



## VUV photoionization of acetamide studied by electron/ion coincidence spectroscopy in the 8–24 eV photon energy range

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### ABSTRACT

A VUV photoionization study of acetamide was carried out over the 8–24 eV photon energy range using synchrotron radiation and photoelectron/photoion coincidence (PEPICO) spectroscopy. Threshold photoelectron photoion coincidence (TPEPICO) measurements were also made. Photoion yield curves and branching ratios were measured for the parent ion and six fragment ions. The adiabatic ionization energy of acetamide was determined as I.E. ( $1^2A'$ ) =  $(9.71 \pm 0.02)$  eV, in agreement with an earlier reported photoionization mass spectrometry (PIMS) value. The adiabatic energy of the first excited state of the ion,  $1^2A''$ , was determined to be  $\approx 10.1$  eV. Assignments of the fragment ions and the pathways of their formation by dissociative photoionization were made. The neutral species lost in the principal dissociative photoionization processes are  $CH_3$ ,  $NH_2$ ,  $NH_3$ ,  $CO$ ,  $HCCO$  and  $NH_2CO$ . Heats of formation are derived for all ions detected and are compared with literature values. Some astrophysical implications of these results are discussed.

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### 1. Introduction

Acetamide,  $H_3C-C(O)-NH_2$ , is one among simple model molecules for the peptide linkage in polypeptides and proteins. Understanding the conformation of these biologically important species can be assisted by knowledge of the structure of this amide. Furthermore, amides are possible precursor molecules in the prebiotic formation of aminoacids that are necessary for the synthesis of proteins [1]. Our previous VUV spectroscopy and photophysics studies on small prebiotic molecules [2], as well as on amino acids [3] and purines and pyrimidines [4], including nucleobases [5], have been carried out in the context of their relevance to exobiological questions. Other groups have been working in this context too [6]. UV and VUV radiation are among the important energy sources impinging on prebiotic and biotic species in astrophysical sites [7].

There have been numerous attempts to prepare these species from simpler compounds under conditions that resemble those

of the primitive Earth. For a review on this subject see Ref. [8]. There have also been experimental and theoretical studies of analogous processes in the interstellar medium (ISM) [9,10]. Acetamide has been observed in the ISM by radioastronomy spectral measurements, in both emission and absorption, in the star-forming region Sagittarius B2(N) [11]. The interstellar formation of acetamide is speculated to occur by the exothermic reaction of the methylene radical  $CH_2$  with formamide, the latter being present in this region of space with an abundance five times that of acetamide [11]. Spin is not conserved in this reaction so that an activation barrier could exist. Shocks and UV irradiation could help overcome a barrier to reaction. Models have also been proposed [10] in which acetamide is formed on interstellar grains by radical–radical interactions. The reacting radicals,  $CH_3$  and  $HNCO$ , require irradiation of the icy mantles for their eventual formation on the grains. The reaction between these radicals is followed by hydrogenation to form acetamide which is then released to the gas phase, where it is observed by radioastronomy, by warm-up mechanisms. Fair agreement with the observed abundance of acetamide in the ISM has been obtained with at least one theoretical model [10].

We remark also that acetamide has been synthesized in laboratory studies involving UV photolysis and proton irradiation of interstellar and pre-cometary ice analogues, such as frozen

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mixtures of H<sub>2</sub>O, CH<sub>3</sub>OH, NH<sub>3</sub> and CO [12]. However, acetamide has not yet been observed in comets.

In this work we have carried out a VUV photoionization study using synchrotron radiation and electron/ion coincidence spectroscopy in the 8–24 eV energy range. The results are important for the determination of survival conditions of this prebiotic molecule to VUV radiation in an astrophysical context. In addition, the study and interpretation of the products of dissociative photoionization of acetamide have potential repercussions, in particular, relative to the use of mass spectrometry in peptide sequencing, which requires an understanding of the chemistry of amides in the mass spectrometer. Earlier photoionization mass spectrometry (PIMS) studies on acetamide have been carried out by Watanabe et al. [13], who measured the ionization energy, and by Schröder et al. [14] who studied keto/enol isomerization of the acetamide cation. In the latter study, quadrupole mass spectrometry has been used and appearance energies (AE) were reported too, but no ion yield curves or branching ratios.

## 2. Structural aspects

### 2.1. The structure of neutral acetamide

The acetamide molecule is considered to be planar and to have C<sub>s</sub> symmetry [15,16]. Electron diffraction data [17] are compatible with a planar structure, but neutron diffraction studies [18] have shown that the peptide moiety in acetamide is slightly non-planar. In the present study we consider acetamide as effectively planar, as is compatible with infrared spectroscopy studies in the gas phase [19,20].

*Ab initio* molecular orbital studies on the structure of acetamide [21] show that the most stable conformation is that in which the methyl group is staggered with respect to the N–C bond. The methyl group is thus eclipsed with respect to the C=O link. The barrier to rotation of the methyl group with respect to the N–C bond is ≈740 meV, determined by NMR for acetamide in solution [22]. Calculated values are 635–890 meV, according to the level of calculation [21], and 542 meV, in *ab initio* calculations which include polarization functions in the basis set [23]. We note that, like formamide, acetamide can be considered to have two resonant structures, which give the C–N bond partial double bond character with a planarised nitrogen atom.

### 2.2. Electronic structure

According to Asbrink et al. [24] the electron configuration of the planar C<sub>s</sub> acetamide molecule is:

$$\dots (5a')^2(6a')^2(7a')^2(8a')^2(9a')^2(1a'')^2(10a')^2(11a')^2 \\ \times (12a')^2(2a'')^2(3a'')^2(13a')^2$$

The *a'* M.O.s are σ orbitals, the *a''* are π orbitals. The two highest occupied orbitals are close together. All interpretations of the photoelectron spectra (PES) of acetamide [24–29] respect the above order of the two highest M.O.s.

## 3. Experimental

Measurements were performed at the undulator beamline DESIRS [30] of the Synchrotron Soleil (St. Aubin, France). The permanent endstation named SAPHIRS, on one of the two monochromatised branches of this beamline, was employed for our measurements. The beamline incorporates a 6.65 m normal incidence monochromator [31] which is equipped with four different gratings. For our measurements, we used the 200 grooves/mm grating which pro-

vides a constant linear dispersion of 7.2 Å/mm at the exit slit of the monochromator. The typical slit width used in our experiments is 100 μm, yielding a monochromator resolution of 0.7 Å for these conditions (about 6 meV at *hν* = 10 eV and 18 meV at *hν* = 18 eV). We also note that the beamline is equipped with a gas filter [32], which effectively removes all the high harmonics generated by the undulator that could be later transmitted by the grating, providing a high spectral purity. In this work, Ar has been used as a filter gas for all measurements below 16 eV.

The DELICIOUS II apparatus has been described in detail recently [33]. Briefly, it consists of a photoelectron photoion coincidence (PEPICO) spectrometer combining velocity map imaging (VMI) of the photoelectrons with a linear time-of-flight mass analyzer operating according to Wiley–MacLaren space focusing conditions. From the electron images, zero kinetic energy electrons can be selected in order to measure Threshold-PEPICO (TPEPICO) mass spectra with resolutions as small as 1 meV. In TPEPICO energy scans, the total resolution is given by the convolution of the monochromator's resolution and the energy resolution of the threshold electrons. The latter can be chosen *a posteriori* by changing the size of the central area of the VMI image used for the coincidence measurement within an interval depending on the selected extraction field (cf. [33] for more details). In PEPICO energy scans, giving partial ion yields, electrons with a maximum kinetic energy (KE<sub>max</sub>) of up to 0.95 eV are used for the coincidence measurements in this study, i.e. there is no ion discrimination up to 0.95 eV above the onsets. KE<sub>max</sub> depends on the extraction field applied in DELICIOUS II (95 V/cm in our case; cf. Ref. [33]). The spectral resolution of these scans is defined only by the slit widths of the monochromator (see above). The step size in the ion yield curves is 5 meV. The energy scale was calibrated using known absorbing Ar lines from the gas filter. The absolute energy precision is better than 3 meV. All photoion yield curves were normalized with respect to the incoming photon flux, continuously measured by a photodiode (AXUV100, IRD).

Due to its low vapour pressure, the solid acetamide powder (from Sigma Aldrich, no further purification) was placed inside an in-vacuum oven heated to 80 °C. The resulting vapour was mixed with 1 bar of He and expanded through a 50 μm nozzle. The molecular beam then traversed a 1 mm skimmer to enter the ionization chamber, where it intersected the VUV photon beam whose transverse dimensions are about 200 μm (horizontal) × 100 μm (vertical).

We remark that our PEPICO fragment ion appearance energies (AEs) correspond to *effective* thermochemical energy values. The two main factors for the possible difference between the measured AE and the 0 K value are (a) the limited detection sensitivity and (b) the thermal energy stored in the parent neutral. Fragmentation dynamics (possible activation barriers, formation of vibrationally excited fragments) also influence the effective AE. This has been discussed in more detail earlier [34]. In the present molecular beam experiment, the expected low temperature (~40 K) should, however, provide a value closer to the AE<sub>0K</sub> than room temperature experiments. Also, compensatory effects may lead to appearance energies that reflect reasonably well their 0 K values as has been pointed out by Chupka [35].

The AEs are determined from semi-log ion yield plots in the threshold region by fitting straight lines to the noise and to the ion signal rise in this region (not shown in our figures). The photon energy at the intersection of these two lines is assigned to the measured AE value. Applying different fits, the precision is estimated by visual inspection of the variation of the intersection and is thus a function of the sharpness of the ion signal rise in the threshold region. Ion yield curves are shown on a linear scale in the figures in order not to distort the shape of the spectrum. The yields for

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