High-resolution Fourier transform infrared synchrotron spectroscopy of the NO₂ in-plane rock band of nitromethane

Mahesh B. Dawadi^a, Sylvestre Twagirayezu^{b#}, David S. Perry^{a*} and Brant E. Billingham^b

^aDepartment of Chemistry, The University of Akron, OH, 44325, USA

^bCanadian Light Source Inc., University of Saskatchewan, 44 Innovation Blvd, Saskatoon,
SK S7N 2V3, CANADA

*Author to whom correspondence should be addressed. Electronic mail:

dperry@uakron.edu.

[#] Present address: Department of Chemistry, Brookhaven National Laboratory, Upton, New York, 11973, USA.

ABSTRACT

The high-resolution rotationally resolved Fourier-transform infrared spectrum of the NO₂ in-plane rock band (440-510 cm⁻¹) of nitromethane (CH₃NO₂) has been recorded using the Far-Infrared Beamline at the Canadian Light Source, with a resolution of 0.00096 cm⁻¹. About 1773 transitions reaching the upper state levels $m' = 0; K'_a \leq 7; J' \leq 50$ have been assigned using an automated ground-state combination difference program together with the traditional Loomis-Wood approach. These data from the lowest torsional state, $m' = 0$, were fit using the six-fold torsion-rotation program developed by Ilyushin et al. [*J. Mol. Spectrosc.*, 259, 26-38 (2010)]. The analysis reveals that the rotational energy level structure in the upper vibrational state is similar to that of the ground vibrational state, but the sign and magnitude of high-order constants are significantly changed suggesting the presence of multiple perturbations.

Key words: Nitromethane, 6-fold internal rotation, high resolution, far infrared spectrum, synchrotron

I. INTRODUCTION

Nitromethane (CH_3NO_2) is a slightly oblate asymmetric top ($\kappa = 0.25$) with a light methyl (CH_3) rotor and a heavier nitro (NO_2) group [1-3]. The very low 6-fold internal rotation barrier, 2.10 cm^{-1} [1-3], makes nitromethane a benchmark system for the studies of large amplitude torsional motion in a 6-fold potential and for the resulting vibrational dynamics [3, 4]. In many other methyl-rotor systems, the torsional potential is dominated by 3-fold terms, which are much larger, typically several hundred cm^{-1} . Since the heavy atoms are co-planar in the equilibrium geometry, symmetry dictates that the 3-fold term in the torsional potential of nitromethane is zero, leaving only the much smaller 6-fold term. However, distortion along a non-totally-symmetric vibrational coordinate relieves this restriction, opening the way for substantial 3-fold coupling terms [5]. Spectroscopic work on CH overtones of nitromethane [4] indicates a large increase in the torsional barrier upon vibrational excitation.

The microwave spectrum of nitromethane has been investigated by several groups [1, 2, 6-9]. Recently, Slingerland et al. [10] have reported low-resolution spectra in the terahertz region (9 to 40 cm^{-1}). In the infrared, low-resolution spectra in the fundamental [11, 12] and overtone [3] regions have been reported. High-resolution infrared spectra of the CN stretch at 917.5 cm^{-1} [13] and in the NO asymmetric stretch at 1584 cm^{-1} [14] have been recorded in the gas phase at 0.005 cm^{-1} resolution with a BOMEM Fourier transform spectrometer, and the transitions of the lowest torsional state ($m = 0$) have been analyzed. For the 1584 cm^{-1} band, high-resolution spectra of jet-cooled nitromethane have been

obtained and analyzed for $0 \leq m \leq 3$ [15-17]. The nitromethane fundamental vibrations are listed in Table 1, all of which are infrared active except the torsion.

Table 1. Fundamental vibrational frequencies for nitromethane.

Normal Mode ^a	Normal Mode ^{b,c}	Symmetry G ₁₂ (D _{3h})	Description ^d	Frequency / cm ⁻¹	Frequency ^b / cm ⁻¹	Frequency ^c / cm ⁻¹	Frequency ^h / cm ⁻¹
v ₁	v ₁	A ₁ '	$\nu(\text{CH})_s$	---	2973.9	2964.3	2972
v ₂	v ₄	A ₁ '	$\nu(\text{C-N})$	917.55 ^e	917.9	917.1	918
v ₃	v ₂	A ₁ '	$\nu(\text{NO})_s$	---	1397.4	1397	1397
v ₄	v ₅	A ₁ '	$\delta(\text{NO})_s$	---	657.4	656	658
v ₅	v ₃	A ₁ '	$\delta(\text{CH})_s$	---	1378.4	1378.8	1377
v ₆	v ₇	A ₁ "	$\nu(\text{NO})_a$	1583.81 ^f	1583.8	1583.3	1586
v ₇	v ₈	A ₁ "	$\rho(\text{NO}_2)_i$	475.360(9) ^g	475.2	----	477
v ₉	v ₆	A ₂ "	$\rho(\text{NO}_2)_o$	---	602.5	----	605
v ₁₀	v ₉	E'	$\nu(\text{CH})_a$	---	3080	3080.4	3065
v ₁₁	v ₁₁	E'	$\rho(\text{CH}_3)$	---	1119	1091	1100
v ₁₂	v ₁₀	E'	$\delta(\text{CH})_a$	---	---	1438	1482

^a The vibrational mode numbering from (Tables 15-5 and A-24) of Ref. [18] will be used in this paper.

^b Vibrational mode numbering and frequencies from Ref.[19].

^c Vibrational mode numbering and frequencies from Ref.[12].

^d ν = stretch; δ = bend; ρ = rock; δ = bend; a = asymmetric; s = symmetric; i = in-plane; o = out-of-plane.

^e From Ref. [13].

^f From Ref.[14].

^g From this work. The uncertainty is given as a standard deviation of the distribution (in parenthesis) in unit of last digit.

^h From Ref.[20].

Most of the vibrational bands of nitromethane remain unexplored at high resolution. Four fundamental bands, the NO₂ in-plane rock, NO₂ out-of-plane rock, the NO-symmetric bend, and CN-stretch fall within the operating range (30-1000 cm⁻¹) of the Far-Infrared Beamline at Canadian Light Source (CLS). This beamline is equipped with a high-

resolution Bruker IFS 125 HR spectrometer (0.00096 cm^{-1}). The brightness and stability of this synchrotron radiation source provides a signal-to-noise advantage over conventional sources within its operating range [21-23]. This paper reports the first high-resolution synchrotron-based FTIR spectrum of the NO_2 in-plane rock band ($440\text{-}510\text{ cm}^{-1}$) of nitromethane, together with detailed assignments and analysis of the transitions of the lowest torsional state ($m = 0$). The analysis of the torsionally excited states ($m > 0$) is underway and will be reported in the future.

II. EXPERIMENTAL

Synchrotron radiation at the CLS Far-Infrared (Far-IR) Beamline was used to record the FTIR spectrum of CH_3NO_2 in the range $440\text{-}510\text{ cm}^{-1}$. The Far-IR Beamline and its capability has been previously described [24-30]. Briefly, synchrotron infrared radiation is collected from the bending magnet via a slotted mirror and focused through a diamond window. Then the light is directed to the entrance of a Bruker IFS 125 HR spectrometer, via a series of flat and elliptical mirrors, where it is finally focused through a 1.15 mm aperture. After passing through the interferometer, the light is directed through a KBr window at the entrance of a 2 m White cell with a total path length of 72 m , containing 197 mtorr of nitromethane at a temperature of 251 K . Finally the light passes through the exit of the White cell, also fitted with a KBr window, and back into the spectrometer where it is finally focused onto a cooled Ge:Cu detector. The observed spectrum (Fig. 1) is the average of 220 interferometer scans measured at an instrumental resolution of 0.00096 cm^{-1} and a sampling rate of 80 kHz . No correction was applied to the internal wavenumber calibration of the FTS, which is thought to be accurate within 0.0005 cm^{-1} . For example, one recent

calibration against known molecular transitions gave a correction that would amount to 0.0002 cm^{-1} in the wavenumber region of the present work. The present spectrum contains more than 20,000 peaks identified by the peak-find program.

Fig.1. The high-resolution synchrotron-based FTIR spectrum in the ν_7 NO_2 in-plane rock region of CH_3NO_2 . A small portion ($\sim 0.40\text{ cm}^{-1}$) of the actual spectrum (black) is shown in black, accompanied by a stick representation of the observed peaks colorized according to their assigned upper state K'_a values and leaving the unassigned features in grey. The notation in the expanded portion of the stick spectrum indicates assigned P lines in the notation, $PJ'_{DK'_a,DK'_c}$.

II. RESULTS & DISCUSSION

A. Symmetry and Selection rules

The molecular symmetry group for CH_3NO_2 is G_{12} , which is isomorphic to D_{3h} and has the irreducible representations $\{A_1', A_1'', A_2', A_2'', E', E''\}$ [1, 2, 8, 18]. The G_{12} group is also isomorphic to C_{6v} and that notation may also be used with the respective symmetry species $\{A_1, B_2, A_2, B_1, E_2, E_1\}$ [31]. Levels with the total species A_1'', A_2'' , and E'' are odd under the interchange of the two ^{16}O atoms and are therefore forbidden [18]. For the vibrational ground state, this means that only levels with $K_a + m = \text{even}$ exist [1, 2, 8, 18], but in the NO_2 in-plane-rock (ν_7, A_1'') vibrationally excited state, only the levels with odd $K_a + m$ exist. The b -type selection rules for the ν_7 band are: $\Delta J = 0, \pm 1$ (except $J = 0 \rightarrow J = 0$); $\Delta K_a = \pm 1, \pm 3, \dots$; $\Delta K_c = \pm 1, \pm 3, \dots$; and $\Delta m = 0$, where m is the internal rotation quantum number. Since nitromethane is more oblate than prolate ($\kappa = 0.25$), prolate-forbidden transitions with $\Delta K_a = \pm 3$ will have substantial intensity.

B. Assignments

The NO_2 in-plane rock of nitromethane (Fig. 1) is a b -type band, dominated by strong R and P Branches. However, the spectrum is very congested by transitions originating in the internal rotor states up to about $m = 9$, which are populated at the sample temperature. Accordingly, assignment of the spectrum required the combined use of an automated ground-state combination difference (GSCD) program together with the traditional Loomis-Wood approach [32]. For this purpose, ground state torsion-rotation energies were obtained from Ilyushin [33] and are in agreement with the limited set of energies ($J'' \leq 20$) previously obtained from Sørensen [2].

The assignment of $m = 0$ transitions was accomplished in three steps. First, the lines in a P or R branch are identified with a Loomis-Woods program [34] based on the anticipated spacing ($2B = \sim 0.39 \text{ cm}^{-1}$). Second, the obtained P or R branch lines are then linked to P , Q , and R lines reaching the same-upper state rotational level using the automated GSCD algorithm [15]. This program searches through the peak-find list for sets of transitions that match the known GSCDs within the experimental resolution (0.0010 cm^{-1}). Figure 2(a) shows one set of 7 transitions from different ground-state levels that reach the same-upper state rotational level. The spacing pattern of these seven transitions is accurately known from microwave spectroscopy and thus provides a very characteristic signature of the identity of the upper state rotational level. Third, the observed GSCDs were fit to the torsion rotation Hamiltonian (as described below). The assignment for a particular GSCD set (Fig. 2(a)) is considered confirmed if the following criteria are met: (a) each GSCD obtained from the present IR spectrum reproduces the GSCD obtained from the fits of the microwave data [33] within 0.0015 cm^{-1} ; (b) the same upper state is reached by at least 4 different IR transitions; and (c) each residual from the fit of the IR GSCDs to the torsion-rotation Hamiltonian (as described below) is less than 0.0011 cm^{-1} .

A total of 1773 transitions, for $m' = 0$; $K_a' \leq 7$; $J' \leq 50$, were assigned based on criteria (a) and (b) above and are tabulated in Table S-1 of the supplementary data. Of these, the assignments of 1576 transitions were confirmed with the combined criteria (a), (b) and (c). The unassigned transitions in Fig. 1 are largely attributable to $m > 0$ lines and also to weaker unassigned $m = 0$ lines including perturbations. Given the congested nature of this spectrum and the presence of a great many blended lines, it is likely that a few assignment errors may remain even in the “confirmed” list. Figure 3 provides a summary of

the assigned $m = 0$ subbands.

Fig.2. (a) An example of the set of ground-state combination differences (GSCD) resulting from the 7 transitions reaching the $J'_{K'_a K'_c} = 5_{33}$ upper state rotational level. (b) An example of the set of upper-state combination differences (USCD) resulting from the 6 transitions originating from the $J''_{K''_a K''_c} = 5_{23}$ lower state rotational level. The prolate-forbidden $\Delta K_a = \pm 3$ transitions, shown as dashed lines, carry significant intensity.

Fig.3. Summary of the *b*-type infrared sub-bands observed for the $m=0$ state of nitromethane.

C. Analysis and Discussion

The upper state term values, $\nu^{J'K_a'K_c'}$, are calculated by adding the known ground state term values $\nu^{J''K_a''K_c''}$ [33] to the wavenumber, ν , of each observed transition,

$$\nu^{J'K_a'K_c'} = \nu + \nu^{J''K_a''K_c''}. \quad (1)$$

To display the pattern of rotational energy levels for both lower and upper states, it is convenient to plot reduced term values. The reduced term values, $\nu_R^{JK_aK_c}$, are obtained by subtracting the J -dependent part of the rigid symmetric rotor energy,

$$\nu_R^{J''K_a''K_c''} = \nu^{J''K_a''K_c''} - \frac{1}{2}(B'' + C'')J''(J'' + 1). \quad (2)$$

The ground state rotational constants [33] were used to compute the reduced term values in both the upper and lower states.

Fig.4. Reduced term values of $m = 0$ rotational levels in the ground (b) and the excited (a) vibrational states. For the vibrationally excited state (a), the plotted term values are represented as the change from the ground states values (b): $\Delta \nu_R^{J' K_a' K_c'} = \nu^{J' K_a' K_c'} - \nu^{J'' K_a'' K_c''}$, where the hypothetical ground state term values for odd K_a'' were computed with the six-fold torsion-rotation program [31] using the ground state constants [33]. Open markers are for $J = K_a + K_c - 1$; closed for $J = K_a + K_c$.

The patterns of the reduced term values, for the upper and the lower states are compared in Fig 4. The $m = 0$ reduced term values lower state (Fig. 4(b)) follow the usual asymmetric rotor pattern with asymmetry splittings that increase with J and decrease with K_a . Since upper state pattern would be essentially identical when plotted on the same scale as Fig. 4(b), only the change of the upper state levels relative to the ground state is plotted in Fig. 4(a).

The present data are fit to the six-fold torsion-rotation Hamiltonian of Ilyushin et al. [31] using their fitting program. In principle, the present $m = 0$ data could be fit with an ordinary asymmetric-rotor centrifugal-distortion Hamiltonian, but for consistency with the future analysis of the $m > 0$ transitions, we use the full torsion-rotation Hamiltonian. Since the program [31] fits only a single vibrational state, it was applied in two stages. First, the GSCDs (e.g., Fig. 2(a)) were fit as a check on the quality of the spectra and the validity of the assignments. Second, the upper state combination differences (e.g., Fig. 2(b)) were fit to determine the upper state rotational constants.

The fit of the GSCDs was approached in steps, beginning with the low $J'' \leq 20$, and then incrementally adding combinations of higher J'' until $J'' = 50$ was reached. At each step, transitions yielding large residuals were eliminated from the fit as possible mis-assignments (supplementary data, Table S.2). Additional sextic and octic centrifugal distortion terms were added as necessary to improve the quality of the fit (Table 2). During the fit, the pure torsional constants and the torsion-rotation interaction constants were held fixed at their ground state values [33] (supplementary data, Table S.3) because the quality of fit was insensitive to these parameters. Equal weights were used for all the transitions. The final fit of 1576 GSCDs included $m'' = 0$ levels in the range, $J'' \leq 50$ and $K_a'' \leq 10$

(Table S.2) and yielded a root-mean-square deviation of 0.00063 cm^{-1} . The ground state constants A''_{eff} , B'' and C'' are in good agreement with the more precise microwave values [33] within the statistical error of our fit. However, the centrifugal distortion constants determined here are significantly different because higher rotational levels and higher-order constants were included in the present fit. Of the sextic and octic constants, some are determined with marginally significant values (Table 2), but they still contribute to the quality of the fit. The root-mean-square deviation ($\sigma = 0.00063 \text{ cm}^{-1}$) is less than the line width (0.0010 cm^{-1}) and just a little larger than the expected instrumental accuracy ($\sim 0.0005 \text{ cm}^{-1}$). The residuals are an apparently random function of J'' , K_a'' and K_c'' and are likely attributable in part to blended lines in the congested spectrum.

On the other hand, the upper-state combination differences (USCDs) are calculated from the assigned infrared transitions that arise from the same ground state reaching the different upper states (Fig. 2(b)). The 497 USCDs involving $m' = 0; K_a'' \leq 7; J' \leq 22$ in the upper vibrational state (supplementary data, Table S.4) have been fit using the same six-fold torsion-rotation program. As for the ground state, the pure torsional constants and torsion-rotation interaction constants were held fixed at their ground state values [33] (Table S.3) and only the upper-state rotational and centrifugal distortion constants were floated. One subband, consisting of the levels $K_a' = 1$ and $K_c' = J'$, is significantly perturbed being shifted to lower wavenumber by as much as 0.6 cm^{-1} at $J' = 22$. Accordingly, those levels for $11 \leq J' \leq 22$ were removed from the fit.

Table 2. The molecular fitted parameters for the NO₂ in-plane-rock band of nitromethane using the six-fold torsion-rotation program^a [31].

Operators	Parameters	Ground state ^{b,c} cm ⁻¹	Excited state ^{b,d} cm ⁻¹
P_a^2	$A_{\text{eff}} - (\frac{1}{2})(B+C)$	0.1711325(60)	0.17096(14)
P^2	$(\frac{1}{2})(B+C)$	0.2738760(27)	0.274592(98)
$P_b^2 - P_c^2$	$(\frac{1}{2})(B-C)$	0.0778731(14)	0.078176(41)
$-P^4$	D_J	$2.30(12) \times 10^{-7}$	$-4.72(82) \times 10^{-6}$
$-P^2 P_a^2$	Δ_{JK}	$1.50(52) \times 10^{-9}$	$6.2(26) \times 10^{-6}$
$-P_a^4$	Δ_K	$1.48(82) \times 10^{-7}$	$-1.34(36) \times 10^{-5}$
$-P^2(P_b^2 - P_c^2)$	δ_J	$9.7(6) \times 10^{-8}$	$1.77(27) \times 10^{-6}$
$-\{P_a^2, (P_b^2 - P_c^2)\}$	δ_K	$4.18(15) \times 10^{-7}$	$2.5(05) \times 10^{-6}$
P^6	H_J	$1.37(28) \times 10^{-10}$	$7.8(27) \times 10^{-9}$
$P^4 P_a^2$	H_{JK}	$-6.2(12) \times 10^{-10}$	$3.1(12) \times 10^{-8}$
P_a^6	H_K	$2.19(30) \times 10^{-9}$	$-6.1(40) \times 10^{-8}$
$\{P_a^4, (P_b^2 - P_c^2)\}$	h_K	$2.71(59) \times 10^{-10}$	$8.45(75) \times 10^{-8}$
$\{P^4, (P_b^2 - P_c^2)\}$	h_J	$6.87(14) \times 10^{-11}$	$5.1(10) \times 10^{-11}$
P^8	L_J	$1.8(41) \times 10^{-15}$	-----
P_a^8	L_K	$-7.80(40) \times 10^{-12}$	$1.7(12) \times 10^{-10}$
$P^6 P_a^2$	L_{JK}	$8.4(32) \times 10^{-15}$	$-6.78(99) \times 10^{-11}$
$P^4 P_a^4$	L_{JK}	$1.11(19) \times 10^{-13}$	-----
	A	0.4450085(61)	0.44558(16)
	B	0.3517491(36)	0.35279(11)
	C	0.1960029(23)	0.19645(11)
No. of GSCD or USCD		1576	497
RMS deviation		0.00063 cm ⁻¹	0.0058 cm ⁻¹
J		$0 \leq J'' \leq 50$	$1 \leq J' \leq 22$
K_a		0,2,4,6,8,10	1,3,5,7

^a The torsional parameters in the torsion-rotation Hamiltonian were held fixed at the ground state values listed in Table S.4.

^b The number in parentheses are standard deviations in units of the last digits.

^c Ground state constants obtained by fitting the GSCDs of the lowest torsional state ($m = 0$).

^d Excited state constants obtained by fitting the USCDs in the lowest torsional state ($m = 0$).

The $m'=0$ upper-vibrational-state molecular constants determined from the fit are given in Table 2. Even fitting a greatly reduced number of rotational levels ($0 \leq J' \leq 22$), the root-mean-square (RMS) deviation of the upper state fit (0.0058 cm^{-1}) was nearly an order of magnitude larger than for the ground state fit. Although lines with J' up to 50 have been assigned (Table S.1), the residuals increase rapidly with J' , and we were not able to achieve a meaningful fit for upper state combinations beyond $J' = 22$. The size and distribution of these residuals relative to those of the ground state, together with the substantial shift of levels in the $K'_a = 1$ and $K'_c = J'$ subband, appear to indicate the presence of multiple perturbations. All combination differences included in the fit for the ground state and for the upper state, in addition to the common upper- or lower-state levels, and the residuals (observed-calculated) are listed in the supplementary Tables S.2 and S.4, respectively.

As expected, the rotational constants, A' , B' , and C' , of the vibrationally excited state (Table 2) are close to, but slightly larger than, those of the ground state. The centrifugal distortion constants are qualitatively different from the ground state (Table 2), with most constants much larger in magnitude and many even having the opposite sign. Such unphysical values of the centrifugal distortion constants are the expected result of trying to fit the level shifts arising from perturbations with a centrifugal distortion Hamiltonian. The identity of the specific perturbing level(s) is not yet known. Since the NO_2 in-plane rock band is the lowest frequency normal mode, the only possible source of perturbations is excited internal rotor states built on the ground state.

Since the fit of the USCDs does not provide a value for the band origin (ν_0), the band origin must be calculated separately. To do this, we subtracted the torsion-rotation energies computed by the fitting program from the experimental upper state term values $\nu^{J'K'_a'K'_c'}$ as determined from Eq. (1). The average value of band origin for the 302 $m' = 0$ upper state levels with $J' \leq 10$ is $475.360 \pm 0.009 \text{ cm}^{-1}$, where the uncertainty is the standard deviation of the distribution of the values obtained.

IV. SUMMARY

The lowest internal rotor state ($m' = 0$) of the NO₂ in-plane rock band of nitromethane has been assigned and analyzed. The rotational constants and centrifugal distortion constants up to octic are derived for the ground and upper states. The pattern of reduced term values indicates that the rotational energy level structure of the upper state is similar to that of the ground state. The unphysical values of the centrifugal distortion constants obtained for the vibrationally excited state, together with the magnitude and pattern of the residuals, suggests the presence of multiple perturbations. Some transitions involving excited internal rotor states ($m' = 3$) have already been assigned. The next stage of the work is to continue assignment of the $m' > 0$ transitions with the aim of probing the coupling of the NO₂ in-plane rock vibration to internal rotation.

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