



## Dissociation of acetonitrile molecules following resonant core excitations

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### ABSTRACT

Dissociation of acetonitrile molecules following resonant core excitations of carbon and nitrogen core electrons to the LUMO orbital was investigated using the electron-energy-resolved photoelectron–photoion coincidence (PEPICO) technique. The fragment ion mass spectra were recorded in coincidence with the resonant Auger electrons, emitted in the decay process of the core-excited states. Deuterated and <sup>13</sup>C-substituted samples were used for fragment identification. The results showed the initial core hole localization to be of minor importance in determining the dissociation pattern of the molecular cation. The participator and spectator Auger transitions produce entirely different fragmentation patterns and the latter indicates that complex nuclear rearrangements take place. Using also the findings from the <sup>13</sup>C labelling, it is suggested that the bending motion, induced in the core-excited state by the Renner–Teller effect, plays an important role in determining the most intense dissociation pathways of the spectator Auger final electronic states.

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### 1. Introduction

Acetonitrile ( $C_2H_3N$ ) is an organic molecule widely used in chemical industry as a solvent. Also known as methyl cyanide, it is the simplest of the organic nitriles. Acetonitrile molecule and a number of its fragments are also present in interstellar medium, where its dissociation is caused by cosmic rays. These molecules and ions play an important role in astrochemistry [1–3]. Dissociation of acetonitrile, both from gas phase and from adsorbed molecules, has been investigated by a number of experimental and theoretical studies [4–15]. It has become clear, that the dissociation process cannot be viewed simply as separation of the molecule into fragments, starting from its ground state geometry, along one or more broken bonds. Instead, nuclear rearrangements take place in the early stages of the dissociation. This process is related to the isomerization and therefore the dissociation and isomerization reactions should be considered together [8,11]. There are several known isomers of acetonitrile: in the neutral ground state the methyl cyanide configuration  $CH_3-C\equiv N$  has the lowest energy, whereas the ionic state the ketenimine isomer  $CH_2=C=NH$  is predicted to be the optimal configuration [11]. According to calculations, a number of other stable linear and cyclic geometries exist for the acetonitrile cation [8,16]. In the present work, the early

stages of various dissociation pathways are discussed in terms of alternative isomerization reactions through theoretically predicted transition states.

Although the outcome of the dissociation reactions has been investigated using both electron [17,18] and photon [15] ionization as well as collision- or surface-induced ionization [7,11–14,16], little is known about how the dissociation depends on the nature of the intermediate short-lived excitation or on the electronic state of the parent molecular cation. Some earlier studies focused on electron–ion coincidences following nitrogen core excitations [9,10], but were lacking the electron energy measuring capability. On the other hand, Sekitani et al. [6] performed electron–ion coincidence (PEPICO) measurements on acetonitrile on gold surface with resolved electron energies and also scanning the photon energy across the core absorption structures, but they detected only the  $H^+$  ions. Preliminary PEPICO results on the fragmentation of gas-phase acetonitrile were published in our instrumental paper [19].

When a photon of suitable energy is absorbed by molecule, electrons from core orbitals can be excited to the lowest unoccupied molecular orbital (LUMO). The resulting neutral core-excited state is energetically very unstable and decays by a resonant Auger process in a few femtoseconds, producing molecular cations. Depending on the fate of the LUMO electron, one can distinguish between the participator and spectator Auger decay. In the former, the LUMO electron is emitted and one valence hole created by filling the core hole; these resulting singly ionized electronic states

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are identical to those reached by direct valence photoionization. In the case of spectator Auger decay the photoexcited core electron remains in LUMO, one valence electron fills the core hole and another is emitted. The spectator Auger transitions to such states have a high probability, but in contrast these states can be only weakly populated (as satellite states) by direct valence photoionization. The presence of the excited electron in the antibonding LUMO orbital can have major consequences for the subsequent nuclear dynamics.

Using the pathway of resonant Auger decay to produce molecular cations thus opens access to a large variety of ionic electronic states which can be identified by the energy of the emitted Auger electron. In order to investigate the dependency of the molecular fragmentation on these states, the kinetic energy of the Auger electron must be recorded in coincidence with the ionic fragments. In this work, soft X-ray synchrotron radiation was used for the initial photoexcitation as its tunability allowed to selectively excite carbon or nitrogen core electrons. The end products were studied by ion mass (time-of-flight) spectroscopy in combination with electron spectroscopy using the electron–ion coincidence (PEPICO) technique.

A problem in PEPICO studies particularly for organic molecules is the unambiguous identification of the fragments based on their mass, since the PEPICO techniques employ rather simple linear ion TOF spectrometers which cannot resolve mass differences in the order of 1/1000th amu. In order to resolve these ambiguities, isotopic substitutions – deuteration and isotopic labelling of the terminal carbon by  $^{13}\text{C}$  – were used in the present work. The latter also allows us to identify, which carbon is contained in a fragment.

## 2. Experiment

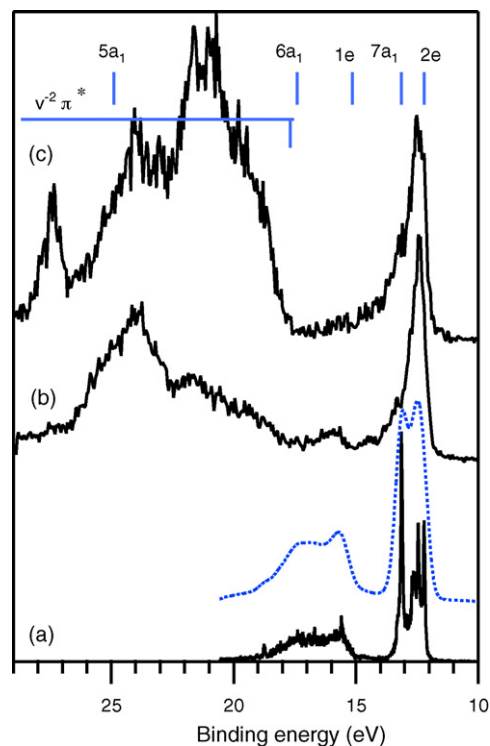
As the experimental PEPICO setup has been described in detail in [19], a brief summary is given here. The setup consists of a modified Scienta SES-100 electron energy analyzer [20], where the original CCD camera was replaced by a resistive anode detector (Quantar), and a homemade Wiley-Mclaren type ion time-of-flight detector with a 400 mm long drift tube. The ion spectrometer is equipped by 77 mm Hamamatsu MCP detector with the anode consisting of 10 concentric rings. The ion TOF is determined by the recharge signal pulse from the MCP stack and the pulses from the anode rings are delayed by 50–100 ns with 5 ns steps. These can be used to determine the radial hit distance from the instrument's axis; in the present work the delayed pulse information was used in the data analysis stage to restrict the active area and improve the true/false coincidence ratio. The ion detection electronics is based on a 1 GHz waveform digitizer card (Signatec PDA 1000). The PEPICO system is operated in the pulsed extraction field mode and in the present experiment the extraction pulse voltage was 260 V across the sample region, with the drift tube held at  $-635\text{ V}$ .

The experiment was performed at beamline I411 at MAX-II synchrotron radiation facility (Lund, Sweden) [21]. Undulator radiation was monochromatized using a modified Zeiss SX-700 monochromator. The samples of acetonitrile, deuterated acetonitrile and isotopically substituted  $^{13}\text{CD}_3\text{-C}\equiv\text{N}$  were purchased from Sigma-Aldrich.

## 3. Results and discussion

### 3.1. Photoexcitation and resonant Auger decay

The photoabsorption spectrum of acetonitrile shows a prominent resonant structure below the  $N\ 1s$  ionization edge at  $h\nu = 399.9\text{ eV}$ , assigned to the excitation of  $N\ 1s$  electron to LUMO



**Fig. 1.** Electron energy spectra for (a) nonresonant photoemission at  $h\nu = 60.5\text{ eV}$ , dotted line-convoluted by  $0.49\text{ eV}$  Gaussian, (b) resonant Auger decay after  $\text{C}1s \rightarrow \pi^*$  excitations at  $h\nu = 286.9\text{ eV}$  and (c) resonant Auger decay after  $\text{N}1s \rightarrow \pi^*$  excitations at  $h\nu = 399.9\text{ eV}$ . Orbital ionization energies and the range of the spectator Auger excitation are marked.

[5,22] that has the  $\pi^*$  character along the  $\text{C}\equiv\text{N}$  bond in neutral acetonitrile (methyl cyanide isomer). Similar excitation feature is identified below the  $\text{C}\ 1s$  edge at  $286.9\text{ eV}$  photon energy [5]. The  $\text{C}1s \rightarrow \pi^*$  and  $\text{N}1s \rightarrow \pi^*$  excitations were induced using  $0.3$  and  $0.4\text{ eV}$  bandwidth (FWHM) monochromatized synchrotron radiation, respectively. Resonant Auger decay spectra of these excitations are shown in Fig. 1 together with a direct valence photoionization spectrum taken at  $h\nu = 60.5\text{ eV}$  with  $10\text{ meV}$  photon bandwidth. In order compensate for the differences in experimental resolution, Fig. 1(a) shows also the valence photoionization spectrum convoluted with a  $0.49\text{ eV}$  FWHM Gaussian.

The Auger electron spectra at the  $\text{C}$  and  $\text{N}$  resonances exhibit a similar structure. The peak in the binding energy range from  $12$  to  $14\text{ eV}$  corresponds to the participator transitions, populating the same single-hole states as in the nonresonant valence spectrum (a). The electronic states in this structure are, according to [24,25]:

$$E_b = 12.20\text{ eV}, (2e)^{-1} - \text{the valence orbital with mostly } \pi_{\text{CN}} \text{ character,}$$

$$E_b = 13.13\text{ eV}, (7a_1)^{-1} - \text{mostly } \text{N } 2p\sigma,$$

The structure between  $12$  and  $13\text{ eV}$  has been assigned to the vibrational progressions of the  $(2e)^{-1}$  band. The vibrational progression is unresolved in the participator Auger spectra (b) and (c) and also the  $(7a_1)^{-1}$  band shows much less resonant enhancement than the  $(2e)^{-1}$  band. Next, the inner valence bands are visible in spectrum (a):

$$E_b = 15.13\text{ eV}, (1e)^{-1} - \text{pseudo } \pi_{\text{CH}_3} \text{ [25],}$$

$$E_b = 17.4\text{ eV} - (6a_1)^{-1} \text{ [26]}$$

Transitions to these inner valence states are very weak in the resonant Auger spectra (b) and (c). The high binding energy region

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