

## The rotational spectrum of acrylonitrile up to 1.67 THz

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### ABSTRACT

The rotational spectrum of acrylonitrile was studied up to 1.67 THz by recording and analysing several extended spectral segments spanning a total of over 540 GHz. The spectra were obtained with cascaded harmonic multiplication techniques, and the ground state data set was extended to over 3000 lines,  $J = 129$ , and includes transitions up to  $K_a = 30$ . At high- $J$  and  $K_a$  several manifestations of a perturbation between the ground state and the lowest excited vibrational state,  $\nu_{11} = 1$ , were observed. The perturbed frequencies were successfully fitted with a coupled fit of the two states resulting in  $E_{11} = 228.29991(2) \text{ cm}^{-1}$ . The results reported for the parent species of acrylonitrile should allow confident prediction of the major features over the whole envelope of the measurable rotational spectrum. New measurements and spectroscopic constants for the ground states of the three single  $^{13}\text{C}$  isotopic species and for the  $^{15}\text{N}$  species are also reported.

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### 1. Introduction

Acrylonitrile (vinyl cyanide,  $\text{H}_2\text{C}=\text{CHCN}$ ) is a relatively rigid planar molecule, and its laboratory rotational spectrum has already been studied on numerous occasions [1–10]. Acrylonitrile is also an established astrophysical species (see Ref. [10]) and the combination of its abundance and sizable dipole moment allowed detection by radioastronomy even of its  $^{13}\text{C}$  isotopic forms [10]. Owing to relatively large values of rotational constants this molecule is expected to be a plentiful contributor to mm- to submm-wave region spectra recorded with the emerging new tools of radioastronomy, such as the Herschel Space Observatory or ALMA (Atacama Large Millimeter/submillimeter Array). The rotational spectrum envelope at laboratory and astrophysically relevant temperatures is shown in Fig. 1 and it can be seen that at high frequencies the spectrum due to the smaller  $\mu_b$  dipole moment component is more relevant. Previous measurements do not extend beyond 458 GHz, with the exception of a total of 40 lines measured with lower precision near 640 and 900 GHz [7]. The principal motivation of the present work has been to use the broadband cascaded harmonic multiplication technique to extend such measurements well into the THz region and to cover a significant portion of the relevant spectral range. This hitherto most comprehensive study of the rotational spectrum of acrylonitrile revealed many surprises that throw additional light on the vibration–rotation interactions in this molecule.

Previous studies of the rotational spectrum of acrylonitrile resulted in determination of its dipole moment components,

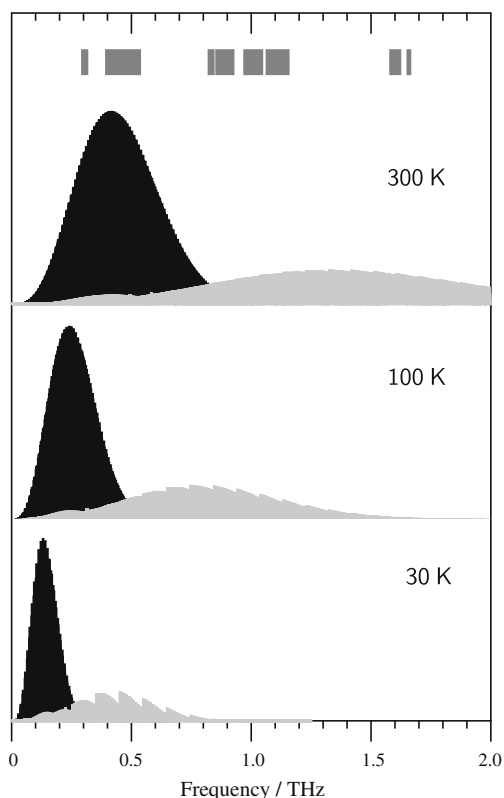
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$\mu_a = 3.815(12) \text{ D}$ ,  $\mu_b = 0.894(68) \text{ D}$  [5], of the molecular geometry [7,9], and in analysis of  $^{14}\text{N}$  nuclear quadrupole hyperfine structure [5,8,9]. Isotopic species were studied in [9,10], rotational transitions in several of the lowest excited vibrational states were assigned in [6], and measurements for the lowest excited state were extended in [7]. The results of earlier work were reviewed in [4], while the most recent constants for the ground states of the parent, the single  $^{13}\text{C}$ , and the  $^{15}\text{N}$  isotopic species have by given in [10], where a brief review of key astrophysical studies has also been made. The infrared spectrum of acrylonitrile and its vibrational normal modes have been surveyed in [11], and the two lowest frequency modes,  $\nu_{11}$  and  $\nu_{15}$ , were later studied in more detail on a gas-phase sample in the far infrared [12]. The lowest vibrational energy levels in acrylonitrile will contribute to the rotational spectrum and their positions are shown in Fig. 2. Initial analysis of the spectra recorded in the present work revealed that there are perturbations between all pairs of neighboring vibrational states, in a chain of perturbations extending from the ground state. The perturbations identified so far are indicated in Fig. 2 and it is clear that a thorough analysis will require a global fit of transitions in all states. In this work we present the first stage of such analysis where we endeavour to account for all of the newly identified effects in the ground state of acrylonitrile.

### 2. Experimental details

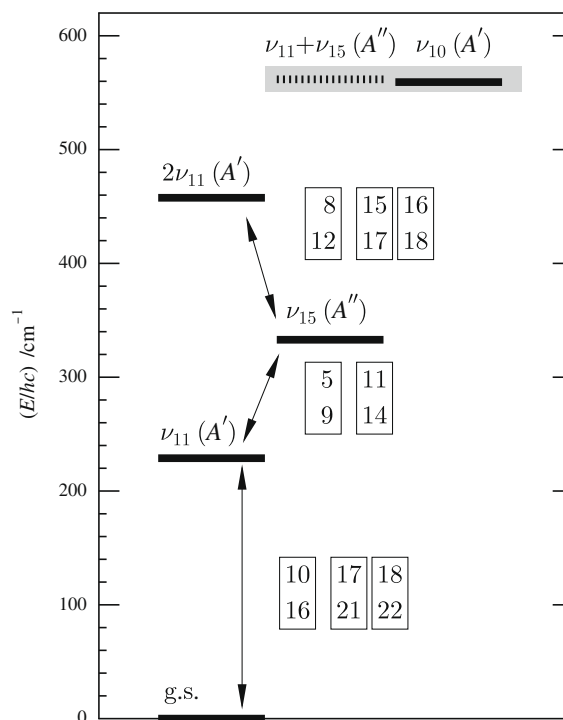
Broadband submillimeter and THz spectra were recorded at JPL by using frequency stabilized harmonic multiplier chains. The spectra covered 290–320, 390–540, 818–930, 983–1160 GHz, and



**Fig. 1.** The temperature dependence of the rotational spectrum of acrylonitrile. The *a*-type transitions (darker) are stronger but peak in intensity at lower frequencies than the *b*-type transitions (lighter). The spectra are normalized in intensity for clarity but, owing to the temperature dependence of the partition function, their peak intensities are in the ratio 50:15:1 for 30, 100, 300 K, respectively. The regions of the spectrum studied in this work are marked at the top of the diagram.

1.58–1.67 THz. Harmonic multiplication numbers of the 11–18 GHz driving synthesizer frequency ranged from  $30 = 6 \times 5$  at 500 GHz, to  $108 = 6 \times 2 \times 3 \times 3$  at 1.6 THz. The radiation was detected after doubly passing the 2.5 m absorption cell. At frequencies up to 540 GHz detection was made with a room temperature Schottky diode detector from Virginia Diodes, and at higher frequencies by using a Si-composite bolometer. Toneburst modulation, with 100 kHz tone and 0.5 kHz burst frequencies, was applied at the FM input of the source synthesizer which allowed lock-in detection ( $1f$  at 0.5 kHz) of 2nd derivative lineshapes. A detailed description of the setup is given in Ref. [13]. All measurements were carried out at room temperature and the pressure in the absorption cell was in the range 3–10 mTorr. Some additional, more limited, measurements in the region 189–275 GHz were also made with the BWO-based spectrometer in Warsaw [14,15].

Experimental uncertainties for the newly measured transition frequencies were assigned in proportion to increasing multiplication harmonic and line width, and were 0.05 MHz for transitions up to 524 GHz, 0.075 MHz for 818–930 GHz, 0.1 MHz for 967–1160 GHz, and 0.2 MHz for 1.58–1.67 THz. These uncertainties were doubled for especially weak lines, such as the highest-*J* and highest-*K<sub>a</sub>* transitions in the parent isotopic species, or transitions for the  $^{13}\text{C}$  and  $^{15}\text{N}$  isotopic species. In integrating the data from previous work, Refs. [4–10], we used their original uncertainties, with two exceptions. All lines cited in Ref. [4] were assigned uncertainties of 0.05 MHz, as was done (but not explicitly stated) in Ref. [6]. The parent species lines from Ref. [10] also had uncertainties as low as 0.003 MHz, which were estimated individually for each line. This is different than was used in other studies where an average uncertainty for a given spectrometer was employed. In order to



**Fig. 2.** Positions of the lowest vibrational energy levels in acrylonitrile. Rectangles enclose values of  $K_a$  for which appreciable perturbations between the two indicated states have been identified. The upper of the two enclosed numbers is the  $K_a$  for the upper interacting state, the lower number is the  $K_a$  for the lower state. The perturbation between  $v_{10} = 1$  and ( $v_{11} = 1, v_{15} = 1$ ) extends over many values of  $K_a$  and relative vibrational energies are in this case drawn on the basis of a preliminary coupled state fit.

weigh the lines measured in Ref. [10] closer to those from similar millimetre-wave spectrometers we increased their nominal uncertainties by a factor of 3. The resulting uncertainties of 0.009–0.045 MHz still weigh those lines more than lines from similar spectrometers (in Ref. [9] or presently in Warsaw, with cited uncertainties of 0.05 MHz), but allow the use of the usual  $3\sigma$  cutoff criterion on the residuals without losing such lines from the fit. The overall rms deviation of the preceding data set for the parent species created in this way was 0.92. For the rare isotopic species we used the data sets reported in Ref. [10] without any modification, since the uncertainties employed therein for the highest- $K_a$  transitions were much closer to those used in the present measurements.

Analysis was carried out by means of the AABS package for Assignment and Analysis of Broadband Spectra [16,17], which was also used to construct the data files for use by the fitting programs. All spectra were first combined into a single spectrum and various graphical techniques for assigning lines and for following the interstate perturbations were then employed, as described in detail in the analysis of the FASSST spectrum of the  $\text{S}(\text{CN})_2$  molecule [18]. Initial fits were made with the ASFIT/ASROT package [17], and final fits and predictions were carried out with Pickett's SPFIT/SPCAT program package [19,20].

### 3. Rotational spectrum

The characteristic features of the high-frequency rotational spectrum of acrylonitrile are illustrated in Fig. 3. The strongest transitions in this region are all *b*-type, and those are at least an order of magnitude more intense than the *a*-types. This is a reversal of the relative intensities observed at lower frequencies. The most

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