High resolution infrared spectroscopy of cyanogen N-oxide, NCCNO

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We report here on the first high resolution infrared absorption spectra of the semistable nitrile oxide, NCCNO. All of the fundamental modes of vibration (except for the lowest-frequency bending mode) and several combination bands have been measured with a Fourier transform spectrometer at a resolution of 0.005 cm^{-1}. In this paper, we present analyses of v_4, the C–C stretching mode at 714.753 94(6) cm^{-1}, v_6, the NCC bending mode at 403.925 97(6) cm^{-1}, v_6+v_7 at 490.123 62(6) cm^{-1}, and the tentatively assigned v_5+v_6 combination band at 826.291 86(8) cm^{-1}. A simultaneous least squares fit of these four bands gives ground state rotational constants of $B_0 = 0.077 085 54(34)$ cm^{-1} and $D_0 = 4.570(30) \times 10^{-9}$ cm^{-1}. © *1996 American Institute of Physics.* [S0021-9606(96)00635-6]

INTRODUCTION

The cyanogen N-oxide (NCCNO) molecule is a semistable member of the nitrile oxide family. Nitrile oxides contain the $-$CNO group and they are named as derivatives of the corresponding nitriles (cyanogen, NCCN, in this case). NCCNO was first prepared in solution by Grundmann and Frommeld[1] in 1966, but were unable to record the characteristic $-$CNO infrared band near 2300 cm^{-1}. Maier and Teles[2] recorded the first infrared spectra of NCCNO in 1987. The vacuum pyrolysis products of chlorocyanoformaldoxime [NC(Cl)C=NOH] were trapped in an argon matrix at 10 K and five low resolution IR bands of NCCNO were reported.[2]

Nitrile oxides are useful reagents in synthetic organic chemistry, where they are generated in solution and used *in situ*.[3,4] For example, NCCNO can be utilized for the stereospecific functionalization of alkenes, specifically as a reagent to effect the vicinal cyanohydroxylation of olefins.[5] In addition, the NCCNO molecule is a candidate for astrophysical observation in dark molecular clouds since it contains only the relatively abundant elements, C, N, and O.

Following our successful measurement of the high resolution infrared spectra of the unstable cyanogen di-N-oxide (ONCCNO) molecule,[6] we have recorded high resolution infrared spectra of NCCNO (this work) and BrCNO.[7] Pasinszki and Westwood[8,9] have recently found that gaseous NCCNO can be generated efficiently and virtually quantitatively by vacuum flow thermolysis of the stable dimer, dicyanofuroxan (dicyano-1,2,5-oxadiazole 2-oxide) in the gas phase at 300 mTorr. By using photoelectron spectroscopy,

He I photoionization mass spectrometry and low resolution mid-infrared spectroscopy, they have confirmed the identity of the NCCNO molecule and have shown that it is the major component in the gas phase. It is surprisingly stable and exists for several hours at low pressure. *Ab initio* theory with a 6-31G* basis set and various levels of correlation [MP3, QCISD, QCISD(T)], predict that the NCCNO molecule has a linear structure,[9] although earlier *ab initio* calculation[10] suggested that NCCNO should exhibit large-amplitude bending motion and have a quasilinear structure. Indeed, the parent nitrile oxide molecule, HCNO, is a well-known quasilinear molecule.[11] The pure rotational transitions of NCCNO have recently been measured at the University of British Columbia with a microwave Fourier transform spectrometer.[12]

In the present work, we have recorded high resolution Fourier transform infrared spectra of the NCCNO molecule from 200 to 4000 cm^{-1}. The NCCNO molecule has seven vibrational modes: $v_1(\sigma)$ 2328 cm^{-1} antisymmetric CNO stretch; $v_2(\sigma)$ 2192 cm^{-1}, CN stretch; $v_3(\sigma)$ 1442 cm^{-1}, CNO symmetric stretch; $v_4(\sigma)$ 715 cm^{-1}, C–C stretch; $v_5(\pi)$ 423 cm^{-1} (tentatively), CNO bend; $v_6(\pi)$ 404 cm^{-1}, NCC bend; and $v_7(\pi)$ 86 cm^{-1}, CCN bend. The vibrational frequencies for v_1, v_2, and v_3 are from the low resolution spectra of Pasinzki and Westwood,[9] and although we have high resolution data, they exhibit severe perturbations in addition to numerous hot bands and are not discussed at this juncture. The values for the lower wave number vibrations (up to 850 cm^{-1}) v_4, v_5, v_6, and v_7 are deduced either directly or indirectly from the high resolution analysis reported here. An
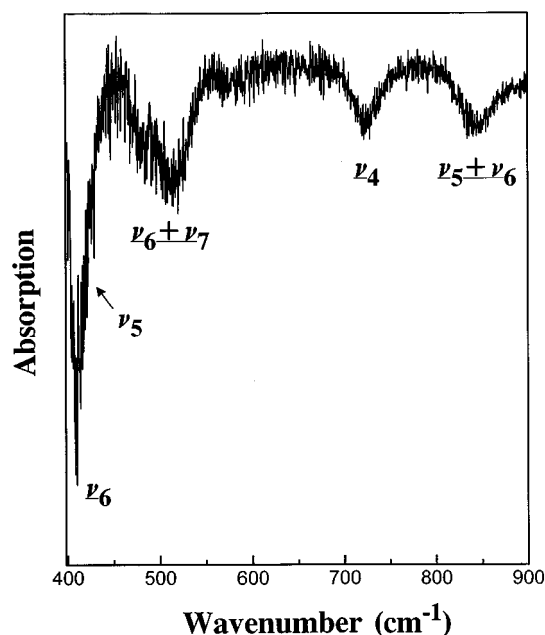
FIG. 1. Overview of the low resolution (0.5 cm^{-1}, 20 cm single path cell, KBr windows), low wave number region of NCCNO. Fundamentals and combination bands underlined are those rotationally analyzed in this work. ν_6 is one to two orders of magnitude weaker than ν_1 at 2328 cm^{-1}.
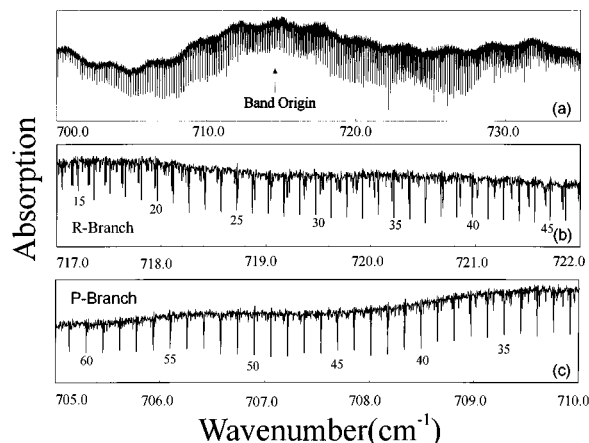

FIG. 2. (a) An overview of the ν_4 (σ) C–C stretching mode of the NCCNO molecule. (b) An expanded portion of the R branch of ν_4. (c) An expanded portion of the P branch of ν_4.

overview of the low wave number region analyzed in this work is presented as Fig. 1.

EXPERIMENT

The NCCNO molecule was generated *in situ* using the same method as described by Pasinszki and Westwood.[8,9] Briefly, the gas phase thermolysis of the stable dimer, dicyanofuroxan, in a quartz tube (8 mm inside diameter by 15 cm long packed with quartz chips) heated to 550 °C yielded NCCNO. The small amounts of N_2O, NO, CO, and CO_2 existed in the spectra, either as the side products of the thermolysis or from subsequent destruction of NCCNO. The experimental setup was typical for absorption work using an external sample cell and glower. The infrared glower was collimated by a parabolic mirror and passed through a 120 cm long absorption cell equipped with KRS-5 windows. The continuum radiation entered the spectrometer through the emission port. The thermolysis products were pumped slowly through the gas cell at a pressure of about 250 mTorr.

The high resolution absorption spectra were recorded with a Bruker FTS 120 HR spectrometer at the University of Waterloo with a resolution of 0.005 cm^{-1} using a liquid helium-cooled Si:B detector. The ν_4 mode near 714 cm^{-1} was recorded using a cold filter that cut off at $\sim$760 cm^{-1} to set the upper limit for the spectral region while the lower limit of 400 cm^{-1} was set by the KBr beamsplitter. There were 50 scans coadded in about 2 h of integration time. The ν_6 mode near 404 cm^{-1} and the $\nu_6 + \nu_7$ combination band at about 490 cm^{-1} were recorded in a similar experiment setup, but a 3.5 μm Mylar beamsplitter was used instead of KBr. The lower wave number limit in this experiment was about

340 cm^{-1}, as determined by the Si:B detector, and the upper limit was set to 760 cm^{-1} with the same cold filter. Fifty scans were coadded in this experiment. The mode near 826 cm^{-1}, tentatively assigned as $\nu_5 + \nu_6$, was recorded with the Si:B detector and the KBr beamsplitter using a bandpass filter to set the spectral range to 750–1250 cm^{-1}.

ANALYSIS

The spectral analysis program PC-DECOMP, developed by Brault, was used for the line measurements. Using this program, the line profiles were fitted with Voigt lineshape functions. The signal-to-noise ratio for the lines in the spectrum was typically about 6:1 and the precision of the line position measurements is better than $\pm$0.0005 cm^{-1} for these lines. However, many of the weaker lines and the blended features were determined only to a precision of about $\pm$0.005 cm^{-1}.

An interactive color Loomis–Wood computer program was used to pick out the branches and to help in the assignments. The measured spectral lines of the ν_4 vibrational mode were calibrated with CO_2 lines using line positions taken from the literature.[13] For the ν_6 vibrational mode and the $\nu_6 + \nu_7$ combination band, we used water absorption lines for calibration.[14] Since there were no impurities spectra in the 750–1250 cm^{-1} region, the $\nu_5 + \nu_6$ combination band was not calibrated. These line positions have an increased absolute error of about 0.002 cm^{-1}, based on the calibration factor used for the ν_4 mode.

The ν_4 fundamental mode

Figure 2 shows the high resolution spectrum of the C–C stretching mode (ν_4) of NCCNO [Fig. 2(a)]. Figures 2(b) and 2(c) are expanded portions of the P and R branch of the ν_4 fundamental. The most intense and regular series picked by the Loomis–Wood program was assigned as the fundamental band.

The main problem in the analysis was the presence of a large number of hot bands that causes a line density as high
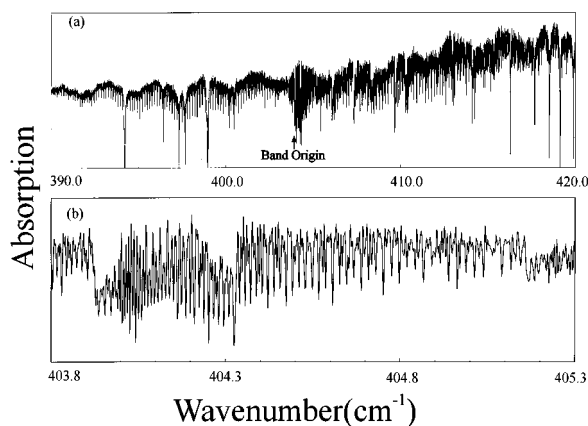
FIG. 3. (a) An overview of the ν_6 (π) NCC bending mode of the NCCNO molecule. The strong broad absorption lines are due to water vapor. (b) An expanded portion of the Q branch of the ν_6 mode.

FIG. 4. An overview of the $\nu_6 + \nu_7$ combination mode of the NCCNO molecule.

as 100 lines/cm^{-1}. It was very difficult to locate the band origin because of overlapping hot bands. However, the intensity pattern did show an "origin gap" in the Loomis–Wood plot, which gave an estimated band origin. The absolute J assignment could only be made by comparing ground state combination differences for two modes, in this case ν_4 and ν_6. In total, 198 rotational lines were assigned in the ν_4 band and they are available from PAPS[15] or by request from the authors.

The ν_6 fundamental mode

An overview of the high resolution spectrum of the NCC bending mode (ν_6) is shown in Fig. 3(a). An expanded portion of the Q branch is shown in Fig. 3(b). The strong Q branch indicates that this band is a bending mode. The *ab initio* calculations[9] predict that the ν_6 mode will be found at 405 cm^{-1}, consistent with the assignment of this band as the NCC bending mode. The fundamental band was picked out with the Loomis–Wood program and was the strongest band in this region. The J assignment was made by matching the ground state combination differences of the ν_4 fundamental. In addition, the location of the Q-branch band head also confirmed the assignment. About 250 lines were assigned and the complete line list is available from PAPS.[15]

The $\nu_6 + \nu_7$ combination band

This band appears near 500 cm^{-1} in the low resolution infrared spectrum.[9] The *ab initio* calculated[9] CNO bending mode frequency is 475 cm^{-1}, so that this 500 cm^{-1} mode was originally assigned as ν_5. However, we could find no trace of a Q branch in the high resolution spectrum (Fig. 4). The combination band $\nu_6 + \nu_7$ does not have a Q branch because the $v_6 = 1$ (π) and $v_7 = 1$ (π) wave functions give rise to Σ^+, Σ^-, and Δ vibrational states ($\Pi \otimes \Pi = \Sigma^+ \oplus \Sigma^- \oplus \Delta$). Only the Σ^+ component has an allowed transition to the ground state, so there will be no Q branch in the $\nu_6 + \nu_7$ band. By subtraction, this assignment gives a value of 86 cm^{-1} for
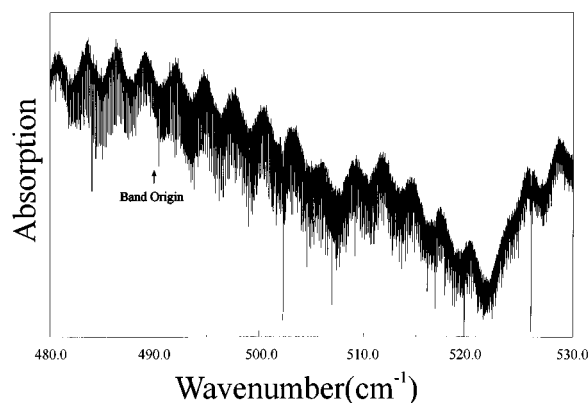
ν_7 to be compared to the *ab initio* harmonic prediction of 54 cm^{-1}. In total, 153 lines have been assigned to this band and they are listed in PAPS.[15]

The $\nu_5 + \nu_6$ combination band

The band around 826.3 cm^{-1} is a relatively weak (as shown in Fig. 5) combination band. This band was easily picked out by the Loomis–Wood program and assigned with the help of the ground state combination differences from the other modes. This mode must be a combination band since there are no fundamental modes calculated in this range.[9] There is no Q branch associated with this mode, so that it must be a parallel transition. We tentatively assign this band as the combination of the CNO bending and NCC bending mode, $\nu_5 + \nu_6$. By subtraction of the ν_6 frequency of 404 cm^{-1}, ν_5 is predicted to be at 422 cm^{-1}. Buried in the stronger ν_6 band region we find a Q branch at 423 cm^{-1}, consistent with this ν_5 assignment and the *ab initio* prediction of 475 cm^{-1}. The assigned lines for $\nu_5 + \nu_6$ are listed in PAPS.[15]
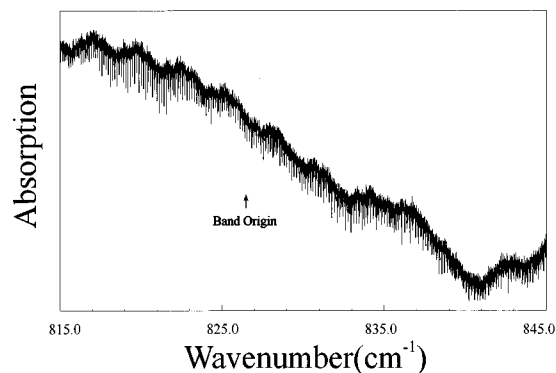

FIG. 5. An overview of the $\nu_5 + \nu_6$ combination mode of the NCCNO molecule.

TABLE I. The rotational constants for NCCNO (in cm^{-1}). One standard deviation is in parentheses.

Level	ν_0	B	$10^9 D$	$10^5 q$	$10^{11} q_D$
Ground	0.0	0.07708554(34)	4.570(30)		
ν_4 (σ)	714.753941(57)	0.07702482(35)	4.583(30)		
ν_6 (π)	403.925967(61)	0.07721463(35)	4.504(30)	3.1477(52)	2.58(88)
$\nu_6 + \nu_7$ (σ)	490.123622(70)	0.07761902(35)	2.643(32)		
$\nu_5 + \nu_6$ (σ)	826.291859(79)	0.07727047(35)	4.208(31)		

The rotational constants

The line positions of all the observed bands were fitted together in a global least-squares fit. The standard energy level expression,

$$F(J) = \nu_0 + BJ(J+1) - D[J(J+1)]^2,$$

was used for the ν_4, $\nu_6 + \nu_7$, and $\nu_5 + \nu_6$ bands. For the ν_6 bending mode, the energy level expression for the excited vibrational level of π symmetry is given by

$$F(J) = \nu_0 + BJ(J+1) - D[J(J+1)]^2$$
$$\pm \tfrac{1}{2} q [J(J+1)] \pm \tfrac{1}{2} q_D [J(J+1)]^2, \qquad (2)$$

with l-type doubling constants q and q_D. We follow the infrared sign convention and report a positive q value. The resulting rotational constants are listed in Table I. The ground state B_0 constant, 0.07708554 cm^{-1} (2.310967 GHz), is in good agreement with the *ab initio* prediction[9] of 2.25 GHz.

DISCUSSION AND CONCLUSION

The semistable cyanogen N-oxide (NCCNO) molecule can be efficiently generated in the dilute gas phase by the gas-phase thermolysis of the dimer, dicyanofuroxan. High resolution spectra of the NCCNO molecule have been obtained for all of the vibrational modes, except the lowest-frequency bending mode. The rotational analysis of the ν_4, ν_6, $\nu_6 + \nu_7$, and $\nu_5 + \nu_6$ bands has been accomplished and reported here. Numerous hot bands associated with these modes need to be analyzed. The higher-frequency modes ν_1, ν_2, and ν_3 show signs of extensive perturbations and further work is necessary on these fundamentals as well as on related combination bands and hot bands.

The ground state rotational constants reported in Table I have already proved useful in narrowing the search for the pure rotational spectrum of NCCNO.[12] The high sensitivity of Fourier transform microwave spectroscopy allowed ^{13}C, ^{15}N, and ^{18}O substituted isotopomers of NCCNO to be detected in natural abundance and a substitution structure to be derived.[12]

The NCCNO molecule behaves like a linear molecule with a low-frequency anharmonic bending mode of about 86 cm^{-1}. Since the low-frequency bending mode has not been characterized yet at high resolution, the possibility of quasilinear behavior cannot be ruled out. However, our preliminary results, the most recent *ab initio* calculations,[9] and the microwave data[12] are consistent with a linear equilibrium geometry.

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