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Synchrotron-based rotation-vibration spectroscopy of imidazole

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Abstract

We report the observation of the far-infrared absorption spectra of the ν_{21} , ν_{20} , ν_{19} , ν_{18} and ν_{17} bands of imidazole in the 480-840 cm^{-1} range, taken at the Canadian Light Source using synchrotron radiation. The ν_{21} , ν_{18} and ν_{17} bands were rotationally assigned and analyzed. Observations of the ν_{20} and ν_{19} bands were limited to their dense, unresolved Q branches. The analysis provided accurate origins for all five bands, and a first rotational characterization of the ν_{18} and ν_{17} levels, as well as a global fit that includes data from recent microwave experiments on the ground vibrational state and low-lying excited vibrational levels [Astron. Astrophys. 628 (2019) A53, J. Mol. Spectrosc. 378 (2021) 111452].

Keywords: imidazole, rotation-vibration, FTIR, synchrotron, far-infrared

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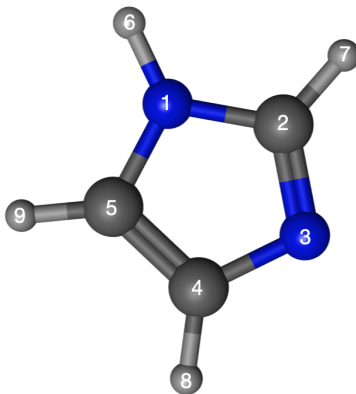
1. Introduction

Imidazole is a planar five-membered aromatic ring doubly substituted with nitrogen (Fig. 1). It has biological significance, appearing frequently as a subunit in larger biologically relevant molecules, and is a candidate for detection in the interstellar medium (ISM) although it has not yet been observed there[1]. Identification in the ISM, should it occur, will most likely be made through observation of spectral lines in the microwave region, and to that end the microwave spectrum of imidazole has been reported a number of times. The first analysis was published in 1967[2], with the results of more comprehensive experiments following in 1976[3] and 1982[4]. Very recent work in 2019 and 2021 has greatly improved the characterization of the ground state[1] and of the three lowest-lying vibrationally excited states[5], as well as providing analysis of ground-state spectra from some isotopically substituted imidazole.

Imidazole has also been studied with infrared spectroscopy, but only at low resolution. To our knowledge only two gas-phase studies have been reported, in 1965[6, 7] and 1992[8]. However, the structures of five-membered rings like imidazole are amenable to accurate calculation, and good estimates of the positions of vibrational energy levels (and the strength of transitions to these levels from the ground state) are available[1, 5, 8, 9].

In this paper we report on the gas-phase far-infrared rotation-vibration spectra of the ν_{21} (509 cm^{-1}), ν_{20} (626 cm^{-1}), ν_{19} (664 cm^{-1}), ν_{18} (725 cm^{-1}) and ν_{17} (812 cm^{-1}) bands of imidazole. The data were taken in absorption on a Bruker IFS125HR Fourier transform spectrometer, using a background continuum of synchrotron radiation from the Canadian Light Source (CLS) facil-

Figure 1: The molecular structure of imidazole. Atoms 1, 3 are nitrogen, 2, 4 and 5 are carbon, and 6-9 are hydrogen.



ity in Saskatoon, SK, Canada. The well-collimated and intense far-infrared light allowed us to collect spectra with reasonable signal-to-noise ratio at the highest resolution available with the spectrometer. Rotational spectra of the ν_{21} , ν_{20} and ν_{19} levels have been reported by Arenas *et al.*[5]; our data provide accurate experimental term energies for these vibrational levels and additional information about their rotational structure. As well, we provide the first rotational characterizations and accurate term energies for the ν_{18} and ν_{17} levels.

2. Experimental

Imidazole was purchased from Sigma Aldrich in the form of a white crystalline powder. The vapour pressure of this compound is very low at room temperature, and as a result the 2-m-long White cell normally used at the CLS, with a volume of about 300 litres, did not produce a measurable spec-

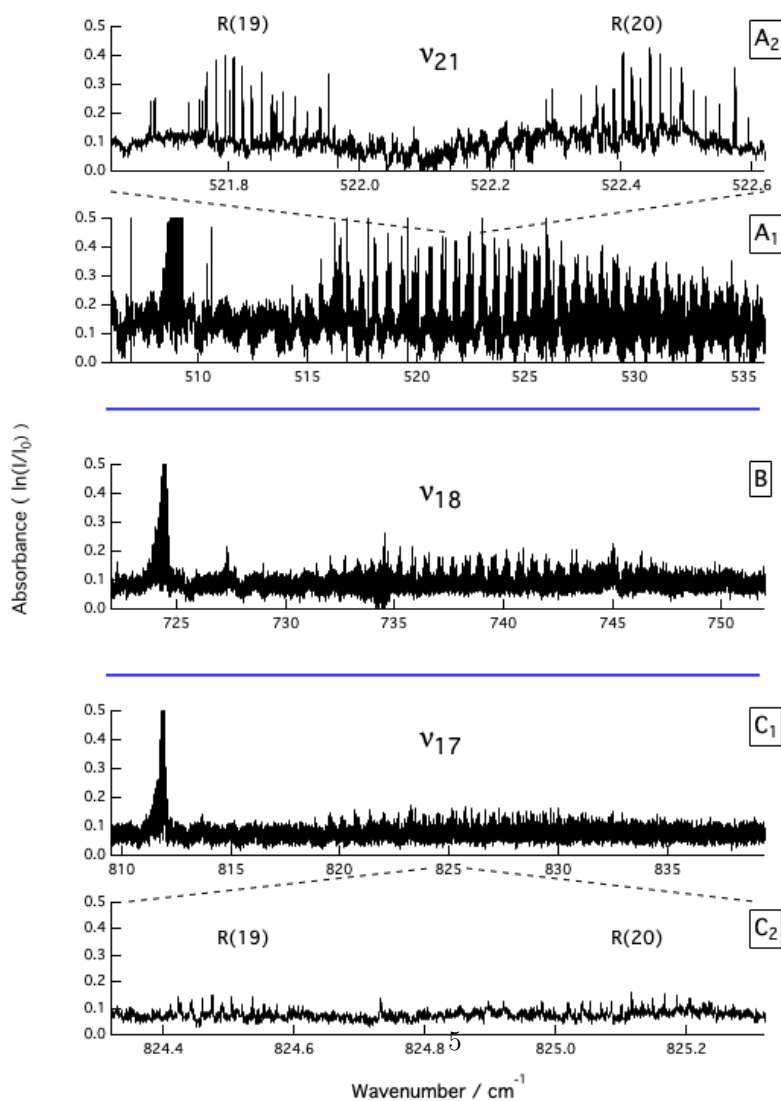
trum when exposed to the imidazole crystals for several hours. Instead, the imidazole was placed in a crucible inside a smaller White cell, 30 cm long and about 20 cm in diameter, set to provide total path length of 9.6 m for the synchrotron light. 8-9 mTorr of N₂O was also admitted into the cell to provide calibration data[10]. The cell was warmed to about 60 °C by wrapping it in heating tape, and after several hours of sublimation, sufficient vapour of imidazole was generated for reasonable detection of the strongest bands. 156 scans were obtained through a 350-750 cm⁻¹ bandpass filter, and 252 scans were collected through a 400-1200 cm⁻¹ filter. Sections of the spectra for which rotational assignments were possible are given in Figure 2; while the low vapour pressure of imidazole significantly reduces the quality of the data, the spectra proved quite suitable for analysis. The ν_{21} spectrum was the strongest, the ν_{18} and ν_{17} spectra were weaker but still rotationally analyzable, while the ν_{20} and ν_{19} spectra were considerably weaker and observed only via their compressed and unresolved Q branches.

The full width at half maximum (FWHM) of strong lines is about 0.001 cm⁻¹, limited by the 5 m length of the scan arm in the Bruker Fourier transform spectrometer at wave numbers below about 630 cm⁻¹ for imidazole at 60°C. Above that wavenumber, the width increases due to Doppler broadening. At 840 cm⁻¹, the upper end of the spectrum we studied, the FWHM is about 0.0013 cm⁻¹.

3. Analysis

All of the five c-type bands studied were characterized by intense, sharp Q-branches. For the ν_{20} and ν_{19} bands these were the only features available

Figure 2: Graphs A_1 , B and C_1 show the Q and R branch regions for the ν_{21} , ν_{18} and ν_{17} bands of imidazole, with the Q branches going off-scale at their peaks. Graphs A_1 , B and C_1 are each 30 cm^{-1} wide. Graphs A_2 and C_2 show 1-cm^{-1} -wide regions of the R branch that include the R(19) and R(20) clusters for the ν_{21} and ν_{17} bands, which respectively have the highest and lowest signal-to-noise ratios of the three bands. Dashed lines locate the 1-cm^{-1} -wide regions within the 30-cm^{-1} -wide regions. The vertical scale is consistent for all of the plots.



to us. In the ν_{21} , ν_{18} and ν_{17} bands we also observed well-structured P and R branches organized into clusters of lines, each of which shared common values of the total angular momentum quantum numbers J'' and J' (see Fig. 2). Since imidazole is very nearly an oblate symmetric top, levels with different K_a but the same K_c for a given J were often unresolved. We conducted the analysis of these bands in a similar way to our work on pyrrole[11], furan[12] and thiophene[13, 14]: ground-state combination differences calculated from the parameters established with microwave spectroscopy were used to set the value of J for each observed P and R branch cluster, and then to determine the K_a and K_c index values for each line within the cluster. The observed transitions followed the expected selection rules $\Delta J = \pm 1$, $\Delta K_a = \pm 1$, $\Delta K_c = 0$. Rotational assignments within the Q branches were not possible due to high spectral congestion.

When a sufficient number of lines had been assigned via combination differences, the PGOPHER program[15] was used to cycle through iterations of fitting and further assignment. Uncertainties were assigned to lines based on their signal-to-noise ratio and status with respect to blending. The positions of the strongest, best resolved lines were assigned uncertainties of 0.0001 cm^{-1} , about one-tenth of the nominal line width, for the ν_{21} band, or 0.0002 cm^{-1} for the weaker ν_{18} and ν_{17} bands at higher wavenumber. Weaker or blended lines were assigned uncertainties 1.25-2 times greater than those of the strongest lines in a given band since their centroids were harder to accurately determine.

Once the bands were assigned as fully as was possible, both far-infrared and microwave transitions were fit simultaneously with the PGOPHER pro-

gram to an S -reduced asymmetric top Watsonian[16] employing the III^l representation. This process revealed problems in the analysis of the microwave data for the ground state[1] from 2019 and in the excited vibrational states[5] from 2021. In the ground state analysis two fits were presented, and in both the constants T_0 , A , B , C and all quartic distortion constants were fitted. The sextic distortion constants H_{JK} , H_{KJ} and h_2 were fitted, while the H_J , H_K , h_1 and h_3 constants were fixed to calculated values in Fit I, and were fixed to zero in Fit II. In both fits, an octic constant labelled L_{JKK} was employed. We found that Fit II reproduced the microwave data given as supplementary data in Ref. [1] (with the octic constant correctly identified as L_{KKJ} [17]), while calculations based on Fit I created significant deviations from the given measurements for many transitions. We speculate that one or more of the four sextic constants fixed to zero in Fit II was misprogrammed in the input file to the Pickett program[18] used to produce Fit I in the 2019 analysis, and that the octic constant employed compensated for the error. We found that when we refit the microwave data using the PGOPHER program the octic constant was unnecessary, and that Fit I ($\sigma_w=0.64$) was superior to Fit II ($\sigma_w=0.75$). The problem with Fit I seems to have extended to the analysis of the excited vibrational states, which fixed the sextic constants to nonzero values, so the fits given in Ref. [5] also fail to reproduce the line lists given as supplementary data.

In the final analysis, we fit our far-infrared transitions from the ν_{21} , ν_{18} and ν_{17} bands with the microwave data for the ground state from 1982[4] and 2019[1] (including only the supplementary data from Table 2, which excluded the lines that exhibited hyperfine structure) and for the ν_{21} level

from 2021[5]. For the ground state we used the Watsonian for Fit I (excluding the octic constant) described in the previous paragraph. In the higher vibrational levels we fixed the sextic constants to those determined for the ground state, as was done in Ref. [5]. The results are collected in Table 1. We have also refit the 2021 microwave data for the ν_{20} and ν_{19} levels, and include the results in Table 2. Rotational analysis of the far-infrared spectra for the latter two bands was not possible since only the congested and unresolved Q branches were observed; however the origins of these bands could still be determined accurately. The bands were calculated in PGOPHER from the constants in References [1] and [5] with a Gaussian broadening of 0.001 cm^{-1} , and the Q-branch regions of each band were exported to a data file. The calculated Q branch structures were then mathematically correlated with our experimental data[19, 20], and the position of the correlation spike was used to determine the shift between the calculated and observed spectra. The observed Q branches and final calculated spectra are shown in Figure 3. We have determined that the origins of the ν_{20} and ν_{19} bands are $628.5348(2) \text{ cm}^{-1}$ and $664.4669(2) \text{ cm}^{-1}$, limited principally by the accuracy of the N_2O calibration lines.

4. Discussion

Each of the vibrationally excited states corresponds to an out-of-plane vibration of imidazole[5, 8, 9]. The ν_{21} vibration is a mix of H6 wagging and ring torsion, the ν_{20} and ν_{19} vibrations are primarily ring torsions, and ν_{18} and ν_{17} vibrations are dominated by H9 and H7 wagging motions. The rotational constants A , B and C for each excited vibrational level are remarkably

Figure 3: Observed Q branches of the ν_{20} and ν_{19} bands of imidazole, along with simulations provided by PGOPHER.

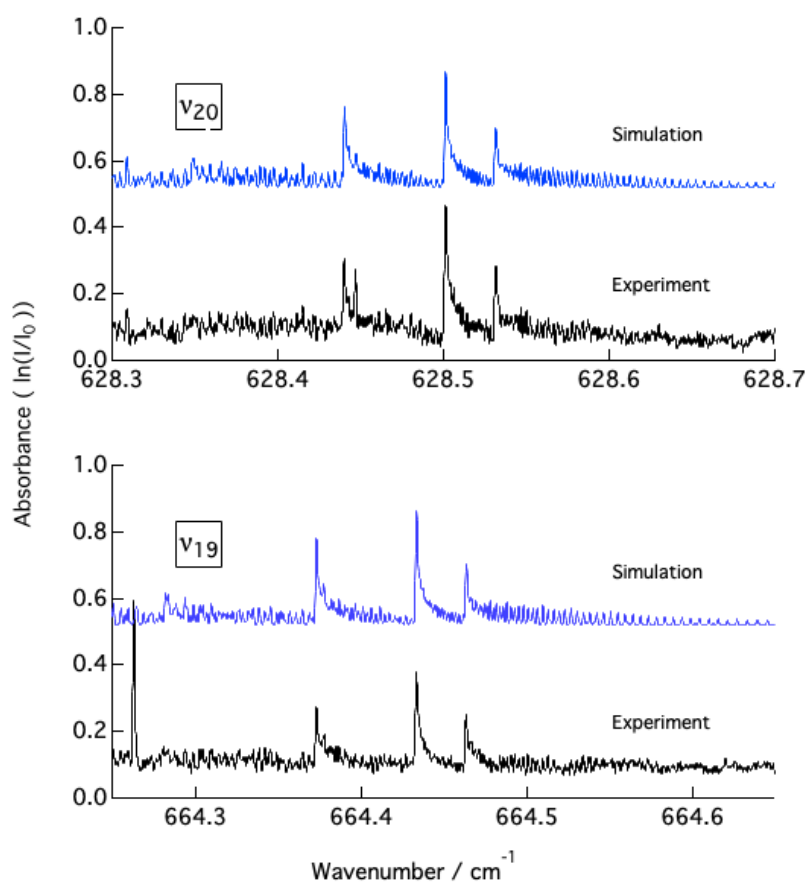


Table 1: Rotational constants and band origins for the ground, ν_{21} , ν_{18} and ν_{17} vibrational states of imidazole from a combined fitting of far-infrared and microwave data. Numbers in parentheses are 1σ uncertainties in the last digits of the value for each parameter. Numbers in square brackets were fixed to values calculated in Ref.[1], or to values obtained in the fit for the ground state for the vibrationally excited levels. Note that the uncertainties in band origins (ΔE) are the statistical uncertainties given by the fitting procedure; these true uncertainty in these values is limited to about 0.0002 cm^{-1} by the uncertainty in the N_2O calibration lines.

Parameter	Ground state	ν_{21}	ν_{18}	ν_{17}
$\Delta E/\text{cm}^{-1}$	0	509.2920714(28)	724.509280(11)	811.934698(27)
A/MHz	9725.30917(20)	9705.93818(41)	9707.4620(17)	9717.4033(45)
B/MHz	9373.99450(19)	9356.37598(36)	9357.1773(18)	9349.5430(49)
C/MHz	4771.91774(22)	4771.23804(18)	4773.7984(13)	4773.5105(45)
D_J/kHz	3.28024(15)	3.27536(15)	3.21348(53)	3.2142(23)
D_{JK}/kHz	-5.17580(21)	-5.15086(20)	-5.0049(14)	-4.9924(72)
D_K/kHz	2.24339(17)	2.22667(14)	2.1382(12)	2.1236(70)
d_1/kHz	0.019853(20)	0.01858(13)	0.02198(54)	0.0401(22)
d_2/kHz	0.016682(12)	0.017066(90)	0.01019(22)	0.02592(98)
H_J/mHz	[1.367]	[1.367]	[1.367]	[1.367]
H_{JK}/mHz	-6.063(61)	[-6.063]	[-6.063]	[-6.063]
H_{KJ}/mHz	7.294(97)	[7.294]	[7.294]	[7.294]
H_K/mHz	[-2.813]	[-2.813]	[-2.813]	[-2.813]
h_1/mHz	[0.0459]	[0.0459]	[0.0459]	[0.0459]
h_2/mHz	-0.0804(60)	[-0.0804]	[-0.0804]	[-0.0804]
h_3/mHz	[-0.0147]	[-0.0147]	[-0.0147]	[-0.0147]
$\mu\text{wave/mm wave lines}$	697	271		
FIR lines		2953	2991	1437
highest J, K_a , K_c	59, 48, 39	45, 45, 37	47, 43, 39	37, 36, 32

Table 2: Rotational constants and band origins for the ν_{20} and ν_{19} vibrational states of imidazole. Rotational constants are obtained by fitting microwave data from 2021[5], while band origins are obtained via correlation, as described in the text. Numbers in parentheses are 1σ uncertainties in the last digits of the value for each parameter. Numbers in square brackets were fixed to values obtained in the fit for the ground state.

Parameter	ν_{20}	ν_{19}
$\Delta E/\text{cm}^{-1}$	628.5348(2)	664.4669(2))
A/MHz	9695.8415(16)	9703.4314(14)
B/MHz	9352.6117(16)	9344.6236(11)
C/MHz	4773.41445(61)	4773.49221(41)
D_J/kHz	3.23088(83)	3.22221(46)
D_{JK}/kHz	-5.02275(140)	-4.98744(52)
D_K/kHz	2.13651(92)	2.11152(35)
d_1/kHz	0.01027(234)	0.0520(12)
d_2/kHz	0.03306(558)	0.0145(23)
H_J/mHz	[1.367]	[1.367]
H_{JK}/mHz	[-6.063]	[-6.063]
H_{KJ}/mHz	[7.294]	[7.294]
H_K/mHz	[-2.813]	[-2.813]
h_1/mHz	[0.0459]	[0.0459]
h_2/mHz	[-0.0804]	[-0.0804]
h_3/mHz	[-0.0147]	[-0.0147]
$\mu\text{wave/mm wave lines}$	130	134
highest J, K_a , K_c	38, 27, 29	40, 24, 30

Table 3: Inertial defects Δ in $\text{amu}\cdot\text{\AA}^2$ for the ground state and five excited vibrational states of imidazole, calculated from the parameters given in Tables 1 and 2.

State	Inertial defect Δ
Ground	0.0287
ν_{21}	-0.1615
ν_{20}	-0.2857
ν_{19}	-0.2929
ν_{18}	-0.2055
ν_{17}	-0.1899

similar. The A and B constants are smaller in the vibrationally excited states than in the ground vibrational state, so the inertia for rotation around the a and b axes is increased upon excitation, likely due to the increased averaged distance from the vibrating nuclei to the axes. On the other hand, the C constant is extremely close in value for the ground and vibrationally excited states, indicating that the perpendicular distances of the nuclei to the c axis changes very little in the excited states as compared to the ground state.

The inertial defect $\Delta = I_c - I_a - I_b$ [17] is given in Table 3 for the six states of imidazole rotationally analyzed so far. As expected, the value of Δ is close to zero for the ground vibrational state, indicating a planar structure, while the values for the excited vibrationally excited states are negative, consistent with the out-of-plane vibrations associated with these states.

5. Conclusions

Our work both complements and extends the recent results on imidazole spectroscopy reported in References [1] and [5]. We have provided accurate term energies for the lowest five excited vibrational states of the molecule, corrected and improved the rotational characterization of the ground, ν_{21} , ν_{20} and ν_{19} levels, and have provided a first rotational analysis of the ν_{18} and ν_{17} levels. As pointed out in Ref. [5], signatures of vibrationally excited states in molecules can play a role in astrophysical spectroscopy both as indicators of the degree of vibrational excitation and as a source of ‘weeds’ - unassigned lines in the spectrum which actually belong to known species. It would be of interest to see if, in retrospect, lines from the ν_{18} and ν_{17} levels appear in the rotational spectrum analyzed in Ref. [5], now that a rotational analysis has been generated from our far-infrared spectrum.

6. Acknowledgements

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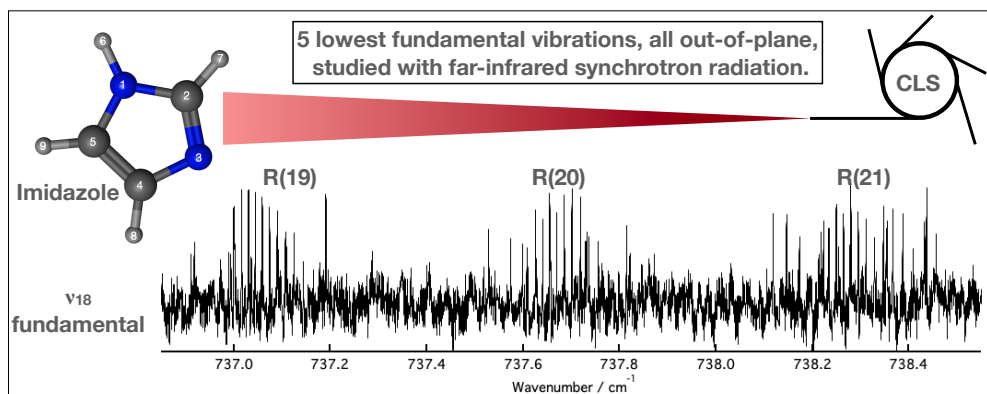
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- Far-infrared absorption spectra of imidazole were obtained with synchrotron radiation
- Three rotationally resolved fundamental vibrational bands were assigned and analyzed
- Origins of two weak vibrational bands were accurately determined
- A global fit of the far-infrared data with previously reported microwave data was performed

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Dennis Tokaryk: conceptualization, methodology, investigation, formal analysis, writing – original draft, data curation, supervision **Jeffery Crouse:** investigation, formal analysis, writing – review and editing **Doyeon Kim:** formal analysis, writing – review and editing

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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