EXPERIMENTAL AND COMPUTATIONAL INVESTIGATIONS OF THE THRESHOLD PHOTOELECTRON SPECTRUM OF THE HCCN RADICAL

B. GANS, CYRIL FALVO, L. H. COUDERT, *Institut des Sciences Moléculaires d'Orsay, Université Paris-Sud, Orsay, France*; GUSTAVO A. GARCIA, J. KÜGER, *L'Orme des Merisiers; Saint Aubin BP 48, Synchrotron SOLEIL, Gif sur Yvette, France*; J.-C. LOISON, *Institut des Sciences Moléculaires, Université de Bordeaux, Talence, France*.

The HCCN radical, already detected in the interstellar medium, is also important for nitrile chemistry in Titan's atmosphere.[a] Quite recently the photoionization spectrum of the radical has been recorded[b] using mass selected threshold photoelectron (TPE) spectroscopy and this provided us with the first spectroscopic information about the $HCCN^+$ cation. Modeling such a spectrum requires accounting for the non-rigidity of HCCN and for the Renner-Teller effect in $HCCN^+$.

In its $^3A''$ electronic ground state, HCCN is a non-rigid molecule as the potential for the $\angle$HCC bending angle is very shallow.[c] Vibronic couplings with the same bending angle leads, in the $^2\Pi$ electronic ground state of $HCCN^+$, to a strong Renner-Teller effect giving rise to a bent $^2A'$ and a quasi-linear $^2A''$ state.[d]

In this paper the photoionization spectrum of the HCCN radical is simulated. The model developped treats the $\angle$HCC bending angle as a large amplitude coordinate in both the radical and the cation and accounts for the overall rotation and the Renner-Teller couplings. Gaussian quadrature are used to calculate matrix elements of the three potential energy functions retrieved through *ab initio* calculations and rovibrational operators going to infinity for the linear configuration are treated rigorously.

The HCCN TPE spectrum is computed with the above model calculating all rotational components and choosing the appropriate lineshape. This synthetic spectrum will be shown in the paper and compared with the experimental one.[b]

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[a] Guélin and Cernicharo, *A&A* **244** (1991) L21; Loison *et al., Icarus* **247** (2015) 218

[b] Garcia, Krüger, Gans, Falvo, Coudert, and Loison, *J. Chem. Phys.* (2017) submitted

[c] Koput, *J. Phys. Chem. A* **106** (2002) 6183

[d] Zhao, Zhang, and Sun, *J. Phys. Chem. A* **112** (2008) 12125