated to collective and delocalized vibrational modes appears as the best region in order to distinguish the vibrational fingerprints of the two most stable conformers of DMMP and TMP. For TEP, the conformational landscape becomes very complicate at ambient temperature and a further analysis at low temperature is required in order to explain the vibrational feature of each conformer.