

Autodetachment dynamics of acrylonitrile anion revealed by 2D electron impact spectra

This content has been downloaded from IOPscience. Please scroll down to see the full text.

2014 J. Phys.: Conf. Ser. 488 052007

(<http://iopscience.iop.org/1742-6596/488/5/052007>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 134.21.16.139

This content was downloaded on 22/10/2014 at 13:30

Please note that [terms and conditions apply](#).

Autodetachment dynamics of acrylonitrile anion revealed by 2D electron impact spectra

Khrystyna Regeta¹ and Michael Allan²

Department of Chemistry, University of Fribourg, Chemin du Musée 9, 1700 Fribourg, Switzerland

Synopsis We have measured the elastic and vibrationally inelastic differential cross sections in acrylonitrile at the scattering angle of 135°. We have found out that the bands at 2.9 and 4.4 eV are shape resonances, while sharp structures in the region 0 – 0.5 eV are either boomerang structure of a shape resonance or vibrational Feshbach resonances. We gain detailed view of the autodetachment dynamics from a 2D spectrum where cross section is plotted against the incident energy and the energy loss.

The interest in acrylonitrile stems from its occurrence in outer space [1] and because it is widely used as a starting material to make polymers. It has a dipole moment of 3.86 D [2] and has been shown to support dipole-bound states [3].

Three shape resonances, due to temporary occupation of three π^* orbitals, are expected in acrylonitrile and were observed in ETS [4]. Qualitative arguments based on the attachment energies of ethene (1.9 eV) and HCN (2.5 eV) lead to expectation of roughly 2.2 ± 2 eV, *i.e.*, 0.2 eV and 4.2 eV for π_1^* and π_3^* (the in-phase and out-of-phase combinations of the vinyl and cyano π^* orbitals) and about 2.5 eV for π_2^* (the in-plane π^* orbital of the cyano group).

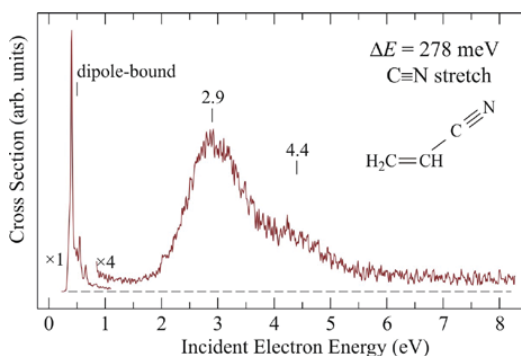


Figure 1. Energy dependence spectrum for CN stretch excitation in acrylonitrile.

The first resonance could be a shape π_1^* resonance, formed by temporary attachment of the incident electron to the π_1^* orbital. But since the dipole moment of acrylonitrile is big enough (above critical), it supports dipole-bound states, therefore the nicely resolved structures at low energy (Figure 1)

could also be due to vibrational Feshbach resonances. In this case the electron is trapped into a very diffuse orbital and is only weakly bound.

One way to distinguish between these two types of resonances (vibrational Feshbach and shape) is to measure other alkyl substituted acrylonitriles and see whether the resonance will go up in energy or not. In case of a shape resonance, alkyl substitution must destabilize the energy of the orbital temporarily occupied in the resonance, thus raising its energy. For this reason we have measured methacrylonitrile (acrylonitrile with one methyl group) and are planning to measure acrylonitrile with two methyl groups. We have seen, that in case of methacrylonitrile the first band has been shifted to higher energy, providing an evidence for a shape resonance, although due to sufficient values of dipole moments, vibrational Feshbach resonances must also be present.

To obtain a deeper understanding of the decay of the resonance we have used the technique of making a 2D picture, where differential cross section is plotted as a function of incident electron energy and the electron energy loss. It revealed a very interesting propensity – no matter what the incident energies and energy losses are, the residual energy of the electron prefers to be constant. In other words we have a preference for a given residual energy, *i.e.*, for certain vibrational modes and quanta (mainly $\Delta v = -1$) driving the autodetachment process.

References

- [1] F F Gardner *et al* 1975 *Astrophys. J.* **195** 127
- [2] C Desfrancois *et al* 1994 *Phys. Rev. Lett.* **73** 2436
- [3] L Suess *et al* 2003 *J. Chem. Phys.* **119** 12890
- [4] P D Burrow *et al* 1992 *J. Phys. Chem.* **96** 7570

¹E-mail: khrystyna.regeta@unifr.ch

²E-mail: michael.allan@unifr.ch