



# Lowest vibrational states of acrylonitrile from microwave and synchrotron radiation spectra



Zbigniew Kisiel<sup>a,\*</sup>, Marie-Aline Martin-Drumel<sup>b,c,1</sup>, Olivier Pirali<sup>b,c</sup>

<sup>a</sup> Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warszawa, Poland

<sup>b</sup> AILES Beamline, Synchrotron SOLEIL, l'Orme des Merisiers, Saint-Aubin, 91192 Gif-sur-Yvette cedex, France

<sup>c</sup> Institut des Sciences Moléculaires d'Orsay, UMR8214 CNRS, Université Paris-Sud, Bât. 210, 91405 Orsay cedex, France

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## ABSTRACT

The high resolution Fourier-transform spectrum of acrylonitrile covering the 40–700  $\text{cm}^{-1}$  spectral region was recorded at the AILES infrared beamline of the SOLEIL synchrotron. The spectrum allowed assignment of vibration–rotation transitions in four different fundamental bands, five hot bands, one overtone band, as well as of some pure rotational transitions. The new infrared data and previous measurements made with microwave techniques have been combined into a single global fit encompassing over 31000 measured transitions. Precise vibrational term values have been determined for the eight lowest excited vibrational states, including  $\nu_{11} = 228.299930(4)$ ,  $\nu_{15} = 332.678207(4)$ ,  $\nu_{10} = 560.716701(5)$ , and  $\nu_{14} = 681.793862(13) \text{ cm}^{-1}$ . The new values are compared with those obtained previously entirely on the basis of rotational perturbations. Several anharmonicity coefficients are determined and compared with *ab initio* anharmonic force field calculations. The assignment of the  $\nu_{10}$  mode is also clarified.

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## 1. Introduction

Acrylonitrile (vinyl cyanide,  $\text{H}_2\text{C} = \text{CHCN}$ ) is a compound with a long history of high resolution studies by rotational spectroscopy carried out for a variety of reasons. Nevertheless, it is the observation of this molecule in interstellar space [1] that has proven to be the main driving force in its more recent high resolution laboratory spectroscopy. The astrophysical relevance of acrylonitrile has been reinforced by the observation even of transitions in  $^{13}\text{C}$  isotopic species and in vibrationally excited states in Sgr B2 [2,3] and in Orion-KL [4] interstellar molecular clouds. The earlier studies of the rotational spectrum of acrylonitrile [5–13] have more recently been considerably extended by taking the coverage well into the THz region [4,14–16]. An intriguing result of these studies was that pursuit of very high- $J$ , moderate- $K_a$  transitions at THz frequencies revealed a plethora of interstate perturbations, affecting even the ground state (g.s.). The initial treatment of perturbations between the ground state and  $\nu_{11}$  [14,15] was later extended to encompass the four lowest vibrational states [16]. In this way vibrational term values for  $\nu_{11}$ ,  $\nu_{15}$  and  $2\nu_{11}$  were determined to the rather high

nominal precision of  $0.00002 \text{ cm}^{-1}$ . Furthermore, several precise energy differences were also determined in higher vibrational polyads of acrylonitrile [4]. Those results could not be compared directly against gas-phase infrared spectroscopy since only low resolution studies of this type have been carried out [17–21]. Only Ref. [19] achieved partial rotational resolution and determined  $\nu_{11}$  and  $\nu_{15}$  to  $0.1 \text{ cm}^{-1}$  accuracy. Presently, we remedy this situation by reporting measurements in the lower infrared region at the highest resolution and sensitivity possible with Fourier-transform infrared spectrometers at synchrotron radiation facilities. The new experimental results are augmented by a new analysis using all available pure rotation and vibration–rotation measurements in the framework of a single global fit, resulting in derivation of a very precise, unambiguous vibrational state picture of acrylonitrile, see Fig. 1.

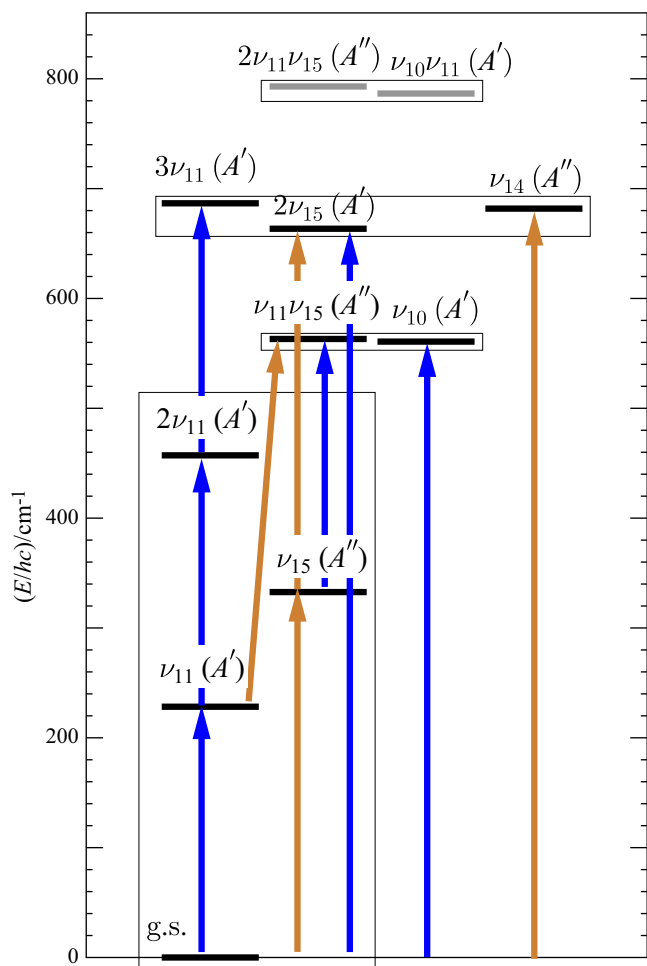
## 2. Experimental details

Acrylonitrile has been studied by high resolution Fourier-transform far infrared (FT-FIR) spectroscopy on the AILES beamline of SOLEIL synchrotron using a Bruker IFS125 spectrometer [22,23]. A room temperature absorption spectrum has been recorded using synchrotron radiation at a resolution of  $0.00102 \text{ cm}^{-1}$  in a White-type absorption cell providing an absorption path-length of about

\* Corresponding author. Fax: +48 22 8430926.

E-mail address: [kisiel@ifpan.edu.pl](mailto:kisiel@ifpan.edu.pl) (Z. Kisiel).

<sup>1</sup> Present address: Harvard – Smithsonian Center for Astrophysics, 60 Garden Street, MS-50, Cambridge, MA 02138, USA.



**Fig. 1.** The lowest vibrational states in acrylonitrile. Boxes identify polyads of states for which rotational transitions have been previously fitted by means of coupled fits accounting for interstate perturbations [4,16]. Arrows indicate vibrational transitions assigned presently in the far infrared spectrum recorded with synchrotron radiation. The molecule is planar, of  $C_s$ -symmetry, and the allowed vibration-rotation transitions are either  $c$ -type (such as  $\nu_{15}$ ) or a combination of  $a$ - and  $b$ -type (such as  $\nu_{11}$ ), as indicated with different colours in the diagram. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

150 m [24]. A Mylar beamsplitter (6  $\mu\text{m}$ -thickness), a 2 mm iris, polypropylene windows, and a 4.2 K liquid-helium-cooled bolometer were used. Sample pressure in the cell was 0.1 mbar, the sample was of stated purity higher than 97% from Aldrich Chemical Co. and was used without further purification. The resulting spectrum covers the frequency region 40–700  $\text{cm}^{-1}$  and was obtained by the co-addition of 242 interferograms. It has been calibrated using the unavoidably present residual water lines and their accurate line frequencies from [25,26].

The fits and predictions were made with the SPFIT/SPCAT package [27,28], which allows practically unlimited freedom in the construction of a Hamiltonian for multiple interacting vibrational states. The AABS package for *Assignment and Analysis of Broadband Spectra* [29] was used as the graphical front-end to SPFIT/SPCAT. The recorded spectrum was first processed with the SVIEW\_L component of the package, and was then compared against collected predictions for all of the studied pure rotation and vibration-rotation transitions as displayed with the linked ASCP\_L component. The actual assignment and data set construction was also carried out with ASCP\_L, with liberal use of its Loomis–Wood display mode. The AABS package and several

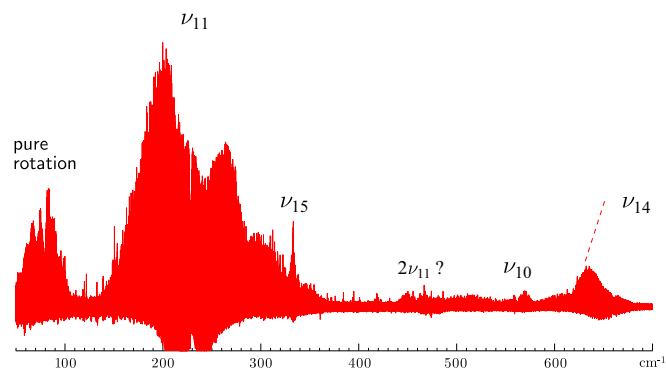
ancillary programs for dealing with the output of SPFIT/SPCAT are freely available from the PROSPE website [30,31]. The more advanced applications of the package have recently been summarised in Ref. [16]. The present work, and the recent studies of combined high resolution data for cyanamide [32] and for  $S(\text{CN})_2$  [33], provided the opportunity to fine tune the package for operation also with both high resolution microwave and vibration-rotation spectra.

The measured rotational transitions were used as published in Refs. [4,16] and incorporated preceding literature data. Those measurements span frequencies from the cm-wave region up to 1900 GHz and were made with different spectrometers and by different authors, so that some care was necessary in choosing measurement uncertainties in order to use such data in a single weighted fit. The adopted scheme was described and tested in Ref. [16]: the preceding literature data was used as published, whereas for measurements carried out in Refs. [4,14,16] frequency uncertainty of 0.1 MHz was used for all transitions up to 640 GHz, 0.2 MHz for 818–1205 GHz, and 0.4 MHz for 1576–1900 GHz. The present infrared data were equally weighted by assuming a wavenumber measurement uncertainty of  $0.0001 \text{ cm}^{-1}$ .

### 3. Infrared spectrum

The recorded spectrum is shown in compressed form in Fig. 2 and the various bands are relatively easy to assign on the basis of previous works. Standard mode numbering is employed, with modes labelled from highest to lowest wavenumber, first for the eleven  $A'$  modes, and then for the four  $A''$  modes, classified according to the  $C_s$  point group for the 7-atom planar acrylonitrile molecule. The lowest wavenumber  $\nu_{11}$  band constitutes the dominating feature in the spectrum. The  $\nu_{15}$  band is positioned on the high wavenumber edge of  $\nu_{11}$ , but is clearly identifiable because of its central Q-branch spike. Both bands are completely resolved, as can be seen in Figs. 3 and 4, and some hot band features are also apparent, even by unaided inspection. The two other fundamentals in this region,  $\nu_{10}$  and  $\nu_{14}$  are also visible. The  $\nu_{14}$  band turns out to be attenuated by the low-pass filter used in the recording to the extent that only  $P$ -branch and  $Q$ -branch lines are measurable.

At this compression there is also some apparent line density at the expected position of the  $2\nu_{11}$  overtone. Unfortunately, low signal-to-noise in that region and the lack of calculated dense spectral features did not allow for analysis and the  $2\nu_{11}$  assignment remains tentative. Nevertheless, at this stage we have already identified vibrational transitions to at least one state in each polyad in Fig. 1.



**Fig. 2.** Overview of the recorded synchrotron radiation spectrum of acrylonitrile. This very compressed spectrum has had the baseline and the water lines removed. The  $\nu_{14}$  fundamental is actually quite strong but is strongly attenuated by the nominal 700  $\text{cm}^{-1}$  low-pass filter used during the recording, which begins to strongly cut in beyond 630  $\text{cm}^{-1}$ .

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