Millimeter-wave Spectroscopy of *syn* Formyl Azide (HC(O)N₃) in Seven Vibrational States

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Abstract

Millimeter-wave spectra for formyl azide (HC(O)N₃) were obtained from 240 to 360 GHz at ambient temperature. For the ground state of *syn* formyl azide, over 1,500 independent rotational transitions were measured and least-squares fit to a complete S-reduced 8th order centrifugal distortion/rigid rotor Hamiltonian. The decomposition of formyl azide was monitored over a period of several hours, the half-life ($t_{1/2} = 30$ min) was determined, and its decomposition products were investigated. Transitions from five vibrational satellites of *syn* formyl azide (ν_9 , ν_{12} , $2\nu_9$, $\nu_9+\nu_{12}$, and ν_{11}) were observed, measured, and least-squares fit to complete or nearly complete octic centrifugally-distorted, single-state S-reduced models. A less complete single-state fit of $3\nu_9$ (509.3 cm^{-1}) was obtained from an unperturbed subset of its

assignable transitions. This state is apparently coupled to fundamental ν_8 (489.4 cm^{-1}) and overtone $2\nu_{12}$ (503.6 cm^{-1}), but the coupling remains unanalyzed. Anharmonic CCSD(T)/ANO1 estimates of the vibrational frequencies of *syn* formyl azide were in close agreement with previously published experimental and computational values. Experimentally determined vibration-rotation interaction (α_i) values were in excellent agreement with coupled-cluster predicted α_i values for the fundamentals ν_9 , ν_{12} , and ν_{11} .

Keywords

Formyl azide, millimeter-wave, rotational spectroscopy, vibration-rotation interaction, centrifugal distortion

1. Introduction

Formyl azide (HC(O)N_3 , **1**) is a highly unstable molecule that has been recently synthesized, isolated, and studied spectroscopically.[1, 2] This newly observed azide is the prototypical acyl azide. Formyl azide is the simplest molecule that can undergo a Curtius rearrangement to produce an isocyanate, isocyanic acid (HNCO , **4**) in this case. Banert *et al.*[1] reported five different successful synthetic routes to formyl azide, allowing for significant flexibility in its generation and its characterization by NMR, UV, and IR spectroscopy. In an attempt to generate oxazirine (*c*- HCON , **5**), a decomposition product of formyl azide (**1**), Zeng *et al.*[2] obtained gas phase and matrix IR spectra, solid-phase Raman spectra, and a single-crystal X-ray structure of formyl azide. In their photochemical experiments, they were unable to directly observe oxazirine (**5**), but did detect isocyanic acid (**4**) and several likely trapping products indicative of the generation of oxazirine. The observed formation of **4** is consistent with the expected Curtius rearrangement of formyl azide.[1, 3] Upon co-deposition of CO in the Ar-matrix, formation of

formyl isocyanate was observed by an incorporation of CO from the matrix, suggesting the possible transient existence of oxazirine (**5**). The *syn* conformation of formyl azide dominates all of the previously published spectra, though the higher-energy *anti* conformer may have been detected as a trace component in a gas phase IR-spectrum.[2]

This present work investigates the gas-phase rotational spectrum of *syn*-HC(O)N₃ (*syn* **1**) and several of its low-energy vibrational states least-squares, which are fit to complete or nearly complete octic centrifugal distortion/rigid rotor Hamiltonians. Many transitions, most presumably from additional vibrational satellites, have been observed but not assigned. Though predicted to have transition intensities above our detection limit (~120 times less abundant than the *syn* conformer), transitions of *anti* formyl azide have not yet been assigned in the dense spectrum. Finally, the decomposition of formyl azide was observed over a few hours to measure its half-life and to determine its decomposition products.

2. Experimental and Theoretical Methods

WARNING. Formyl azide is expected to be a highly explosive compound. Full personal safety equipment was worn and extreme caution was exercised when working with this substance. To further minimize risk of injury, only small quantities of this compound were generated.

Samples of HC(O)N₃ (**1**) were prepared *via* nitrosation of formylhydrazine with sodium nitrite in acid using a procedure adapted from Banert *et al.*[1] Formylhydrazine was purchased from Alfa Aesar and used without further purification. A typical reaction involved dissolving formylhydrazine (8.3 mmol) in water (1.5 mL), then cooling the solution in an ice/salt mixture to between -5 and -10 °C. A solution of sodium nitrite (8.3 mmol) in water (1.2 mL) was then

prepared and slowly added dropwise to the cooled solution of formylhydrazine over a five minute period, stirring throughout. Upon complete addition of the sodium nitrite, the reaction mixture was acidified to a pH of 1 - 2 using chilled concentrated perchloric acid and immediately frozen in liquid nitrogen. After the head space was evacuated, the contents were allowed to warm to room temperature. The evolving condensable gases were cryopumped into a thick-walled glass trap held at liquid nitrogen temperature. The condensable gas sample prepared in this way had H₂O as the major impurity. To remove the water, the sample was allowed to warm towards room temperature and passed through an ethylene glycol slurry-cooled U-trap, held at a temperature of -15 °C, immediately prior to spectroscopic study. This method was successful in generating formyl azide, removing water or other impurities of lower volatility, and collecting sufficiently clean rotational spectra. Although formyl azide in our spectrometer at room temperature has an apparent $t_{1/2} = \sim 30$ min (*vide infra*), freezing the sample in liquid nitrogen until introduction into the sample chamber allowed the sample to survive for several days with little obvious decomposition. Typical reactions yield 4000 - 5600 mTorr • L of gas and generate sufficient formyl azide for a few days of data collection, over several different fills of our spectrometer sample chamber (approximately 80 L).

The millimeter-wave spectrometer used to obtain the formyl azide spectrum from 240 to 360 GHz has been described in previous publications.[4, 5] The spectrometer sample chamber was typically filled with formyl azide to a pressure of 12 - 15 mTorr at room temperature (293 K). Spectral data were immediately collected over an approximately 2.5 hr period, yielding up to five GHz of the spectrum with each filling of the spectrometer volume. Transitions in the collected spectra were assigned, analyzed, and least-squares fit using Kisiel's AABS programs[6, 7] with ASFIT and ASROT.[8, 9]

The CCSD(T)[10]/ANO1[11] geometry optimizations of the *syn* and *anti* conformations of formyl azide and subsequent harmonic or anharmonic 2nd order vibrational perturbation theory (VPT2) frequency calculations were carried out using CFOUR.[12] The CCSD(T)/ANO1 optimized geometries were found using analytic gradients[13, 14] with the frozen core approximation. From the optimized geometries of formyl azide, the quartic distortion constants were estimated *via* a harmonic frequency calculation, and the vibration-rotation interaction values (α_i) and fundamental vibrational frequencies were estimated by calculating the cubic force constants using analytical second derivatives at displaced points, using the method of Stanton *et al.*[15, 16] The vibration-rotation interaction constants were used to predict and assign the transitions of the vibrational satellites of *syn* formyl azide. The B3LYP/6-31G(d) [17-19] optimizations and harmonic frequency calculations were carried out in Gaussian 09[20] with the WebMO interface.[21] Natural Bond Orbital (NBO) and Natural Resonance Theory (NRT)[22, 23] calculations were performed using NBO 6.0[24] implemented in Gaussian 09. High resolution molecular images were generated in POV-Ray.[25] The output summaries of each theoretical calculation and analysis can be found in the supplementary content.

3. Computational Analysis and Spectral Prediction

As observed in previous spectroscopic and computational studies,[1-3] formyl azide can exist in two stable conformers (*syn* and *anti* **1**); the structural parameters of their CCSD(T)/ANO1 equilibrium geometries are provided in Table 1. The single-crystal X-ray structure has been previously reported for the *syn* conformer of formyl azide;[2] its parameters are reproduced in Table 1. There is excellent agreement between the heavy atom bond distances and angles of the

coupled-cluster gas-phase and experimental solid-phase crystal structures; all distances (except the C–H) differ by less than 0.007 Å and the angles differ (excluding θ_{O-C-H}) by less than 0.8 °. The poor agreement of the H-atom locations between the coupled-cluster and crystal geometries is not surprising, since X-ray crystallography tends to underestimate C–H bond lengths and the H-atom locations in the *syn* formyl azide crystal structure were not explicitly treated as part of the structural refinement.

Table 1.

Computed (*syn* and *anti*) and X-ray (*syn* only) structural parameters of formyl azide.

	<i>syn</i> formyl azide (1)		<i>anti</i> formyl azide (1)
Parameter	CCSD(T)/ANO1	X-ray[2]	CCSD(T)/ANO1
R_{C-H} (Å)	1.094	0.950 ^a	1.103
R_{C-O} (Å)	1.207	1.204(2), 1.198(2)	1.199
$R_{C-N\alpha}$ (Å)	1.419	1.418(2), 1.420(2)	1.425
$R_{N\alpha-N\beta}$ (Å)	1.260	1.256(2), 1.260(2)	1.253
$R_{N\beta-N\gamma}$ (Å)	1.127	1.121(2), 1.119(2)	1.132
θ_{O-C-H} (°)	124.7	117.4 ^a	124.0
$\theta_{O-C-N\alpha}$ (°)	126.0	125.21(16), 125.23(15)	121.6
$\theta_{C-N\alpha-N\beta}$ (°)	111.6	112.28(14), 112.07(13)	112.8
$\theta_{N\alpha-N\beta-N\gamma}$ (°)	174.7	174.49(17), 174.11(17)	173.9
A_e	15911.3		51349.6
B_e	4284.9		2839.6
C_e	3375.8		2690.8
A_0	15841.2		51024.3
B_0	4264.0		2826.9
C_0	3354.7		2677.2
μ_A (D)	0.22		2.07
μ_B (D)	1.54		1.50

^aNo standard uncertainty values were determined as these two parameters were not included in the structure refinement.

The B3LYP/6-31G(d) relative energies of key species on the conformational potential energy surface of formyl azide and its expected decomposition pathways are shown in Figure 1. The *syn* conformation is the most stable with the *anti* conformation predicted to be higher in energy by 2.2 kcal/mol at B3LYP/6-31G(d) or 2.8 kcal/mol at CCSD(T)/ANO1. The coupled-cluster energy difference predicts a population of *anti* formyl azide roughly 120 times less than *syn* formyl azide at our observation temperature of ~ 293 K, which is consistent with the previously reported gas phase infrared observation of an abundance of less than 2 % at 298 K.[2] *Syn* formyl azide exhibits strong *b*-type transitions ($\mu_b = 1.5$ D, CCSD(T)) and much lower intensity *a*-type transitions ($\mu_a = 0.22$ D). *Anti* formyl azide has large dipole components along both axes ($\mu_a = 2.1$ D and $\mu_b = 1.5$ D, CCSD(T)) and would exhibit intrinsically strong *a*- and *b*-type transitions. Due to the larger μ_a dipole component and the somewhat more favorable rotational partition function, the strongest intensity rotational transitions of the *anti* conformer are predicted to be only 60 times less intense than the strongest intensity rotational transitions of the *syn* conformer in a given spectral region.

The anharmonic VPT2 calculation at the CCSD(T)/ANO1 level produced fundamental infrared absorption frequencies that are in very good agreement with the previously published experimental results.[2] The fundamental frequency predictions and assignments are in reasonable agreement with those assigned based upon previous high level calculations (CCSD(T)-F12a),[2] with the exception of ν_5 and $2\nu_{11}$, where the frequency ordering of $2\nu_{11}$ and ν_5 are reversed. For those two vibrations, the experimental absorption frequencies and their intensities match the CCSD(T) -F12a method more closely. The CCSD(T)/ANO1 predicted fundamental frequencies of *anti* formyl azide are available in the supplementary content.

Fig. 1. Experimentally observed and theoretically predicted decomposition pathways of formyl azide on the singlet potential energy surface. Relative energies (kcal/mol) including ZPVE calculated at B3LYP/6-31G(d) in blue and CCSD(T)/ANO1 in red.

Table 2.

Computed and experimental vibrational frequencies for *syn* formyl azide.

Mode (sym)	CCSD(T)/ANO1 Fundamental (cm ⁻¹) ^b	CCSD(T)-F12a Fundamental (cm ⁻¹) ^b [2]	Solution phase CCl ₄ 298 K (cm ⁻¹) [1]	Gas phase 298 K (cm ⁻¹) [2]	Ar matrix 16 K (cm ⁻¹) [2]	Raman Solid 77 K (cm ⁻¹) [2]
2ν ₃ (A')	3424.4 (4.1)	3416 (4)		3423 vvw	3402 vw	
ν ₂ +ν ₅ (A')	3293.2 (7.7)	3402 (1)		3301 vvw		
ν ₃ +ν ₄ (A')	3105.6 (13.0)	3095 (3)		3093 vvw	3098.5 vw	3067 m
ν ₁ (A')	2921.9 (32.0)	2938 (52)	2932 w	2937 w	2939.9 w	2964 s
2ν ₅ (A')	2312.9 (25.2)	2288 (29)		2288 w	2282.3 w	2267 vw
ν ₂ (A')	2153.5 (130.8)	2172 (192)	2152 s	2164 vs	2159.7 vs	2172 s
ν ₅ +ν ₆ (A')	2094.4 (249.4)	2087 (15)		2085 w, sh	2079.2 w	
2ν ₆ (A')	1873.7 (9.5)	1887 (8)		1883 w	1875.4 w	
ν ₃ (A')	1722.0 (217.6)	1718 (258)	1699 s	1717 s	1708.1 s	1674 s
ν ₄ (A')	1368.1 (1.6)	1360 (<1)			1370.1 vvw	1374 ms
ν ₅ +ν ₉ (A')	1337.0 (4.2)	1332 (4)		1323 vw	1322 vvw	
2ν ₁₁ (A') ^a	1159.4 (103.5)	1175 (163)	1169 s	1174 s, sh	1173.1 s	1171 w
ν ₅ (A') ^a	1167.3 (357.5)	1151 (357)	1146 s	1151 vs	1149.1 vs	1142 vw
ν ₁₀ (A'')	996.2 (0.1)	993 (<1)				1006 vw
ν ₆ (A')	940.2 (85.8)	947 (101)	942 m	945 ms	941.3 s	956 vs
ν ₁₁ +ν ₁₂ (A')	840.1 (69.1)	844 (9)		847 w, sh	842 vw	
ν ₇ (A')	823.2 (6.4)	829 (42)	827 w	820 m	824.6 m	831 s
ν ₁₁ (A'')	582.6 (9.5)	584 (8)		582 vw	581.4 w	581 vw
ν ₈ (A')	489.4 (0.3)	491 (<1)				496 m
ν ₁₂ (A'')	250.6 (14.6)	251 (14)				286 w
ν ₉ (A')	169.7 (1.1)	171 (<1)				190 s

^a Frequency ordering of 2ν₁₁ and ν₅ are reversed in the CCSD(T)/ANO1 VPT2 calculation compared to the experimental values and

CCSD(T)-F12a calculation.[2] ^b Computed infrared intensity in parenthesis (km/mol).

The barrier to interconversion from *syn* to *anti* formyl azide is approximately 10.5 kcal/mol (B3LYP/6-31G(d)) and involves an out-of-plane rotation of the azide group (**TS_{syn 1-anti 1}**). This is similar to predictions of the rotational barrier from previous studies[1, 3, 26] and to the recent coupled-cluster predicted rotational barrier of carbonyl diazide.[5] There are at least four viable pathways for decomposition of formyl azide on the singlet potential energy surface, two of which (*via* **TS_{syn 1-4}** and **TS_{anti 1-5}**) have been reported previously.[1] The lowest energy decomposition pathway is *via* a concerted Curtius rearrangement (**TS_{syn 1-4}**) of *syn* formyl azide to the isocyanate **4**. This reaction has a barrier of approximately 26 kcal/mol and is highly exothermic to isocyanic acid (HNCO, **4**) and N₂ (-58 kcal/mol). From *anti* formyl azide, a loss of N₂ results in the formation of oxazirine (*c*-HCON, **5**) over a barrier of 34 kcal/mol (**TS_{anti 1-5}**) and is endothermic by 28 kcal/mol. On the triplet surface, this HCON isomer exists as a ring-opened acyl nitrene (**³5**), but on the singlet surface is best described as a cyclic molecule. The computed bond distance between O and N for the singlet oxazirine (**5**) is approximately 1.79 Å, with a total NBO bond order of 0.98. An NRT analysis reveals that the dominant resonance form is the one shown in Figure 1, accounting for 84 % (B3LYP/6-31G(d)) of the molecular character. Singlet *c*-HCON (**5**) is the ground state electronic configuration by a small energy difference (approximately 4 kcal/mol, B3LYP/6-31G(d)). There is a third potential decomposition pathway of the *syn* conformer of formyl azide that leads to hydrazoic acid (HN₃, **3**) and carbon monoxide, though the transition state barrier is 59.1 kcal/mol and this decomposition is endothermic by approximately 10.1 kcal/mol. This transition state features a slightly bent (163 °) H–C–O angle formylium-like fragment in which the H-atom is slightly tilted toward an azide-like fragment. In fact, NBO/NRT calculations reveal the formylium-azide zwitterionic resonance form to be the dominant one, accounting for approximately 25 % of the

overall character (B3LYP/6-31G(d)). A molecule on the HCON₃ surface which is not discussed in the previous experimental works with formyl azide is 1,2,3,4-oxatriazole (**2**). Other than *anti* formyl azide, oxatriazole (**2**) can form by the smallest transition state barrier (17.0 kcal/mol *via* TS_{syn 1-2}) from *syn* formyl azide. The *syn* conformation of formyl azide is aligned for a thermally-allowed 6 π electron electrocyclization, explored computationally by Abu-Eittah *et al.*[27] The intramolecular reaction produces this oxatriazole, a heteroaromatic molecule, which lies only 14 kcal/mol above *syn* formyl azide. The fourth decomposition pathway explored in Figure 1 involves a retro-1,3-dipolar cycloaddition *via* TS_{2decomp} (50.9 kcal/mol), yielding HCN and N₂O. This computational analysis of formyl azide and its possible decomposition products provided the foundation of our spectroscopic analysis and motivated a simple kinetic study of the spontaneous decomposition.

4. Spectral Data and Analysis

The absorption signals collected over the range of 240-360 GHz showed a very dense spectrum resulting from formyl azide, as well as a handful of other small molecules, including known or suspected decomposition products of formyl azide. An image of the predicted stick spectra for all satisfactorily least-squares fit *syn* formyl azide vibrational states and the experimental spectrum from 299 – 304 GHz is provided in Figure 2. The most intense transitions of the ground state are intentionally off-scale to facilitate the detection of many of the lower intensity absorptions of the vibrational satellites. Co-products or decomposition products, carbon monoxide, hydrazoic acid (HN₃),[28], isocyanic acid (HNCO),[29] hydrogen cyanide (HCN), [30] and nitrous oxide (N₂O)[31] have all been identified in the collected spectrum. Although several transitions associated with these light molecules are fairly intense relative to

formyl azide, due to the sparse nature of their spectra (small partition function), their presence in the sample did not hinder the analysis of the formyl azide spectrum.

Fig. 2. Experimental spectrum (upper) and predicted stick spectrum of formyl azide species (lower) from 299 to 304 GHz. The most intense transitions in the experimental spectrum are off-scale.

The most intense transitions of the *syn* conformer are *b*-type R-branch transitions, which, for the ground state, are also some of the most intense transitions observed throughout the spectrum. These transitions present themselves as part of R-branch bands (separated by approximately 6.7 GHz for the ground state, *i.e.*, $2C$) which begin with four degenerate transitions (two $^aR_{0,1}$, $^bR_{1,1}$ and $^bR_{-1,1}$) and then progress to higher frequency as $K_{prolate}$ increases. Upon moving to higher frequency in the R-branch, these four transitions lose degeneracy, and one *a*-type and one *b*-type

transition progress separately to lower frequency, while their counterparts continue toward higher frequency. Due to the small value of μ_a for the *syn* conformer, the $^aR_{0,1}$ transitions were much weaker than the $^bR_{1,1}$ and $^bR_{-1,1}$ transitions. For the ground state of *syn* formyl azide, R-branch transitions range from $J' = 9$ to $J' = 89$ across the spectral window. A full list of each type of transition for each of the observed and least-squares fit states can be found in Table 3, and Figure 3 provides a data set distribution plot of J'' and $K_{prolate}''$ for observed transitions for the ground state of *syn* formyl azide. Similar distribution plots, which display the diversity of transitions included in the least-squares fits, are available in the supplementary content for all other least-squares fit states.

Table 3.

Summary of transitions for each *syn* formyl azide vibrational state observed and least-squares fit.^a

Transition Type	ground state	ν_9	ν_{12}	$2\nu_9$	$\nu_9+\nu_{12}$	$3\nu_9$	ν_{11}
$^aR_{0,1}$	579	468	354	302	140	49	21
$^bR_{1,1}$	174	172	166	155	144	40	108
$^bR_{-1,-1}$	138	139	124	102	100	3	51
$^bR_{1,-1}$	73	75	66	65	64		40
$^bR_{-1,3}$	19	0	4	0	0		
$^bQ_{1,-1}$	905	802	694	646	455	162	243
$^bQ_{3,-3}$	17	8	6	10	7		
$^bP_{1,-1}$	116	72	47	29	3		
$^bP_{1,-3}$	116	72	47	29	3		
Total							
Independent Measurements	1573	1328	1097	990	733	149	317

^aIn cases where two or more transitions were degenerate, each transition is counted individually in the transition type counts. Due to degeneracies, the total number of independent measurements is not the sum of the line counts above.

Fig 3. Data set distribution plots of J'' and $K_{prolate}''$ for R-branch (blue circles), P-branch (green triangles) and Q-branch (purple circles) transitions for the ground state of *syn* formal azide.

The next most-prominent features in the rotational spectrum of *syn* formyl azide are the *b*-type Q-branch series ($^bQ_{1,-1}$) with constant values of $K_{prolate}'$ (from $J' = 12$ to $J' = 101$ for the ground state). The Q-branch series that begin at higher frequency (such as $K_{prolate}' = 14$) display a bandhead at high frequency, where the first few transitions in the series increase in frequency with increasing J , and the rest decrease. In each Q-branch the transitions lose their degeneracy at higher values of J . The band origins for these Q-branches are separated by approximately 24 GHz, *i.e.*, $2(A-(B+C)/2)$, allowing for the observation of almost five complete Q-branch series within our spectral region. Higher J transitions of all the lower $K_{prolate}$ bands also form more widely separated, but easily recognizable, series in the observed spectral region. A small number

of ${}^b\text{Q}_{3,-3}$ transitions are observable for $K_{\text{prolate}}' = 6, 7, \text{ and } 8$, where the prolate or oblate symmetric rotor approximations are least appropriate.

Additionally, over one hundred pairs of weak P-branch (${}^b\text{P}_{1,-1}$ and ${}^b\text{P}_{1,-3}$) transitions were observed and included in the least-squares fit for the ground state. As is shown in Figure 3, they provide access to transitions with a different range of J ($J' = 26$ to $J' = 72$) and K ($K_{\text{prolate}}' = 20$ to $K_{\text{prolate}}' = 36$ for the ground state) than the R- and Q-branch transitions. All these transition types combined resulted in a large data set in which a total of 1573 independent transitions were observed, measured, and included in the least-squares fit of the ground vibrational state of *syn* formyl azide. The rotational and distortion constants for *syn* formyl azide and each other vibrational state least-squares fit were determined in both the S-reduction and A-reduction, the results of the S-reduced fits can be found in Table 4, while the results of the A-reduced fits can be found in the supplementary content. For both the A- and S-reduced least-squares fits, any transition with $\text{obs} - \text{calc}$ value greater than 100 kHz was excluded from the data set. The removal of these worst-fitting lines assures that any absorptions that fall on top of significant underlying features are not included in the data set, without significant loss of information regarding the centrifugal distortion terms. The diversity of transitions and the broad range of J and K values allowed for a complete determination of the rotational and all distortion constants through 8th order in the S-reduction fit for the ground state *syn* formyl azide. For the A-reduction of this data set, the values determined for two octic terms (l_{JK} and l_{KJ}) were not statistically significant. In the S-reduction fit all of the quartic and sextic distortion constants are very precisely determined (quartic to greater than five significant digits and the sextic to greater than four). The diagonal octic constants are also precisely determined, but the off-diagonal octic terms are less well determined, especially l_2 and l_4 .

Table 4.

S-Reduced rotational constants for *syn* formyl azide and its vibrational satellites, I^r representation.

	CCSD(T)/ ANO1	ground state	ν_9 (A', 169.7 cm ⁻¹) ^a	ν_{12} (A'', 250.6 cm ⁻¹) ^a	$2\nu_9$ (A', 339.5 cm ⁻¹) ^a
A_v (MHz)	15841.2 ^b	15992.41613(25)	16046.94391(33)	16044.63077(44)	16102.18660(63)
B_v (MHz)	4264.0 ^b	4299.01818(11)	4305.47766(17)	4288.81823(18)	4312.16322(31)
C_v (MHz)	3354.7 ^b	3383.19532(11)	3382.58384(17)	3382.41086(19)	3382.13356(33)
D_J (kHz)	4.174	4.289255(54)	4.28598(10)	4.27970(10)	4.28684(28)
D_{JK} (kHz)	-36.66	-37.62983(24)	-37.90938(34)	-38.03108(47)	-38.20449(78)
D_K (kHz)	141.5	147.96891(86)	152.2387(13)	149.8230(20)	156.6065(33)
d_I (kHz)	-1.366	-1.412258(11)	-1.423558(18)	-1.404877(23)	-1.436524(25)
d_2 (kHz)	-0.07848	-0.0867857(54)	-0.0945227(74)	-0.0861390(98)	-0.1026382(60)
H_J (Hz)		0.014326(10)	0.014464(27)	0.014184(25)	0.01445(10)
H_{JK} (Hz)		-0.107621(72)	-0.11270(10)	-0.09920(11)	-0.11776(17)
H_{KJ} (Hz)		-0.69697(30)	-0.73289(61)	-0.7399(13)	-0.7764(26)
H_K (Hz)		4.2785(10)	4.6076(18)	4.4139(27)	4.9729(42)
h_I (Hz)		0.0074536(44)	0.0076056(76)	0.0074935(97)	0.0077284(76)
h_2 (Hz)		0.0010561(33)	0.0010929(49)	0.0010228(62)	0.0012158(18)
h_3 (Hz)		0.00026819(56)	0.00031296(85)	0.00026900(75)	0.00035242(79)
L_J (mHz)		-0.00006270(71)	-0.0000634(22)	-0.0000665(19)	-0.000047(14)
L_{JK} (mHz)		0.0010471(82)	0.001059(12)	0.001037(14)	0.001094(19)
L_{JK} (mHz)		-0.010577(53)	-0.01053(12)	-0.01129(18)	-0.01027(37)
L_{KKJ} (mHz)		0.05848(19)	0.06397(21)	0.05612(72)	0.0783(17)
L_K (mHz)		-0.19073(46)	-0.21895(78)	-0.1912(14)	-0.2645(25)
l_I (mHz)		-0.00004116(63)	-0.0000515(10)	-0.0000563(13)	-0.00005117(72)
l_2 (mHz)		0.00000144(56)	0.00000776(89)	0.0000088(10)	[0]
l_3 (mHz)		-0.00000729(15)	-0.00000982(26)	-0.00000923(21)	-0.00000886(21)
l_4 (mHz)		-0.000000195(17)	-0.000000209(32)	[0]	-0.000000790(48)
Δ_i (u Å ²)		0.221189(6)	0.531944(9)	0.079093(10)	0.84187(2)
κ		-0.85474	-0.85425	-0.85683	-0.85377
N_{lines}		1573	1328	1097	990
σ_{fit}		0.032	0.036	0.035	0.035

^a Anharmonic vibrational frequencies calculated at the CCSD(T)/ANO1 level. ^b VPT2 predicted B_0 values.

	$\mathbf{v_9+v_{12}}$ $(\text{A}'', 419.7 \text{ cm}^{-1})^a$	$\mathbf{3v_9}$ $(\text{A}', 509.3 \text{ cm}^{-1})^a$	$\mathbf{v_{11}}$ $(\text{A}'', 582.6 \text{ cm}^{-1})^a$
A_v (MHz)	16098.4637(10)	16157.385(57)	16082.2718(30)
B_v (MHz)	4294.63486(39)	4318.7989(91)	4296.06788(89)
C_v (MHz)	3381.65080(41)	3381.7647(64)	3382.4496(11)
D_J (kHz)	4.27494(33)	4.1799(71)	4.29071(92)
D_{JK} (kHz)	-38.2799(11)	-39.550(49)	-38.0349(21)
D_K (kHz)	154.2852(75)	163.45(59)	157.022(32)
d_1 (kHz)	-1.413700(40)	-1.4044(52)	-1.41561(14)
d_2 (kHz)	-0.093319(19)	-0.0929(13)	-0.09151(11)
H_J (Hz)	0.01506(12)	-0.0269(37)	0.01348(40)
H_{JK} (Hz)	-0.10605(30)	-0.014(14)	-0.11863(67)
H_{KJ} (Hz)	-0.8208(33)	-5.89(30)	-0.6293(90)
H_K (Hz)	4.530(21)	18.3(25)	6.40(15)
h_1 (Hz)	0.007235(18)	-0.0082(27)	0.007432(71)
h_2 (Hz)	0.001132(13)	-0.0028(11)	0.001669(73)
h_3 (Hz)	0.0002860(24)	0.00052(27)	0.000335(15)
L_J (mHz)	-0.000172(16)	0.00340(58)	0.000218(68)
L_{JK} (mHz)	0.001091(33)	-0.0424(15)	0.00306(12)
L_{JK} (mHz)	-0.01467(69)	0.009(34)	[0]
L_{KKJ} (mHz)	0.1490(17)	8.39(61)	-0.180(11)
L_K (mHz)	0.062(17)	-20.9(40)	-2.42(27)
l_1 (mHz)	-0.0000139(27)	0.00003(41)	0.000051(13)
l_2 (mHz)	-0.0000046(25)	-0.00114(18)	-0.000077(14)
l_3 (mHz)	-0.00000281(81)	-0.000660(69)	-0.0000089(45)
l_4 (mHz)	-0.00000050(10)	-0.0000989(51)	0.00000206(52)
$\Delta_i (\text{u } \text{\AA}^2)$	0.37760(2)	1.1454(4)	0.34995(6)
κ	-0.8564	-0.853	-0.8561
N_{lines}	733	149	317
σ_{fit}	0.037	0.059	0.040

Using the observed rotational constants of the ground vibrational state of the *syn* conformer, as well as predicted vibration-rotation interaction terms, assignments for three fundamental excited vibrational states (ν_9 , ν_{12} , and ν_{11}) of this conformer were made, and least-squares fits were obtained (Table 4). These vibrational states are all similar in their spectral patterns to the ground vibrational state. The lower intensity transitions ($^aR_{0,1}$, $^bP_{1,-1}$, $^bP_{1,-3}$), which were very beneficial in achieving a full octic fit in the ground state, become more and more difficult to observe as the vibrational state population decreases. Since no computational method was available to estimate the octic distortion terms, in the few instances in which they could not be satisfactorily determined by least-squares fitting, they were set to zero. A comparison between the coupled-cluster estimated vibration-rotation interaction values for each rotational constant in each measured fundamental state and the experimentally measured values is provided in Table 5. As expected at the CCSD(T)/ANO1 level, there is excellent agreement between the computationally predicted and the observed vibration-rotation interaction (α_i) values, which were determined by the difference between the fundamental state rotational constant and the corresponding ground state rotational constant.[5, 28, 32] The CCSD(T)/ANO1 constants allowed for close initial prediction of vibrational satellite spectra and unambiguous assignment of each of these three fundamental vibrational satellites. For ν_9 , the experimental α_i values are in excellent agreement (approximately 1%) with the CCSD(T)/ANO1 theoretical predictions. Vibrational states ν_{12} and ν_{11} also show very good agreement between prediction and experiment, with the largest discrepancy of 4.5 MHz (5 %) for α_C of ν_{11} . Also provided in Table 5 are the CCSD(T)/ANO1 results for the total vibration rotation interaction correction ($B_e - B_0$) for each rotational constant. From the experimental A_0 , B_0 , and C_0 values, these corrections lead to $A_e = 16062.5086$ MHz, $B_e = 4319.8814$ MHz, and $C_e = 3404.2765$ MHz. The inertial defect

from these mixed experimental/computational equilibrium constants is $\Delta_i = 0.0018 \mu\text{\AA}^2$, which is sufficiently near the expected value of zero for a planar molecule.

Table 5.

Experimental and calculated vibration-rotation interaction (α_i) values for three fundamental vibrational states of *syn* formyl azide.

	ν_9 (A', 169.7 cm ⁻¹) in-plane C–N–N bend		ν_{12} (A'', 250.6 cm ⁻¹) HC(O)–N ₃ torsion		ν_{11} (A'', 582.6 cm ⁻¹) out-of-plane C–N–N bend		CCSD(T)/ANO1 $B_e - B_0$ (MHz)
	Exp.	CCSD(T)	Exp.	CCSD(T)	Exp.	CCSD(T)	
α_A (MHz) ^a	54.5277	55.07	52.2146	49.08	89.8565	85.4	70.08
α_B (MHz) ^a	6.4591	6.54	-10.2002	-9.87	-2.9510	-2.70	20.90
α_C (MHz) ^a	-0.6118	-0.61	-0.7848	-0.72	-0.7460	-0.77	21.11

^a $\alpha_B = B'' - B_0''$

Fundamental vibrational mode ν_9 is responsible for the most intense vibrational satellite of *syn* formyl azide and corresponds to the in-plane C–N–N bending mode. Free of observable coupling to other modes, the transitions of ν_9 were, like those of the ground state, effectively fit to a full octic single-state S-reduced Hamiltonian. Due to its low fundamental frequency of 169.7 cm⁻¹, two overtone satellites of this vibration were observable ($2\nu_9$, $3\nu_9$), and transitions have been assigned and fit for these states too. For the first overtone ($2\nu_9$) the data set was still extensive, and the fit was quite successful, although one of the off-diagonal octic constants (l_2) could not be determined. Unfortunately, the assigned transitions for $3\nu_9$ (509.3 cm⁻¹) could not satisfactorily be least-squares fit to a single-state model, presumably due to substantial coupling to two other nearby vibrational states (ν_8 , 489.4 cm⁻¹, and $2\nu_{12}$, 503.6 cm⁻¹). All three states have A' symmetry and are subject to various c-type Coriolis coupling interactions, while ν_8 and $2\nu_{12}$ exhibit a classic strong Fermi resonance perturbation ($k_{12,12,8} = 28.1 \text{ cm}^{-1}$, CCSD(T)/ANO1). An

incomplete, single-state, least-squares fit, including only the least perturbed transitions, was obtained for $3\nu_9$ and is presented in Table 4. In the 8th order S-reduced Hamiltonian reported in Table 4, all constants are included, but the constants L_{JK} and l_I are determined to be near zero. The physical meaning of the sextic and octic distortion constants is, however, dubious (*vide infra*).

The rotational constants of the ν_9 series are very linear from the ground state to $3\nu_9$ for changes in A ($R^2 = 0.999991$) and B ($R^2 = 0.99995$), but are less linear for the changes in C ($R^2 = 0.987$). If the linear fit is only for $\nu_9 = 0, 1, 2$, then the linearity of the changes in the C constant improves, but only slightly ($R^2 = 0.992$). Since it cannot be expected that all of the constant changes for this fundamental will be linear, quadratic fits have been applied for the rotational and quartic distortion constants for $\nu_9 = 0, 1, 2$, as shown in Figure 4a. The linearity of the changes in the A and B values and the smooth changes for the values of C indicate the reliability of the rotational constants determined for $3\nu_9$, despite the incomplete fit for that state. As shown in Figure 4b, the quartic distortion constants from $\nu_9 = 0, 1, 2$ extrapolated to $\nu_9 = 3$ do not agree with the observed values as well as the rotational constants do. The deviation from the extrapolated values for the quartic distortion terms of $3\nu_9$ are most likely due to the impact of unmodeled coupling to the other two states (ν_8 and $2\nu_{12}$), but to some extent due to the attenuated data set. While the deviations of the $3\nu_9$ experimental quartic constants compared to those predicted by extrapolation are noticeable, the deviations of the sextic constants are much more dramatic (Figure 4c and 4d). For $\nu_9 = 0, 1$, and 2, the sextic distortion constants vary slightly for most terms relative to the ground state and provide some confidence that the values of these constants have physical meaning. When the quadratic extrapolation is used to predict values of the sextic constants for $3\nu_9$, several of the predicted values bear little resemblance to those

generated by the single-state, least-squares fit. The experimental value of H_J is approximately the correctly predicted magnitude, but has the

Fig 4. Trends in the relative S-reduction rotational constants (a) and quartic distortion constants (b) for the ν_9 vibrational states. Trendlines are the quadratic fit of $\nu_9 = 0, 1, 2$. Trends in the relative sextic distortion constants (c and d).

wrong sign, compared to the extrapolation. The values of H_{JK} , H_{KJ} , and H_K all differ from the respective predictions by an order of magnitude. As each of these constants is statistically-well determined by the least-squares fitting, yet differ so dramatically from the extrapolated values, it seems clear that these sextic constants are being used by the least-squares fitting routine to account for the un-modeled coupling between $3\nu_9$ and ν_8 and $2\nu_{12}$.

The second most intense vibrational satellite is due to fundamental mode ν_{12} , which is a torsional vibration between the azide and formylium fragments of formyl azide at 250.6 cm^{-1} . With no perturbations due to coupling with near-lying vibrational states, the transitions of ν_{12} were successfully least-squares fit to nearly complete octic S-reduced centrifugal distortion Hamiltonian, where only the off-diagonal constant l_4 had to fixed to zero. Its first overtone, $2\nu_{12}$, however could not be fit to a single-state model, as it is part of the aforementioned coupled vibrational state triad: ν_8 (489.4 cm^{-1}), $2\nu_{12}$ (503.6 cm^{-1}), and $3\nu_9$ (509.3 cm^{-1}). Even the initial R-branch transitions in each $K_{prolate}$ band show substantial perturbations, making even a partial single-state fit unattainable for this overtone.

There is an observable combination state $\nu_9+\nu_{12}$ at 419.7 cm^{-1} for which transitions have been assigned and fit. The observed total vibration-rotation interaction shifts for the $\nu_9+\nu_{12}$ rotational constants are, as expected, very nearly the summation of the experimental α_i values determined for ν_9 and ν_{12} . Initially, the changes in all of the distortion constants for ν_9 and ν_{12} relative to the ground state were used as a prediction of the distortion constants of the combination state. This allowed for a very accurate *a priori* prediction and subsequent assignment of transitions for this state. A complete octic centrifugally-distorted S-reduced Hamiltonian fit of these transitions for $\nu_9+\nu_{12}$ is given in Table 4.

Unfortunately, like $2\nu_{12}$, the initial R-branch transitions of fundamental ν_8 in each band show substantial perturbations. While the α_i values for this state can be used to predict the transition frequencies, and tentative line assignments can be made, the most intense lines of each R-branch cannot be even partially fit to a single-state model. It is clear that a multi-state fit would be needed to adequately treat all three states. Nevertheless, many R-branch transitions and several Q-branches have been identified and tentatively assigned to these states. It is possible that with further careful assignment of transitions from all three states a multi-state fit including Coriolis and/or Fermi coupling terms will be feasible.

The highest-energy vibrational satellite, fundamental ν_{11} (582.6 cm^{-1}), observed in this study has been fit to a nearly full octic S-reduced Hamiltonian (Table 4), although L_{JK} is not determined in the current model. The relative low intensity of this state, less than 6% the intensity of the ground state, resulted in relatively few transitions being measured well enough to be included in the fit. Although ν_{11} has been fit to a single-state model, it is apparent that some of the unobserved or unfit transitions are coupled to the closely lying vibrational state $2\nu_9 + \nu_{12}$ (588.9 cm^{-1}). A two-state fit will probably be necessary to completely fit these two states. The 317 line data set did result in a fit with a σ of 0.040 MHz, which is the highest of any of the states (other than the highly perturbed $3\nu_9$) reported in this work, but still approaching experimental error. Very few independent *a*-type, R-branch transitions could be included in this fit, and no P-branch transitions could be included, due to their very low intensity.

Kinetics and Mechanism of Decomposition

Several molecules, other than formyl azide, feature prominently in our experimental spectra. These molecules, HN_3 (**3**), HNCO (**4**), N_2O , HCN , and CO , have consistently been observed in

our spectra from different synthetic batches of sample and different fractions within each sample. As such, we can conclude that these small molecules are present in the formyl azide sample as either contaminants of the reagents used, co-products of the formation of formyl azide, or decomposition products of formyl azide in the solution or gas phase. The Curtius rearrangement product, isocyanic acid (HNCO, **4**) was easily identifiable with transitions at about the same intensity as the most intense *syn* formyl azide ground state transitions. Its presence in the product mixture is expected and corresponds to the lowest-energy pathway (26.5 kcal/mol barrier, B3LYP/6-31G(d)) for thermal decomposition of formyl azide. Additionally, intense transitions due to HN₃ are present in all of our observed spectra of formyl azide. Unlike HNCO, its presence is more likely due to its co-production with formyl azide from a small hydrazine impurity in formyl hydrazine rather than its generation from the decomposition of formyl azide. While a decomposition of formyl azide to HN₃ is possible through **TS_{syn1-3}**, the 59 kcal/mol energy barrier precludes thermal decomposition from formyl azide. Our synthesis, following the work of Banert *et al.*[1] utilized formyl hydrazine as the starting material. As HN₃ has long been known to form by sodium nitrite oxidation of hydrazine,[33] the most likely source of HN₃ was from a trace hydrazine impurity in the formyl hydrazine or the *in situ* decomposition of formyl hydrazine during the course of the reaction. The CO and HCN detected in the spectra are known decomposition products of isocyanic acid.[34] Finally, N₂O was most likely generated by the reaction of HN₃ with nitrite during the liquid phase oxidation.

Although there was trapping evidence of the existence of oxazirine (**5**) produced in the matrix-isolated photodecomposition of formyl azide,[2] oxazirine was not detected in our spectrum. In the previous photochemical decomposition, it was postulated that the UV photons may be energetic enough to induce decomposition to oxazirine from the *anti* conformer of

formyl azide. The inability to detect oxazirine is not surprising given the above mentioned large thermal barrier (33.9 kcal/mol, B3LYP/6-31G(d)) to oxazirine from *anti* formyl azide and its endothermicity (27.7 kcal/mol relative to *syn* **1**). Furthermore, with a reverse barrier of only circa 6 kcal/mol, oxazirine would react rapidly with N₂ producing an equilibrium that heavily favors the existence of formyl azide. While we cannot exclude the presence of trace quantities of oxazirine in the sample of formyl azide, but it is not present at a sufficient quantity to be detectable.

Through an electrocyclization of *syn* formyl azide (**1**), the as of yet uncharacterized 1,2,3,4-oxatriazole (**2**) should be accessible. Oxatriazole (**2**) was not detected in our current experiment despite a favorable predicted dipole moment ($\mu = 2.9$ D, B3LYP/6-31G(d)) due to its vanishingly low population. The thermal barrier (**TS**_{syn 1-2}) to cyclization is a moderate 17.0 kcal/mol, and the cyclic structure is 14.4 kcal/mol more unstable than *syn* formyl azide despite the formation of an aromatic π -system upon cyclization. Furthermore, the barrier to ring-opening back to oxatriazole is less than 3 kcal/mol, making it impossible to observe oxatriazole even if it were generated directly. Due to the very low population of the cyclic isomer, its rapid ring-opening to *syn* **1**, and the density of the *syn* formyl azide spectrum, it is likely that a gas phase spectrum of oxatrizaole is virtually unattainable.

A simple kinetics experiment was used to monitor the intensity changes of transitions of formyl azide, CO, HN₃, HNCO, HCN, and N₂O over a three hour window that started shortly after the chamber was filled with a fresh gaseous sample of formyl azide. As shown in Figure 5a, the formyl azide signal intensity fell rapidly in our spectrometer as HCN and CO became more abundant. The apparent first-order kinetics is evident from the plot of ln(I) versus time in

Figure 5b, which is consistent with a unimolecular decomposition as the dominant decomposition pathway, and which

Fig. 5. a) Experimental intensities of key species versus time. Intensities are all adjusted to the maximum signal intensity of formyl azide. b) Plot of the natural log of intensity of *syn* formyl azide versus time fit to a linear model.

leads to a half-life of $t_{1/2} = 26.4 \pm 0.8$ min. This is approximately four times smaller than the value of the half-life previously determined by Zeng *et al.* ($t_{1/2} = 132$ min), suggesting that the decomposition mechanism may be influenced by surface effects (different materials to which the sample is exposed within the experimental apparatus) or by residual impurities in the systems. Consistent with the previous works and computational analysis, the isocyanic acid (**4**) signal intensity increases as the formyl azide decomposes and then falls as it is no longer being replenished, and is itself decomposing. The expected decomposition products of isocyanic acid

(4), CO and HCN, increase in signal strength as the isocyanic acid intensity falls. The N₂O signal intensity remains nearly unchanged during the approximately three-hour window, an observation that supports the assertion that it was generated in solution before the sample was placed into the chamber. The intensity of HCN absorptions increase independently of the N₂O absorptions, which is consistent with the lack of a decomposition pathway through oxatriazole (2).

5. Discussion

Although for the ground state and several unperturbed low lying vibrational states of the normal isotopic form of *syn* formyl azide the rotational spectra are now well understood, further progress can be envisioned in three directions: assignment of the spectrum of the *anti* formyl azide conformer, analysis by multi-state fitting of the triad ($3\nu_9$, ν_8 , and $2\nu_{12}$) and diad (ν_{11} , and $\nu_9+2\nu_{12}$), and measurement of the ground state spectra of additional isotopologues allowing for a structure determination. Further efforts towards assigning the spectrum of *anti* formyl azide and the coupled excited vibrational states would be greatly facilitated by improvements in signal intensity. The most obvious route to accomplish this goal would be to generate a sample of formyl azide with higher purity. Comparing the current observed intensities of the *syn* formyl azide transitions in our spectrometer to other molecules whose purity is well-documented, it is clear that the formyl azide spectrum could be enhanced by increasing its mole fraction in the gaseous sample. Based upon our CCSD(T)/ANO1 predicted energy difference of 2.8 kcal/mol, a factor of 120 in the intensity is lost due to the lower population of the *anti* conformer. On the other hand, the dipole moment for the *anti* conformer is larger than that of the *syn* conformer ($\mu_a = 2.1$ D versus $\mu_b = 1.5$ D) and the rotational partition function is somewhat more favorable for

the *anti* conformer. Together, these two effects produce a roughly two-fold gain in the intensity. Thus, we predict that the strongest *anti* conformer transitions will be approximately 60 times weaker than the strongest *syn* conformer transitions. Detection of the *anti* conformer will be difficult, but not impossible, especially if sample purity could be improved.

To observe the ^{13}C -isotopologue in natural abundance, improved sample purity would be clearly beneficial, but cooling the gas sample to $-80\text{ }^{\circ}\text{C}$ would also be helpful, enhancing the ground state population and signal intensity and decreasing the spectral clutter of highly excited vibrational states. Even so, enriched samples would very likely be required for all other singly-substituted isotopologues.

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