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Laser spectroscopy of nicotine and related analogues - perturbations and puckering in pyridine and pyrrolidine rings

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Abstract

Nicotine has many physiological effects due to its neurotransmitter binding properties, associated with its usage as a recreational drug. Despite the great number of solution phase studies, very little has been published about gas phases spectroscopic properties. We report the first electronic spectra, obtained via two colour resonant two-photon ionisation spectroscopy. Evidence of two distinct conformers is supported by conformer specific IR-UV ion depletion spectra, interpreted with the aid of quantum chemistry calculations. Unconventional CH $\cdots$ N type hydrogen bonds between the rings play a key role in determining the conformational structures and giving rise to “blue-shift” perturbations in their IR spectra that facilitate their assignment. It is striking that the conformers are structurally very similar in the ground state, but upon excitation one of them undergoes a significant change in pyrrolidine puckering giving rise to an electronic spectrum of quite different character.

Nicotine analogue 2-phenylpyrrolidine serves as a useful comparison, having a much more accessible conformational space defined by pyrrolidine puckering. It is also one of the few such molecules in which both gas and solution phase conformational preferences are analysed. Resonant two-photon ionization (R2PI), microwave, and NMR spectroscopic techniques were employed, supported by *ab initio* calculations. There is a significant change in the conformational preference between the gas and solution phases, with the CH $\cdots$ N type hydrogen bonds affected by the presence of solvent molecules.

Keywords: Nicotine analogues, molecular conformation, R2PI spectroscopy, IR-UV laser spectroscopy