PROBING VIBRATIONAL WAVE PACKETS IN ORGANOPHOSHOROUS MOLECULES USING FEMTOSECOND TIME-RESOLVED MASS SPECTROMETRY

DERRICK AMPADU BOATENG, KATHARINE MOORE TIBBETTS, *Chemistry, Virginia Commonwealth University, Richmond, VA, USA*.

Organic phosphates and phosphonates share a basic structure with organophoshorous chemical warfare agents and cellular components such as DNA. To understand ultrafast nuclear dynamics in isolated organic phosphates and phosphonates, Femtosecond Time Resolved Mass Spectrometry (FTRMS) was employed. FTRMS applies the pump-probe technique with mass spectrometric detection. In our experiment an ionizing 10^{14} W cm^{-2}, 1500 nm, 18 fs pump and a non-ionizing 10^{13} W cm^{-2}, 800 nm, 25 fs probe pulse were used. Experiments were performed on four related compounds: dimethyl methylphosphonate (DMMP), diethyl methylphosphonate (DEMP), diisopropyl methylphosphonate (DIMP) and trimethyl phosphate (TMP). The yields of parent molecular ions generated by the pump pulse exhibited ultrafast oscillations with the period depending on the parent molecule. These oscillations indicate the presence of a vibrational wave packet that is excited upon ionization. In DMMP, a well resolved peak of 45 fs (732 ± 28 cm^{-1}) was observed with a weak feature at 610-650 cm^{-1}, while DIMP exhibits bimodal oscillation with frequencies of 554 ± 28 and 670-720 cm^{-1}. Oscillations for DEMP were barely visible due to rapid decay. The high- and low- frequency oscillations in DMMP and DIMP were assigned to coherent excitation of O-P-O bend and P-C stretching respectively based on DFT calculations. Bimodal oscillations at 770 and 880 cm^{-1} in TMP were also observed and are tentatively assigned to the symmetric and asymmetric P-O stretching modes. These results suggest that this group of compounds exhibits similar coherent vibrational excitation upon ionization. These results may have applications to development of new organophosphorous chemical warfare agent detection and destruction techniques based on the coherent control and may point to reaction pathways in organophosphorous compounds of biological relevance.