LARGE AMPLITUDE BENDING MOTION AND METHYL GROUP TORSION IN THE TPE SPECTRUM OF METHYL ISOCYANATE CH$_3$NCO

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Methyl isocyanate is a non-rigid quasi-symmetric top molecule displaying a torsion of its methyl group and a large amplitude CNC bending mode. The torsion is nearly free as the hindering barrier is only 20 cm$^{-1}$. The barrier to linearity, also very low, is on the order of 920 cm$^{-1}$. Although the $a$-type transitions of methyl isocyanate have already been recorded up to the submillimeter wave domain, spectroscopic information is still lacking, especially concerning the cationic species CH$_3$NCO$^+$. Threshold photoelectron (TPE) spectroscopy has been used to obtain spectroscopic information on CH$_3$NCO$^+$. The spectrum recorded from 84000 to 94000 cm$^{-1}$ (10.4 to 11.6 eV) using VUV synchrotron radiation displays several sharp features superimposed on a broad feature spanning nearly 8000 cm$^{-1}$. As shown by the ab initio calculations, the ground electronic state of the cation is doubly degenerate and is split into a lower $\tilde{X}^+$ and an upper $\tilde{A}^+$ substate by vibronic couplings. The $\tilde{X}^+$ substate is characterized by a barrier to linearity of 1180 cm$^{-1}$ and a barrier hindering the internal rotation of 203 cm$^{-1}$. For the $\tilde{A}^+$ substate, an equilibrium configuration with a linear CNC chain arises.

Treating simultaneously the two large amplitude motions and the overall rotation, a calculation of the rovibronic energies of the neutral and cationic species has been carried out to model the TPE spectrum. This calculation accounts for the singularity at the linear configuration and relies on a model designed for asymmetric-top molecules to evaluate the intensity of the TPE spectrum lines. The strong dependence on the methyl group internal rotation barrier on the CNC bending angle is also taken into account. In the poster, the results of the rovibronic energy calculation will be reported and the experimental TPE spectrum will be compared to the theoretical one.


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