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VUV and soft X-ray spectroscopy of an interstellar molecule: Fulminic acid HCNO

To date, over 300 molecules have been detected in interstellar space [1]. These molecules range from small molecules such as H_2 [2] to large molecules such as the fullerene molecule C_{60} [3]. One of these molecules is HCNO, fulminic acid, which was first detected in 2009 [4]. In the field of astrochemistry, HCNO is an intriguing molecule to detect, since it is, like its isomers isocyanic acid, HNCO, and cyanic acid, HOCN, the smallest molecule to contain the essential atoms for organic life and may also play a role in the formation of important biomolecules. HCNO is, however, also a molecule with a fascinating history [5]. HCNO was likely first synthesized in 1800 by Edward Howard, who combined nitric acid, ethanol and mercury oxide [6]. A white crystalline solid with a “saline taste” was produced [6]. Upon addition of sulfuric acid, a violent explosion ensued. Now convinced that he had not synthesized a muriate salt, he named this new compound fulminating mercury. Today we know that Howard synthesized explosive $Hg(CNO)_2$ and the addition of sulphuric acid lead to an exothermic release of fulminic acid, which ignited unreacted $Hg(CNO)_2$. The composition and structure of fulminic acid and its salts puzzled chemists for close to 150 years. In 1824, it was involved in the formulation of isomerism by Berzelius in the wake of the “Liebig-Wöhler controversy” [7] and in an early example of quantum chemical theory, Pauling computed that the structure of fulminic acid is HCNO and not CNOH as previously assumed [8].

In my PhD thesis, which I completed in the group of Prof. Dr. Ingo Fischer in Würzburg, we investigated how HCNO interacts with interstellar radiation, particularly VUV- and soft X-ray radiation. We synthesized HCNO by preparative gas-phase pyrolysis according to Wentrup *et al.* (shown in Fig. 1) [9].

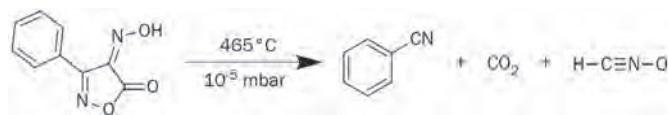


Fig. 1: Gas-phase preparative pyrolysis to produce HCNO from 3-phenyl-4-oxo-4H-isoxazol-5-ylidene, according to Ref. [9].

We hoped to gain a better understanding of the fate of interstellar HCNO, especially possible destruction pathways induced by these high-energy photons. Additionally, these studies allowed us to elucidate processes of fundamental spectroscopic inter-

est, such as the Renner-Teller distortion and the Auger-Meitner effect. We investigated the normal and resonant Auger electron spectra [10], the subsequent dissociation of the produced cations and dications [11] as well as the photoelectron spectrum and dissociative photoionization [12], which I want to discuss in more detail in this article.

Dissociative photoionization of HCNO

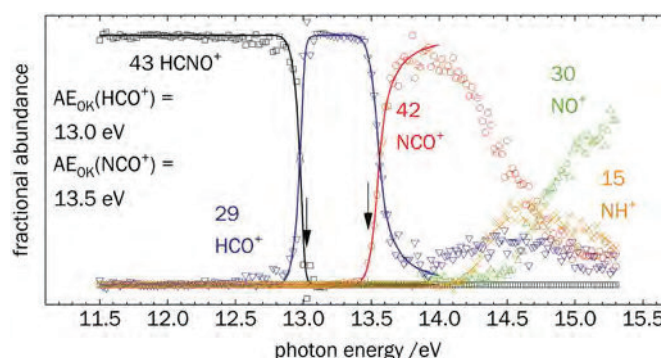
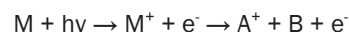


Fig. 2: Breakdown diagram of HCNO showing the dissociative photoionization up to photon energies of 15.3 eV. Experimental data is shown as colored symbols, the fit data produced by minimalPEPICO for the first two dissociation steps is shown as solid lines. Taken from Ref. [12]. Reprinted with permission from AIP Publishing.

UV photons in the interstellar space can induce photoionization, photodissociation and even a combination of both processes called dissociative photoionization:



This process occurs, when the photoionization produces a photoion M^+ with sufficient energy, that one or more bonds can be broken leading to the formation of a charged fragment A^+ and a neutral fragment B. This process can play an important role in the depletion of HCNO, while also producing highly reactive neutral and cationic species.

We investigated the dissociative photoionization of HCNO at the synchrotron radiation facility Swiss Light Source (SLS) in Villigen, CH. At the VUV beamline of the SLS, an i^2 PEPICO setup is available, enabling the simultaneous measurement of photoelectrons and photoions produced by interaction with VUV radiation in the range of 5 up to 21 eV [13]. The resulting breakdown diagram of the dissociative photoionization of HCNO up to photon energies of 15.3 eV is shown in Fig. 2. Below 12.8 eV, the HCNO cation is stable, and we detect it at $m/z = 43$.

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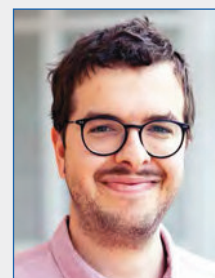
With the onset at 12.8 eV, HCNO^+ dissociates to $m/z = 29$, which we assign to HCO^+ . This is the dominant species up to an energy of around 13.5 eV, where we also observe the formation of $m/z = 42$, which we assign to NCO^+ based on enthalpies of formation tabulated in the ATcT [14]. At energies of 14.2 and 14.5 eV HCNO^+ may also fragment to $m/z = 30$, NO^+ , and to $m/z = 15$, NH^+ . The dissociation to HCO^+ and NCO^+ surprised us, since both fragments contain a C-O bond, while the parent ion HCNO^+ does not. This told us that before these fragments can be formed HCNO^+ must undergo some isomerization reaction. The global potential energy surface of the $[\text{H,C,N,O}]^+$ system has been investigated comprehensively by Luna *et al.* in 1996 using density functional theory, providing us the required energies and geometries of the intermediates and transition states [15]. With the transition state frequencies as input parameters, we were able to use the modeling program minimalPEPICO [16] to fit the experimental data. The resulting fit is shown in Fig. 2 as a solid lines. The model reproduces the experimental data well and allows to extract the experimental barrier energies for both reactions as the appearance energy at 0K $\text{AE}_{0\text{K}}$ for HCO^+ and NCO^+ from HCNO at 13.0 and 13.5 eV.

In interstellar environments, photons above 13.6 eV are quickly absorbed by ionization of the abundant H-atom, making only processes occurring below this energy relevant. We can show that the major dissociation product of HCNO^+ is HCO^+ with a small contribution of NCO^+ . We believe that the inclusion of these fragmentation pathways is important for astrochemical models. The data also shows the importance of experimental investigations, as it would have been difficult to predict the branching ratios solely based on theoretical models.

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Marius Gerlach studied chemistry at the University of Würzburg from 2014 to 2019. In Würzburg, he also completed his PhD in 2023 in the group of Prof. Dr. Ingo Fischer at the Institute for physical and theoretical chemistry. Since February 2024, he works as a postdoctoral researcher in the group of Prof. Dr. Sandra Brünken at HFML-FELIX in Nijmegen, NL. There, he investigates the Infrared spectroscopy and reaction kinetics of potentially interstellar ions trapped at cryogenic temperatures, mimicking the cold and dilute conditions in space.

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