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The Rotational Spectrum of Propynal in the 250-700 GHz range using Coherent Synchrotron Radiation Fourier Transform Spectrometry.

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Abstract. The Coherent Synchrotron radiation obtained at SOLEIL has allowed, for the first time, measurement of broad band absorption, Fourier Transform spectra in the sub-THz range at 0.001 cm^{-1} resolution, with a signal-to-noise ratio of 100 attained in a few hours. The technique has been applied to the observation of the pure rotational spectrum of propynal ($\text{HC}\equiv\text{CCHO}$) in the 250 -700 GHz range. The new data have allowed the determination of more precise values for rotational constants and for higher order rotational constants. The potential of the technique for rapid recording of rotational spectra in this energy range is outlined.

Introduction.

Propynal, also known as propiolic aldehyde, is a mildly reactive molecule, which has been detected in interstellar molecular clouds, using its rotational spectrum in the 15-40 GHz range [1-3]. The first microwave laboratory studies [4,5] allowed a first determination of rotational constants and some centrifugal distortion constants. Later, Winnewisser extended the analysis of the ground state (GS) to the millimeter wave region (95-200 GHz) and obtained a refined set of rotational and centrifugal constants [6]. More recently, McKellar and coworkers have recorded the IR spectrum in the 650 cm^{-1} region at 0.003 cm^{-1} resolution, allowing an analysis of the ν_7 , ν_8 and ν_{11} bands. In the course of this latter investigation, the authors noted discrepancies between GS levels predicted using the reference 6 constants and combination differences from the observed infrared transitions, especially for higher K values. The data were thus refitted using Watson's α -reduced Hamiltonian to yield a slightly different set of rotational and quartic centrifugal distortion constants and improved values for the sextic constants including an H_k term[7]. Even more recently, Jaman and coworkers obtained new millimeter

wave data of propynal in a DC discharge containing propargyl alcohol as a precursor and measured new lines in the 36-180 GHz range. In their analysis, they refitted the rotational and centrifugal distortion constants, this time using the s-reduced Hamiltonian instead but not making use of the ground state combination differences from McKellar and coworkers. In view of these discrepancies, it seems desirable to extend the range of observation of the rotational spectrum at higher resolution than the IR work to help determine more precise higher order centrifugal distortion constants. Also, the direct observation of GS rotational lines should yield a higher accuracy than the use of combination difference of infrared lines measured at lower resolution. In view of the importance of the 100-900 GHz spectral range for new ground-based radioastronomy instruments [9], it is of importance to illustrate with a concrete example the capabilities of synchrotron radiation (SR)-based, broad band, interferometric techniques for recording survey absorption spectra in the sub 1 THz range.

The synchrotron provides a source of infrared radiation that combines the advantages of a high brilliance and a wide spectral coverage [10 and reference therein]. To enhance its intensity in the THz range, a number of synchrotron radiation facilities around the world have studied the production of Coherent Synchrotron Radiation (CSR) obtained by reducing the bunch length so that it becomes comparable to the emitted wavelength [11-17]. Although this operation mode allows a large flux enhancement in the THz range ($\bullet 10^4$), the interaction of the electrons with their own electromagnetic field causes a microstructure (microbunching) in the electron bunch, resulting in bursts of THz radiation and with accompanying source instabilities [14]. The reported applications of CSR mostly exploit the intensity increase of this source for low resolution studies, where the stability has less impact on the signal-to-noise (S/N) ratio. For high resolution measurements, the use of CSR can be greatly hampered by these micro-bunching instabilities [10]. Recent developments at SOLEIL, however, demonstrated the potential advantages of CSR (brightness, stability, small beam divergence) which improve the S/N allowing the observation of weak bands even at high resolution [16,17]. Even though the ultimate available resolution (20 – 30 MHz) using this technique is far from the sub-MHz resolution of the millimeter wave monochromatic scanning set-up, such studies present complementary properties: the whole spectral range is measured simultaneously, which is useful for the study of reactive species, the line intensities are easier to extract and the large number of lines recorded is advantageous in obtaining accurate constants. Here, such a study is presented for which the CSR emission is ideally suited: the rotational structure of propynal in the sub-THz range.

Experimental.

The absorption measurements of the propynal molecule were performed on the AILES beamline with the CSR source. The flux of this emission between 250 and 750 GHz (about 0.4 to 1.2 mm wavelength) is advantageous for performing broad band interferometric spectroscopy measurements (here about nine hours). For high resolution measurements, (here $\bullet 30$ MHz resolution) the signal-to-

noise has been optimized through minimizing the source instabilities [14,16,17]. These optimal conditions allowing for an intense emission over a wide frequency range are found for a momentum compaction factor: $\alpha = \alpha_0/25$ (with α_0 the nominal compaction factor), corresponding to a theoretical bunch length at zero current of around 3 ps (1 mm), and a current per bunch of 70 μA . The Synchrotron was operating in the so-called hybrid mode with an isolated electron bunch (in one quarter of the orbit) and 312 equally small bunches. With these conditions, the CSR appears quasi-stable in the 7 to 21 cm^{-1} range, allowing for high resolution measurements.

The AILES beamline of SOLEIL has been designed to minimize known sources of instabilities, specifically in the far-infrared and THz ranges [18,19], these characteristics are briefly summarized here. Near the bending magnet output, the edge and constant field radiations of the bending magnet are extracted by a slotted mirror. The collected solid angle is 78 mrad horizontally and 20 mrad vertically, allowing 10^{16} to 10^{17} photons to be extracted per 0.1 % band pass of coherent radiation. The transfer optics placed in the ring vacuum chamber are fixed to the highly stable ground of the storage ring. The experimental beamline is under vacuum (pressure less than 10^{-6} mbar) and equipped with a Bruker IFS 125HR high-resolution interferometer (882 cm maximum optical path difference) coupled to two 4.2 K Infrared Laboratories composite bolometers with a specified theoretical noise equivalent power of about 10^{-13} $\text{W}/\sqrt{\text{Hz}}$. The use of separate bolometers for sample and reference allows the non random noise generated in the CSR to be removed from the final spectrum. In the following, the synthesis of the propynal sample is summarized, the experimental measurement conditions are given and the results of this study presented.

To obtain propynal with high purity, we used a synthesis technique based on the retro-ene reaction of propargyl ether, described by McNab et al. [20] followed by a purification procedure. For this purpose 7 g of propargyl ether (98% from Sigma Aldrich) were placed in a flash pyrolysis chamber under vacuum allowing for thermal decomposition at 750°C into two products, the propynal, and allene ($\text{H}_2\text{C}=\text{C}=\text{CH}_2$). After the pyrolysis, the reaction products were trapped at near liquid nitrogen temperature and gradually warmed under static vacuum. At around -34 ° C as the allene evaporates, the gas is pumped away and liquid propynal remains. This purification procedure was performed twice and the purity was checked using both mass spectrometry and infrared absorption, until only propynal was detected.

For the present measurement, 0.225 mbar of propynal was introduced into a White cell aligned to an 8.85 m optical path. The interferometer was equipped with a Si/Mylar composite beamsplitter and the moving mirror scanned at the highest possible velocity of 5.06 cm/s (80 kHz He-Ne laser fringe modulation), as the highest Fourier frequency in the wavenumber range of interest (about 125 Hz) falls well below the detector roll-off (full response here up to 200Hz). This enables averaging over a larger number of interferograms. The detector was fitted with a 200 cm^{-1} cold low pass filter and the spectrometer with a 12.5 mm entrance aperture, but the SR effective source diameter was measured at

the interferometer entrance focal plane to be about 4.5mm FWHM with 100% of the incoming energy at 8mm diameter. This results in a source diameter fulfilling the resolution criterion. For the propynal spectrum and reference spectrum (empty cell), 186 scans at maximum resolution were recorded for about 9 hours. The calculation of the transmittance may ideally be obtained when measuring both empty and gas filled cell in strictly the same optical conditions, aiming at suppressing the fine structures discussed previously[14]. The S/N ratio at the peak of the bandpass (around 10 cm^{-1}) can be estimated to about 57. It should be noted, however that, during the course of preliminary measurements, an increase in signal was observed, causing one detector to saturate. This gradual increase in coherent emission was obtained as the electron bunch length distribution narrowed as a result of the topping-up procedure and gave rise to a 20% general increase of the signal, causing the detectors to reach saturation point. In order to operate the detector in non-saturated conditions, we chose to slightly misalign the cell to record the gas filled cell spectra. The signal to noise ratio of the transmission, based on this ratio, was then about 45 at best. The spectrum calibration was performed using CH_3Cl lines measured just prior to this study. Water lines were not exploited for this purpose as this molecule is present in both the spectrometer and the cell, to be avoided for a precise line determination [21]. Using CH_3Cl data in the HITRAN [22] database, from the microwave measurements of Wlodarczak et al. [23], a recalibration shift of $3.5\times 10^{-4}\text{ cm}^{-1}$ (10.5 MHz) was determined. This adjusts for a small systematic error in the frequency axis, with random errors on line positions of the calibration gas of the order of $5\times 10^{-5}\text{ cm}^{-1}$ (1.5 MHz). This small systematic error is commonly due to slight non parallelism of the alignment laser and IR moving mirror axis and for a small part (estimated to about $2.2\times 10^{-4}\text{ cm}^{-1}$ here) to slight distortion of the line shape due to off-focus and off-axis radiation [21,24].

Results and Analysis.

The geometry of propynal makes it a near prolate asymmetric top with the A rotational constant much larger than the B and C constants, which are of the same order of magnitude (Figure 1) and a dipole moment with μ_a and μ_b components. As a result, the rotational

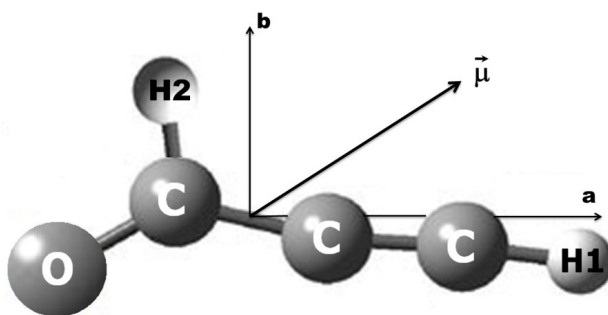


Figure 1. Molecular structure of propynal with the main axis and the dipole moment vector. The interatomic distances and angles are given in Table 1 (from references 5, 25 and 26).

spectrum recorded here in the 8 to 19 cm^{-1} range displays quite regularly spaced ${}^qR_{Ka}$ stacks arising from the μ_a selection rule, and also a few ${}^rQ_{Ka}$ sub branches from the μ_b selection rule, where the overlapping lines lead to strong absorption corresponding to the high intensity features, with the rQ_3 sub branch saturating in the spectrum.

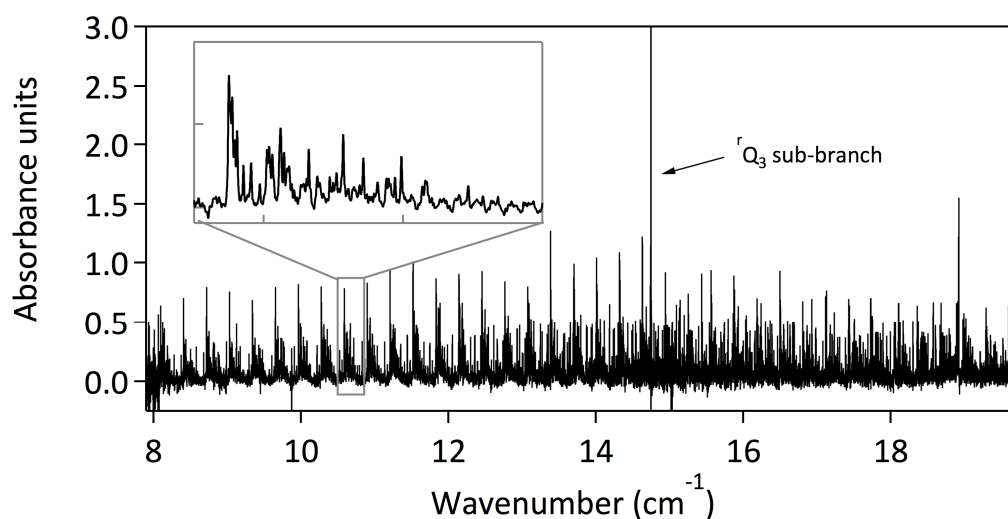


Figure 2. Survey of the rotational spectrum of propynal in the 8-19 cm^{-1} region, recorded at room temperature with 0.001 cm^{-1} resolution, using CSR at Beamline AILES (SOLEIL), 0.225 mbar sample pressure and 8.85 m path length.

Propynal has several low lying fundamental vibrations (in particular ν_{12} and ν_9 below 300 cm^{-1}) with a substantial population at room temperature, responsible for the intricate pattern of weaker lines between the well-defined K stacks.

The analysis was carried out as follows: since very good starting parameters were available in the literature, we first carried out a simulation in the spectral region of interest, using the parameters from reference [7] and the same A-reduced asymmetric rotor Hamiltonian [27] and I^r representation as in this earlier work. Simulations were performed using C.M. Western's PGopher program [28] and a first set of about 600 transitions could be assigned in a straightforward manner.

The RMS error produced when using the ground state parameters from literature to calculate assignable transitions in the 250-700 GHz region were relatively large (about 0.002 cm^{-1} for constants from ref [6], about 0.01 cm^{-1} for constants from ref [7] and about 0.0025 cm^{-1} for constants from ref [8]). As expected, examination of the residuals showed that although the results for the already measured microwave lines were, as expected, excellent, systematic deviations appeared in the higher

quantum number regions. Thus, using our experimental data, a new fit of the molecular parameters was carried out using H.B. Pickett SPFIT and SPCAT program suites [29]. This produced a new set of parameters which allowed a better match of predicted line positions with higher quantum number lines. New sets of lines were progressively introduced and this procedure repeated until about 1200 transitions (941 a-type and 257 b-type lines) could be reproduced with an average RMS deviation of about $2 \times 10^{-4} \text{ cm}^{-1}$. A total of 140 pure rotational lines from refs [4-6,8] were also included in the combined fit. An example comparison of simulated and observed spectrum is given in Figure 3.

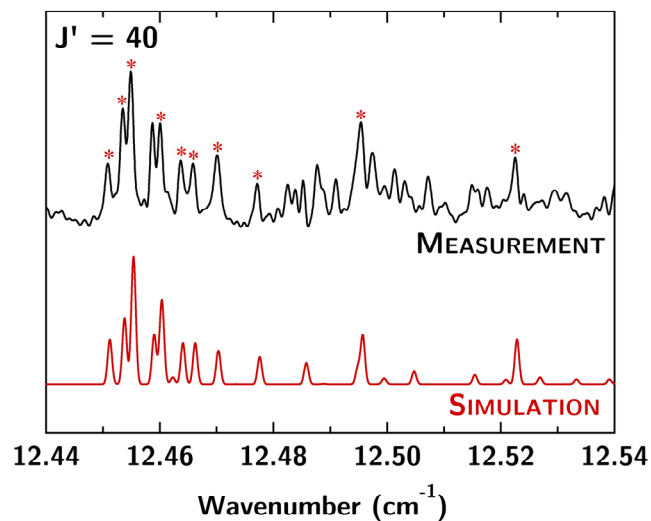


Figure 3. Detail of the rotational spectrum of propynal for the $J = 40 \leftarrow 39$ region. Only lines marked with an asterisk have been retained in the fit, most others being excited vibrational state transitions. Experimental conditions are the same as in Fig. 2. Gaussian line shapes with $4.5 \times 10^{-4} \text{ cm}^{-1}$ HWHM were assumed for the ground state line simulations.

The results are also compared to literature values using the residuals plots in figure 4. The new set of effective constants is presented in table 1 and compared with literature values.

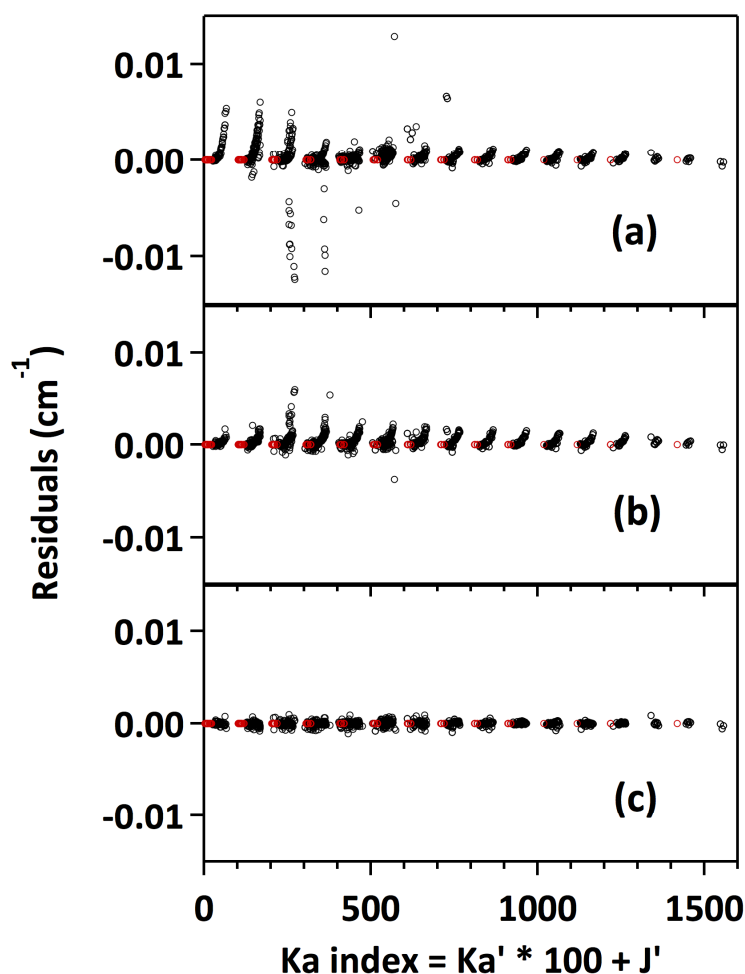


Figure 4. Plot of the fit residuals (observed minus calculated line positions) using (a) constants, reduction and representation as in reference [8], (b) constants from reference [7], (c) this work, constants from table 3. In red, sub-200 GHz lines from references [6] and [8], in black, 250-700 GHz lines from this work.

On the whole, the precision of the rotational and centrifugal distortion constants is improved. Some quartic and all sextic constants now have improved values, well outside the defined error bars from earlier work and a H_J sextic constant is added. Addition of other, higher order, constants did not significantly improve the fit and were not determined with enough certainty anyway, and these have not been retained. It should also be noted that the RMS error using these parameters is close to the precision of our frequency determination (about 10^{-4} cm⁻¹), and that the residuals are now evenly distributed around zero without systematic deviation.

In the simulation process, the relative intensities of the a-type and b-type transitions were manually adjusted to yield the best visual agreement. Although this procedure does not take into account the instrument function rigorously, it gives however, an acceptable approximation of the relative

intensities for weak (unsaturated) lines. From the relative intensities, we could thus derive a $\mu_a/\mu_b = 1.57 \pm 0.1$ dipole moment component ratio. This determination compares favourably with the $\mu_a/\mu_b = 2.36 \pm 0.02/1.47 \pm 0.02 = 1.60 \pm 0.04$ ratio, determined previously with great precision from Stark effect measurements by Brown and Godfrey [25]. This also implies that, using with standard procedures with precise optical path, pressure and temperature measurements [30], line strength measurements could be carried out and from this, estimation of total dipole moments. Here, as an illustration, an approximate measurement of intensity over four isolated lines with moderate intensity (about $1.9 \times 10^{-22} \text{ cm}^2 \cdot \text{molec.}^{-1} \text{ cm}^{-1}$) around 10 cm^{-1} leads to a dipole moment estimate of $2.7 \pm 0.3 \text{ D}$ (compared to 2.78 D experimentally [25]). Clearly, measurements over several pressures are needed for an adequate measurement of the dipole moment or, in other cases, the vibrational partition function, but this illustrates this possibility.

As explained earlier, many lines pertaining to vibrationally excited states are observed in the spectrum, these could be extracted by subtracting out the ground state predicted lines [31], but in this paper no attempt was made to analyse these data.

Conclusions

This study shows that Coherent Synchrotron Radiation can be used to obtain, in a few hours, rotational spectra of a light, reactive molecule such as propynal in the sub-THz range using FT-based instrumentation. Although this technique has limited resolution capabilities compared to purely electronic or opto-electronic scanning devices, it is shown here that the large number of observable lines in this spectral range enables molecular constants to be retrieved with good precision, as a new, improved set of effective molecular constants could be derived. In a similar manner, improvement in the rotational constants was achieved using FIR data for ethylene oxide, a lighter molecule where the higher frequency lines are available using normal synchrotron radiation[32]. Also, the multiplex advantage of the technique may be of use when studying reactive or elusive molecules with lifetime of the order of an hour. Intensity measurements are also possible using the same methods as in the IR region, which can be an advantage for sub-mm wave/ IR cross calibration studies, as switching between these two spectral ranges can be easily done, using the very same instrumentation.

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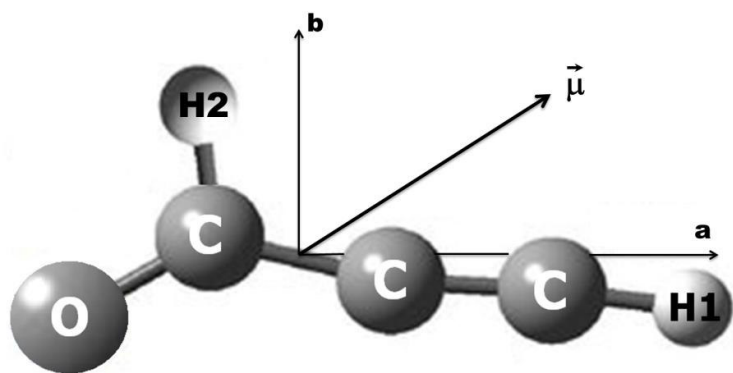
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Table 1. Comparison of ground state parameters for Propynal using Watson's a-reduced Hamiltonian in the I^r representation (1σ uncertainty in parenthesis).

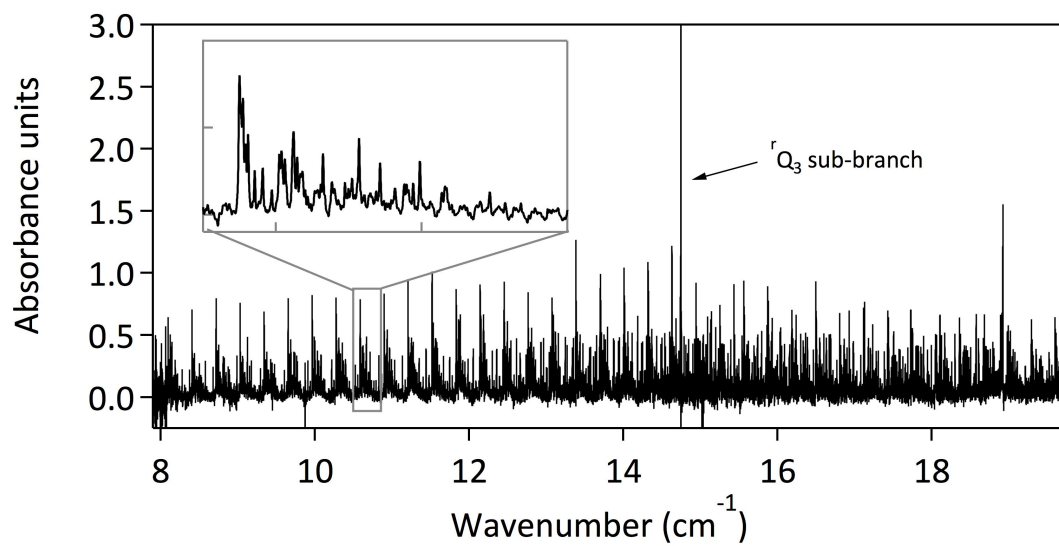
<i>Constant (MHz)</i>	<i>This work</i>	<i>Ref [6]^a</i>	<i>Ref [7]</i>
<i>A</i>	68035.308 (25)	68035.299 (43)	68035.263 (39)
<i>B</i>	4826.28805 (97)	4826.3014 (73)	4826.293 (6)
<i>C</i>	4499.52695 (95)	4499.5107 (69)	4499.51 (6)
<i>Δ_J</i>	$1.91792 (111) \cdot 10^{-3}$	$1.917 (012) \cdot 10^{-3}$	$1.913 (4) \cdot 10^{-3}$
<i>Δ_{JK}</i>	-0.1481185 (186)	-0.148102 (47)	-0.148044 (39)
<i>Δ_K</i>	9.0033 (57)	8.99124 (97)	8.9926 (87)
<i>δ_J</i>	$3.3742 (15) \cdot 10^{-4}$	$3.458 (14) \cdot 10^{-4}$	$3.4564 (12) \cdot 10^{-4}$
<i>δ_K</i>	0.03396 (26)	0.0390 (32)	0.0347 (28)
<i>H_J</i>	$7.549 (214) \cdot 10^{-9}$	--	--
<i>H_{JK}</i>	$-0.8348 (082) \cdot 10^{-6}$	$-7.41 (59) \cdot 10^{-7}$	$-7.11 (48) \cdot 10^{-7}$
<i>H_{KJ}</i>	$-8.245 (107) \cdot 10^{-6}$	$-8.310 (130) \cdot 10^{-6}$	$-8.264 (12) \cdot 10^{-6}$
<i>H_K</i>	$3.190 (147) \cdot 10^{-3}$	--	$2.36 (6) \cdot 10^{-3}$
<i>J max</i>	77	23	<50 ^{-b}
<i>Ka max</i>	14	14	-b
<i>Kc max</i>	75	21	-b
<i>Number of a-type Lines</i>	941	91	-b
<i>Number of b-type Lines</i>	257	44	-b

a. Converted from the older set of centrifugal distortion constants. Here $\delta_k = -2R_5$ see ref [33].

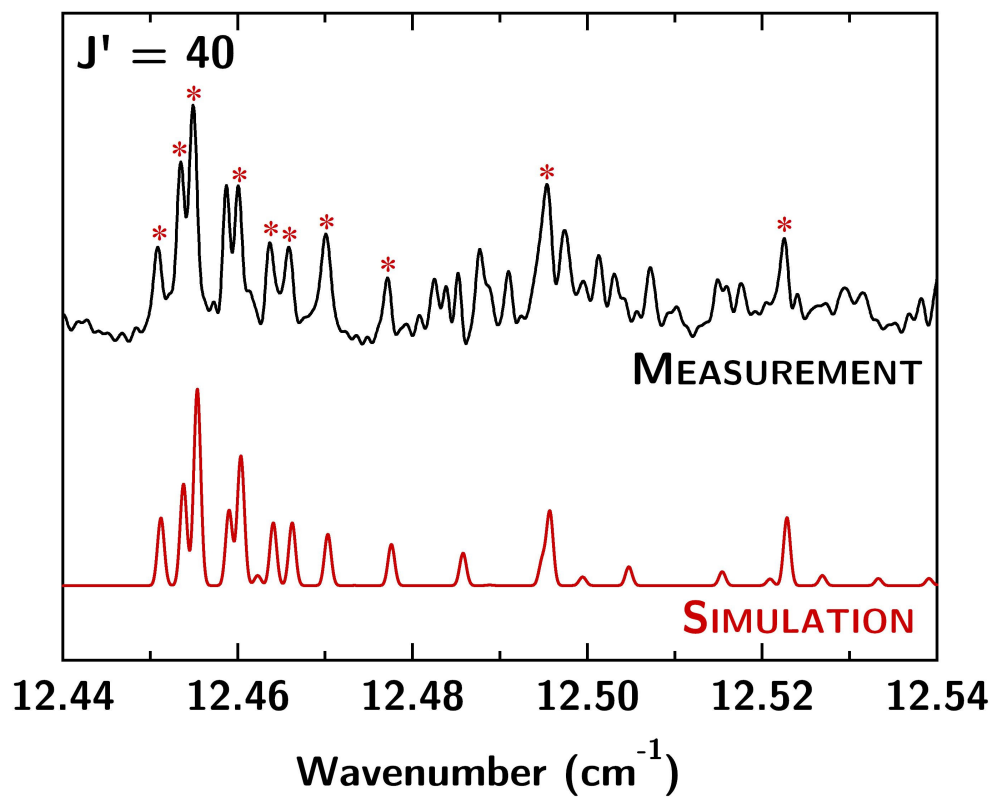
b. Not specified. From MW lines of ref [6] and combination differences in IR bands.

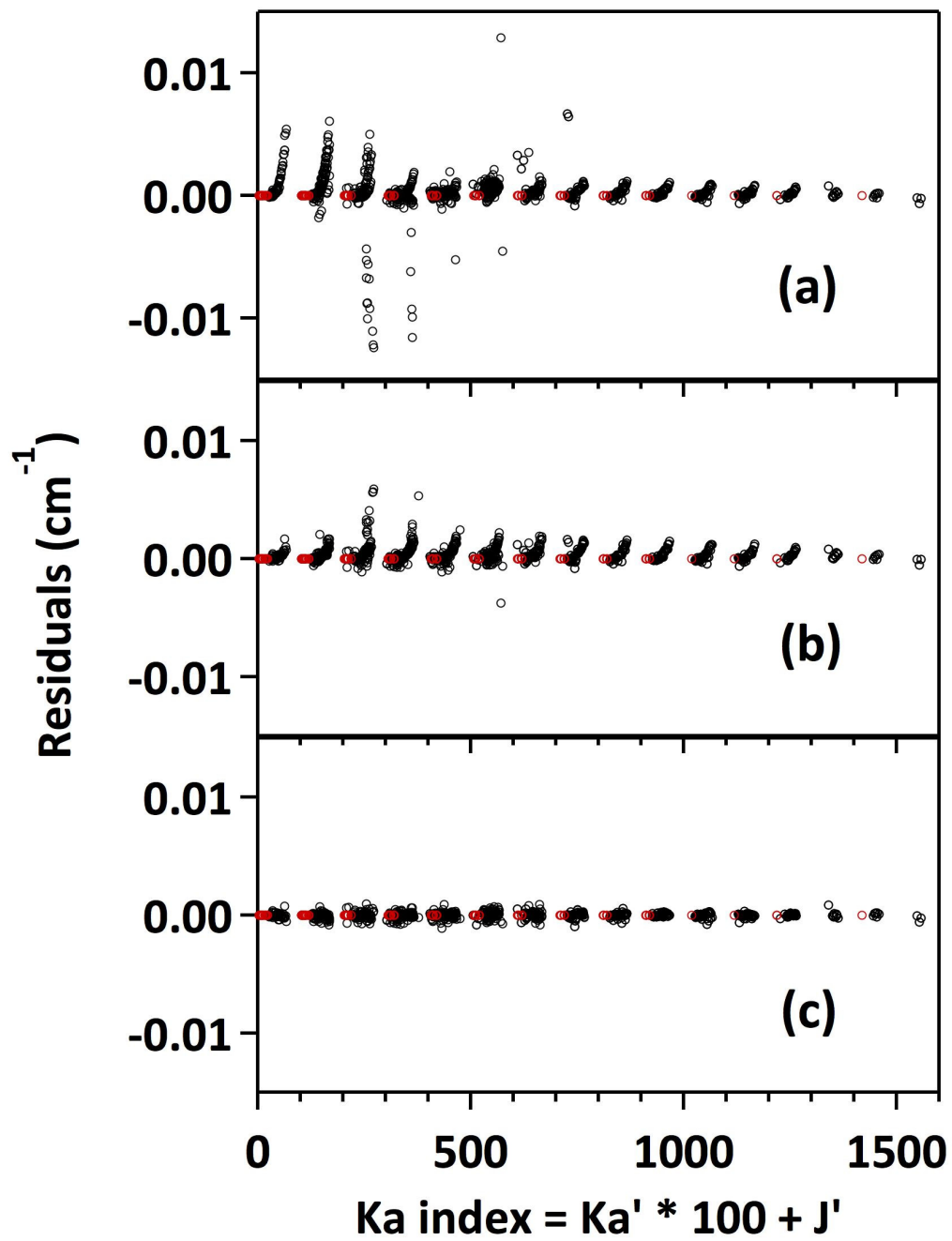


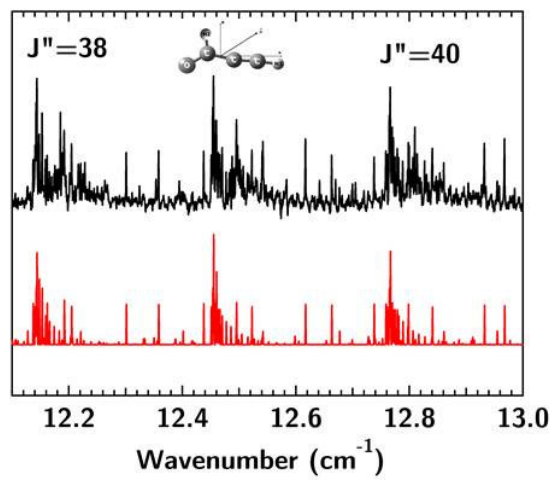
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Highlights

- Improved molecular constants for Propynal
- Use of Coherent Synchrotron radiation for broad band rotational spectroscopy
- Fourier Transform spectra in the 250 -700 GHz range at 0.001 cm^{-1} resolution

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