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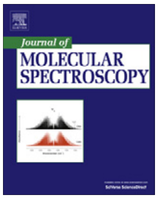

Broadband rotational spectroscopy of acrylonitrile: Vibrational energies from perturbations

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ABSTRACT

The coverage of the room-temperature rotational spectrum of acrylonitrile has been expanded to a total of 1170 GHz, by recording broadband spectral segments at frequencies ranging 90–1900 GHz. This corresponds, in total, to 61.6% coverage of the rotational spectrum up to 1.9 THz and facilitated an in depth study of rotational transitions in the lowest vibrational states of acrylonitrile and up to large values of rotational quantum numbers. Multiple perturbations between the four lowest vibrational states of the molecule have been identified and successfully fitted within the framework of a coupled four state Hamiltonian. The fit encompasses over 12 500 measured transition frequencies, and delivers precise wavenumbers for the three lowest excited vibrational states entirely on the basis of perturbations in the rotational spectrum: $v_{11} = 228.29986(2)$, $v_{15} = 332.67811(2)$, and $2v_{11} = 457.17496(2)\ \mathrm{cm}^{-1}$. The new results are compared with *ab initio* anharmonic force field calculations and the techniques used to deal in an efficient manner with a broadband, high-resolution spectrum of this type are also described in some detail.

1. Introduction

Acrylonitrile is a molecule with a strong rotational spectrum, which has been the subject of many, successively more refined studies [1–12]. Much of that work has been stimulated by the astrophysical relevance of acrylonitrile, and it has been demonstrated that transitions in interstellar ^{13}C isotopic acrylonitrile can also be detected [10]. This observation, and the evolution of the experimental tools of radioastronomy into the THz region renewed the interest in the laboratory spectrum of acrylonitrile. Two recent investigations extended the frequency coverage of this spectrum well into the THz region, both for the parent [11] and for the main singly substituted isotopic species [12]. The access to THz- region frequencies also allowed identification of several resonances affecting the rotational transitions of the vibrational ground state. Even though the lowest excited vibrational state, $v_{11} = 1$, is a relatively distant 228 cm^{-1} above the ground state, it turns out that the large value of the A rotational constant for acrylonitrile (1.66 cm^{-1}) allows resonances with the ground state for relatively low values of the K_a quantum number. For the dominant ^{a}R-transition type the affected transitions are generally for values of J in the region of 100 and at frequencies closer to 1 THz so that they were not encountered in the earlier studies. The analysis of the observed perturbations with a coupled two-state fit allowed precise determination of the wavenumber for the v_{11} mode in several isotopic species of acrylonitrile, with isotopic variation that was consistent with anharmonic force field calculations [12].

The two-state fits performed in [11,12] showed that a considerable number of transitions in v_{11} could not yet be fitted. Further resonances affecting this and other low-lying excited vibrational states were preliminarily identified in Fig. 2 of Ref. [11]. This suggested that there may be a ladder of resonances extending from the ground state upwards, that would ultimately allow determination of vibrational energies of all lowest vibrationally excited states entirely on the basis of perturbations in pure rotational transitions. The resonances usually affect a relatively small number of lines and their frequencies are only predicted with confidence on evolution of a perturbation fit. The optimum approach to solving this type of problem is to make as large a region of the rotational spectrum as possible available for analysis. The main enabling task performed in the present work was, therefore, to obtain the most extensive broadband coverage of the rotational spectrum of acrylonitrile. Its analysis was then performed with tools optimised for dealing with broadband spectra and allowed more confident identification of the main resonances between the four lowest

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vibrational states, as shown in Fig. 1. The frequencies of the corresponding perturbation maxima for ^aR-type transitions range from 420 GHz to 980 GHz, and many other, less complete resonances have also been identified. The final step was fitting the measurements with an appropriate coupled-state Hamiltonian and the results are reported below.

2. Experimental details

The rotational spectrum was measured with different broadband spectrometers operated in the four participating laboratories, and the achieved coverage is summarised in Table 1. The measurements made at JPL for the parent species were updated in parallel with the isotopic study reported in [12]. The remaining measurements were recorded as part of the present investigation. All measurements were made at room temperature, on commercially available acrylonitrile, which was used without further purification. Free-space absorption cells 2–6 m long were used, sample pressures were in the region of 10 mTorr, and second derivative type detection was employed. Most of the spectral segments were recorded by using radiation from selective cascaded multiplication of output from a centimetre-wave region synthesizer. This method has been described in some detail in [13] and the same general scheme was used in all such cases. The distinguishing feature between the various implementations was the type and the number of frequency multipliers generating the radiation, as illustrated by the multiplication factors listed in Table 1. Some measurements were also made in direct generation with a BWO-based spectrometer [14,15]. The final result is that the spectrum has been covered by means of a relatively small number of broadband segments, spanning a total of 1170 GHz of the spectrum, and including continuous coverage of the 182–640 GHz region. The acquired spectra correspond to coverage of 61.6% of the rotational spectrum up to the highest studied frequency of 1.9 THz.

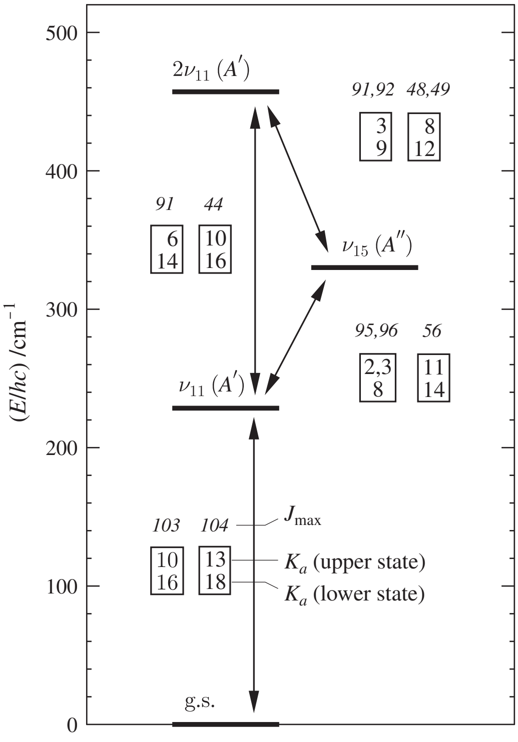

Fig. 1. Summary of the main resonances identified between the lowest four vibrational states of acrylonitrile. The K_a quantum numbers involved in the perturbation and values of J at the perturbation maximum are indicated. In each of these cases the final data set encompasses the region of the perturbation maximum in both states, always for ^aR-type transitions, and sometimes also for other transition types.

The measured spectrum extends from 0.09 to 1.9 THz so that it involves a large variation of apparent linewidths, as documented in Table 1. Efficient incorporation of thousands of lines measured in such a spectrum into a weighted least-squares fit requires a simplified treatment of the measurement uncertainties. The scheme introduced in [12] was used, according to which only three different uncertainty values were adopted. In the present case we used 0.1 MHz for all transitions up to 640 GHz, 0.2 MHz for 818–1205 GHz, and 0.4 MHz for 1576–1900 GHz. Data for the ground state and for $\nu_{11} = 1$ measured prior to Ref. [11] were transferred from the data set reported in [11]. For $\nu_{15} = 1$ and $\nu_{11} = 2$ the previous data from [6] were also used, with their cited uncertainties. Numerical tests made in [12] have shown that the resulting deviations of fit and values of the derived parameters were comparable to those obtained with the more complex weighting scheme used in [11]. The specific values of the uncertainties used here lead to a weighted deviation of the presently reported four state fit of close to unity.

All fits and predictions were carried out with Pickett's SPFIT/SPCAT program package [16,17]. Analysis was carried out by means of the AABS package for "Assignment and Analysis of Broadband Spectra" [18], which is freely available on the PROSPE website [19,20]. The package incorporates multiple techniques developed in response to the need to effectively handle and reduce broadband spectra, and these are described in some detail below.

3. Techniques of broadband analysis

Broadband rotational spectra pose multiple challenges to analysis. The spectra have very high resolution so that broadband coverage is associated with considerable number of data points. The spectra can contain a very large number of lines so that efficient transition frequency measurement and construction of data sets are important. Equally as important is the ability to keep track of what has already been assigned, to compare the spectrum with predictions, and to navigate the spectrum in ways that are consistent with the principal characteristics of a given spectroscopic problem. The AABS package had its origin in the need to deal with the data overload introduced by broadband FASSST spectroscopy [14,21], which gave birth also to the CAAARS analysis package [22]. The broadband handling needs at JPL stimulated writing the SMAP program [23]. The present choice of the AABS package, apart from familiarity to the corresponding author, is that since its inception it was applied to a varied range of broadband spectra and spectroscopic problems, many of which involved interstate perturbations. This enforced steady development of several generic features that are necessary for such work, as discussed in more detail below. The applications of the discussed features are also summarised for reference in Table 2.

3.1. Spectrum handling

The broadband spectra can, as in the present case, come from different spectrometers, will have different point spacing and intensity scaling, and will not necessarily be contiguous in frequency. On the other hand, it is advantageous to use just a single spectrum for analysis. The spectral display and manipulation program SVIEW_L of the AABS package is used for this purpose. All spectra from Table 1 have been combined into a single spectrum consisting of 36 million data points at 50 kHz point frequency spacing. Suitable software constructions allow efficient handling of such spectra irrespective of their length. Constant point spacing