

LARGE AMPLITUDE MOTION EFFECTS IN THE TPES SPECTRUM OF METHYL ISOCYANATE CH₃NCO

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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.^a 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,^b spectroscopic information is still lacking, especially concerning the cation.

Threshold photoelectron spectroscopy has been used to obtain spectroscopic information on the cationic species (CH₃NCO⁺) of methyl isocyanate. 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 carried out in this work, 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 ground electronic state of the neutral and the \tilde{X}^+ substate of the cation are characterized by similar values of the methyl group internal rotation barrier. As for the \tilde{A}^+ substate of the cation, a much larger value shifted by $\pi/3$ was calculated.

Accounting for the two large amplitude motions and for the overall rotation,^a a calculation of the rovibronic energies of the neutral and the cationic species is in progress and should allow us to model the TPES spectrum. This calculation relies on Gaussian quadrature to treat the singularity at the linear configuration.^c The strong dependence on the methyl group internal rotation barrier on the CNC bending angle is also taken into account.^a In the talk, the results of the rovibronic energies calculation will be reported and the experimental TPES spectrum will be compared to the theoretical one.

^aKręglewski, *J. Molec. Spectrosc.* **105** (1984) 8; and Koput, *ibid.* **106** (1984) 12

^bKoput, *J. Molec. Spectrosc.* **115** (1986) 131; and Cernicharo *et al.*, *A&A* **587** (2016) L4

^cCoudert, Gans, Holzmeier, Loison, Garcia, Alcaraz, Lopes, and Röder, *J. Chem. Phys.* **149** (2018) 224304