The 130–370 GHz rotational spectrum of phenyl isocyanide ($\text{C}_6\text{H}_5\text{NC}$)

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ABSTRACT

The analysis of phenyl isocyanide ($\text{C}_6\text{H}_5\text{NC}$, $\mu_a = 4.0$ D) in its ground vibrational state and two lowest-energy excited vibrational states, ν_{22} (141 cm^{-1}) and ν_{33} (155 cm^{-1}), in the 130–370 GHz frequency region has been completed. Over 4500 new rotational transitions have been measured in the ground vibrational state for the most abundant isotopologue, resulting in the determination of the spectroscopic constants for a partial octic Hamiltonian with low error. The Coriolis-coupled ν_{22} – ν_{33} dyad reported herein, containing over 3500 new transitions for each vibrational state, has been analyzed for the first time. The coupled-state least-squares fit utilizes seven coupling terms (G_a , G_a^I , G_a^K , G_a^J , G_a^{JK} , F_{bc} , and F_{bc}^K) to address perturbation between the two vibrational states, including resonances and several nominal interstate transitions. This work results in precise determination of the energy separation between the two states, $\Delta E_{22,33} = 9.682\,248(3)\text{ cm}^{-1}$, and the Coriolis coupling coefficient, $|\zeta_{22,33}^a| = 0.858(9)$. The precise rotational and distortion constants determined in this work provide the foundation for an astronomical search for phenyl isocyanide across the radio band.

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INTRODUCTION

The recent detection of benzonitrile ($\text{C}_6\text{H}_5\text{CN}$)¹ in Taurus Molecular Cloud 1 (TMC-1)²—the first detection of a simple derivative of benzene in the interstellar medium (ISM) by radioastronomy—invites consideration of the isomeric molecule, phenyl isocyanide ($\text{C}_6\text{H}_5\text{NC}$). In the current study, we describe a detailed analysis of the rotational spectrum of phenyl isocyanide in its ground vibrational state and two lowest-energy excited vibrational states, ν_{22} (141 cm^{-1}) and ν_{33} (155 cm^{-1}), in the 130–375 GHz frequency region. Phenyl isocyanide ($\text{C}_6\text{H}_5\text{NC}$, Fig. 1) is a planar, prolate ($\kappa = -0.832$),³ asymmetric top rotor with its dipole moment along the a -inertial axis ($\mu_a = 4.0$ D),⁴ resulting in a spectrum dominated by ^aR -type absorptions. Its infrared,⁵ Raman,⁵ and 12–40 GHz microwave³ spectra have been studied, the latter leading to a microwave substitution structure based upon measurement of four isotopologues ($\text{C}_6\text{H}_5\text{NC}$, 2- $[\text{2H}]$ - $\text{C}_6\text{H}_5\text{NC}$, 2,4- $[\text{2H}]$ - $\text{C}_6\text{H}_5\text{NC}$, 2,4,6- $[\text{2H}]$ - $\text{C}_6\text{H}_5\text{NC}$). Kasten *et al.* later analyzed the ^{14}N nuclear quadrupole hyperfine splitting using transitions in the 5–8 GHz frequency range.⁴ No previous studies, however, examined the rotational spectrum of phenyl isocyanide at frequencies

higher than 40 GHz. The precise determination of its rotational and distortion constants using an extended frequency range provides the information necessary for an astronomical search for phenyl isocyanide in the ISM by radioastronomy. Its identification and measurement of abundance relative to its nitrile counterpart could help inform our understanding of interstellar chemistry.

Detecting aromatic molecules in the ISM by radioastronomy and understanding the role of aromatic compounds in interstellar chemistry are goals of longstanding interest in astrochemistry.^{6–8} The small, 2π -electron aromatic compounds cyclopropenylidene^{9,10} and cyclopropenone¹¹ have been detected by radioastronomy, and larger aromatic compounds (benzene, C_{60} , C_{70}) have been detected by infrared spectroscopy.^{12,13} Benzonitrile has long been an alluring target for radioastronomers due to its strong dipole moment ($\mu_a = 4.5$ D)¹⁴ and the fact that many nitriles have been detected in the ISM.¹⁵ It has been suggested as a tracer molecule for benzene in the ISM and, as previously mentioned, was recently detected by radioastronomy¹ in TMC-1.²

Several nitriles and their corresponding isocyanides have been observed in the ISM: the SiCN and SiNC radicals,^{16,17} the MgCN and MgNC radicals,^{18–20} cyanogen (inferred from the observation

FIG. 1. Phenyl isocyanide structure with principal rotation axes.

of its protonated form)²¹ and isocyanogen,²² cyanoacetylene and isocyanoacetylene,^{23–27} hydrogen cyanide and hydrogen isocyanide,^{27–31} their deuterated counterparts,³² and methyl cyanide and methyl isocyanide.^{33–35} In some cases where both isomers are detected, their relative abundances have been estimated. Cernicharo *et al.* detected CH₃NC toward Sagittarius B2 (Sgr B2) and approximated its abundance relative to CH₃CN to be 0.05:1.³³ Remijan *et al.* later estimated this ratio to be 0.02:1 and suggested that the isocyanide is formed by nonthermal processes.³⁴ Gratier *et al.* approximated the two species to be in a 0.15:1 ratio in the photodissociation region of the Horsehead mane.³⁵ In general, an organic isocyanide (R–N≡C) is ~21 kcal/mol higher in energy than the corresponding nitrile (R–C≡N), and this energy difference is remarkably insensitive to the nature of the substituent (R).³⁶ Hudson and Moore conducted proton bombardment and UV photolysis experiments on ices containing nitriles and demonstrated that both treatments, in the absence of water, resulted in the generation of the corresponding isocyanides.³⁷ It is plausible that phenyl isocyanide may be detectable in the interstellar medium, particularly in regions whose chemistry is governed by pulse shocks, irradiation, or other nonthermal processes.

In the current study, we collected the rotational spectrum of phenyl isocyanide in the 130–370 GHz frequency region. The ground vibrational state was fit to a single-state distorted rotor model using over 4500 transitions. The two lowest-energy excited vibrational states, ν_{22} (141 cm⁻¹, B₁ symmetry) and ν_{33} (155 cm⁻¹, B₂ symmetry), are reported for the first time. They exhibit strong Coriolis coupling and are least-squares fit to a two-state model. This model addresses resonances and allows the measurement of several nominal interstate transitions, resulting in a highly precise determination of their energy separation. An unperturbed ground vibrational state separated by approximately 150 cm⁻¹ from a dyad of low-lying, coupled vibrational states is observed for similar molecules, e.g., phenylacetylene³⁸ and benzonitrile.³⁹

EXPERIMENTAL METHODS

A sample of phenyl isocyanide was prepared as described later. Spectra were collected on a broadband spectrometer using 5–10 mTorr sample pressure at room temperature. The 250–370 GHz spectrum was collected using the instrument described previously.^{39–41} The 130–230 GHz frequency spectrum was collected on the same apparatus using a Virginia Diodes amplification and multiplication chain (WR5.1AMC 140–220 GHz) and

a Virginia Diodes zero-bias detector (WR5.1ZBD 140–220 GHz). The spectra were combined into a single broadband spectrum using Assignment and Analysis of Broadband Spectra (AABS) software.^{42,43} Pickett's SPFIT/SPCAT programs were used to conduct least-squares fitting and spectral prediction, respectively.⁴⁴ PIFORM, PMIXC, PLANM, and AC programs were used for data analysis, to reformat output files, and to generate various plots.⁴⁵

In our least-squares fits, we assume a uniform frequency measurement uncertainty of 50 kHz for our own data, as well as for the data reported by Kasten *et al.*⁴ (Uncertainties were not provided in the original publication.)

Computational Methods

All computations were performed at the B3LYP/6-311+G(2d,p) level of theory using Gaussian 16.⁴⁶ An optimized geometry for phenyl isocyanide was obtained using very tight convergence criteria and an ultrafine integration grid. Anharmonic vibrational frequency calculations provided the fundamental vibrations and the vibration-rotation interaction constants (α_i). For comparison to the observable rotational constants, A_0 , B_0 , and C_0 , the A_e , B_e , and C_e equilibrium rotational constants obtained from the B3LYP calculation were corrected by one half the sum of the computed vibration-rotation interaction constants. Optimized geometry and anharmonic vibrational frequency calculations for benzonitrile, using the same criteria and level of theory, were obtained for comparison. Computational output files are provided in the [supplementary material](#). Tables of the vibration-rotation interaction constants for the two isomers are also provided in the [supplementary material](#).

Synthesis

Phenyl isocyanide was prepared using a procedure adapted from the work of Leifert *et al.*⁴⁷ (Scheme 1). In a 1-L round-bottom flask under nitrogen and cooled in an ice/acetone bath (–10 °C), 15 g formanilide (124 mmol, 1 equivalent) was dissolved in 200 ml tetrahydrofuran (THF). To the solution was added 103.6 ml triethylamine (743 mmol, 6 equivalents). Subsequently, 17.3 ml phosphoryl trichloride (POCl₃; 185 mmol, 1.5 equivalents) was added dropwise to avoid vigorous reaction. The solution changed from clear, light yellow to orange and opaque to dark brown over the course of the addition. The acetone/ice-cooled reaction was stirred for 2 h. A 10% aqueous solution of Na₂CO₃ was added slowly with stirring (200 ml). The mixture was then warmed to room temperature and allowed to stir for 1 h. The organic layer was separated, and the aqueous layer was extracted with dichloromethane. The combined organic layers were dried over MgSO₄, filtered, and concentrated by rotary evaporation. Phenyl isocyanide (bp 52–53 °C at 12 Torr)⁴⁸ was purified by vacuum distillation (~50 °C) and collected

SCHEME 1. Preparation of phenyl isocyanide (C₆H₅NC).

in a receiving flask cooled with a dry-ice/acetone bath. The ^1H and ^{13}C -NMR spectra appeared as expected based on literature data^{49,50} and are provided in the [supplementary material](#), along with a mass spectrum.

As is characteristic of many isocyanides,⁵¹ phenyl isocyanide has a very strong, repulsive, pungent odor and should be treated with caution. All materials that came in contact with phenyl isocyanide were promptly and thoroughly rinsed with 5% sulfuric acid in methanol to remove the stench and then washed.

ANALYSIS OF ROTATIONAL SPECTRA

Ground state

The phenyl isocyanide spectrum, like that of its nitrile isomer, exhibits numerous vibrational states in the 130–370 GHz region, resulting in a high spectral line density. A portion of the experimental spectrum in the 166 220–167 200 MHz region is provided in Fig. 2, which highlights the ground vibrational state and its two lowest-lying fundamentals, ν_{22} and ν_{33} . The phenyl isocyanide spectrum is predominantly composed of $^a\text{R}_{0,1}$ bands (separated by approximately 2500 MHz, $\sim 2C$); no P- or Q-branch transitions were observed in this work due to their very low intensity in the frequency range examined. The $^a\text{R}_{0,1}$ sub-bands begin with $K_a = 0$ at low frequency and spread out to higher frequency with increasing K_a and concurrently decreasing J . In the observed region, the lead line is composed of two degenerate transitions that have equal values of K_c . As a result, the two degenerate transitions have quantum

numbers $K_a + K_c = J$ and $K_a + K_c = J + 1$, referred to below using a + or – superscript on the value of K_a , respectively, for brevity. With increasing K_a , the transitions lose degeneracy after which point the band undergoes a turnaround. At even greater values of K_a , pairs of + and – symmetry lines become degenerate with equal values of K_a . Many of these K_a -degenerate $^a\text{R}_{0,1}$ transitions are observable in the lower frequency range, 130–220 GHz. The higher frequency bands become more compact, and the loss of degeneracy and turnaround occur at higher K_a . The loss of degeneracy occurs at $J'' + 1 = 59$ in the ground state band depicted in Fig. 2. The turnaround for this band occurs after $K_a = 10$ ($J'' + 1 = 55$).

The vibrational ground state of phenyl isocyanide has been least-squares fit to a single-state distorted rotor model including ^{14}N hyperfine-resolved transitions from the work of Kasten *et al.*⁴ The transitions of Bak *et al.*³ were not available and thus not included in this work. We have measured over 4500 new lines; J'' ranges from 42 to 144 and K_a ranges from 0 to 66. The resulting spectroscopic constants (A -reduction, I^r representation)⁵² are presented in Table I, along with those of Bak *et al.*³ and Kasten *et al.*,⁴ those predicted by an anharmonic frequency calculation at the B3LYP/6-311+G(2d,p) level of theory, and the spectroscopic constants of benzonitrile³⁹ for comparison. A data distribution plot of the ground vibrational state is presented in Fig. 3, which shows the scope of data collected. In such a plot, the size of the circle corresponds to the magnitude of the error for the line measurement. The plot in Fig. 3 shows that there are lines with somewhat high error scattered throughout the data set, suggesting that there may be underlying features or other nonsystematic error in the spectrum collected. The

FIG. 2. Phenyl isocyanide rotational spectrum from 166 220 MHz to 167 200 MHz (bottom) and stick spectra of the ground vibrational state, ν_{22} , and ν_{33} transitions (top). The upper state J (i.e., $J'' + 1$) values are marked for ground state lines (blue), whereas all three upper rotational state quantum numbers are marked for ν_{22} (gold) and ν_{33} (green). Many transitions belonging to other vibrational satellites are also visible in the spectrum.

TABLE I. Experimental and computational spectroscopic constants for the ground vibrational state of phenyl isocyanide (C_6H_5NC) and experimental spectroscopic constants for the ground vibrational state of benzonitrile (C_6H_5CN).

	Bak <i>et al.</i> ³ and Kasten <i>et al.</i> ^{4,a,b}	Current work ^c	B3LYP ^d	Benzonitrile ³⁹
A_0 (MHz)	5659.5190(56)	5659.337 4(13)	5658.4	5655.265 371(75)
B_0 (MHz)	1639.7757(12)	1639.771 667(59)	1635.8	1546.875 780 4(76)
C_0 (MHz)	1271.1538(12)	1271.154 548(49)	1268.7	1214.404 077 2(67)
Δ_J (kHz)	0.0473(27)	0.049 448 9(40)	0.047 2	0.045 265 3(27)
Δ_{JK} (kHz)	0.853(12)	0.912 873(36)	0.878	0.937 906(27)
Δ_K (kHz)		0.260 5(17)	0.265	0.242 34(77)
δ_J (kHz)	0.0187(14)	0.012 465 0(22)	0.011 8	0.011 015 89(73)
δ_K (kHz)		0.601 34(13)	0.572	0.609 088(74)
Φ_J (Hz)		0.000 002 62(17)	0.000 002 52	0.000 000 51(22)
Φ_{JK} (Hz)		0.001 813 4(85)	0.001 67	0.001 543 5(46)
Φ_{KJ} (Hz)		−0.009 494(31)	−0.008 68	−0.007 849(17)
Φ_K (Hz)		[0.007 55]	0.007 56	[0]
ϕ_J (Hz)		0.000 001 206(86)	0.000 001 18	0.000 001 412(38)
ϕ_{JK} (Hz)		0.000 855 5(58)	0.000 842	0.000 743 1(30)
ϕ_K (Hz)		0.006 51(13)	0.006 41	0.007 106(76)
L_J (μHz)		[0.]		0.000 058 5(56)
L_{JK} (μHz)		−0.003 943(94)		−0.002 085(52)
L_{JK} (μHz)		[0.]		
L_{KKJ} (μHz)		−0.032 7(35)		−0.042 8(18)
L_K (μHz)		6.38(15)		4.468(90)
Δ_i (uÅ ²) ^e		0.073 921(28)	0.079 96 ^f	0.080 084(3)
N^g		4723		4073
σ_{fit} (MHz)	0.004	0.034		0.025

^aKasten *et al.*⁴ included the rotational constants of Bak *et al.*³^bDistortion constants reported as T_4 and T_5 converted to A -reduction distortion constants.^cGlobal fit to the present millimeter-wave measurements and the available literature data.⁴^dEvaluated with the 6-311+G(2d,p) basis set and with constants converted to a right-handed coordinate system by reversing the signs of all off-diagonal (lowercase) distortion constants.^eInertial defect, $\Delta_i = I_c - I_a - I_b$.^fCalculated from the B_0 constants using the PLANM program.^gNumber of fitted transition frequencies.

fact that a large proportion of such lines occurs at high K_a and J'' may suggest an unaddressed systematic issue, although attempts to incorporate additional spectroscopic constants into the least-squares fit were unsuccessful in improving the error.

Despite a lack of Q-branch transitions, the very large data set enabled us to determine several purely K -dependent terms: Δ_K , δ_K , ϕ_K , and L_K . The precision of all of the determined constants except A_0 have been improved by at least two orders of magnitude compared to those previously determined.³ The older constants are reasonably confirmed by those determined in the current work. The previously determined values of A_0 , Δ_{JK} , and δ_{JK} , however, do differ from the more precisely determined constants by somewhat more than their quoted error limits. We have newly determined Δ_K , all of the sextic centrifugal distortion constants except Φ_K and three of the on-diagonal octic centrifugal distortion terms (L_{JK} , L_{KKJ} , and L_K). Unlike in the case of benzonitrile,⁵³ however, we were unable

to improve upon the precision of the quadrupole coupling constants for phenyl isocyanide. The experimentally determined constants are also in excellent agreement with those predicted by the anharmonic calculation at the B3LYP/6-311+G(2d,p) level of theory. The relative errors of the B3LYP predictions are 0.02% for A_0 , 0.2% for B_0 , and 0.2% for C_0 . We were unable to determine Φ_K , which we fixed to the B3LYP-predicted value, but the quartic and other sextic centrifugal distortion constants reported in this work show remarkable agreement (to within 10%) with those predicted computationally.

In comparing benzonitrile and phenyl isocyanide, the A_0 rotational constants are quite similar. That of phenyl isocyanide is approximately 4 MHz greater than that of benzonitrile. Interestingly, the values of one half the sum of the vibration-rotation interaction constants for the two isomers are nearly equal (41.856 MHz for phenyl isocyanide and 41.992 MHz for benzonitrile). Since this

FIG. 3. Data distribution plot for the least-squares fit of spectroscopic data from the current work (black circles) and measurements from the work of Kasten *et al.*⁴ (blue circles) for the vibrational ground state of phenyl isocyanide. The size of the plotted symbol is proportional to the value of $|(f_{\text{obs.}} - f_{\text{calc.}})/\delta f|$, where δf is the frequency measurement uncertainty (50 kHz), and all values shown are smaller than 3.

value is expected to be accurate from these B3LYP computational predictions,^{54,55} the observed difference between the A_0 rotational constants appears to be indicative of a slight contraction of the phenyl isocyanide aromatic ring toward the a principal axis relative to that of benzonitrile (corresponding to <0.0004 Å in the b coordinate of each off- a -axis C atom). The B_0 and C_0 rotational constants, on the other hand, are markedly different between the two isomers (~ 93 MHz and ~ 57 MHz, respectively, greater for phenyl isocyanide than for benzonitrile). The difference arises because the C and N atoms whose positions differ are located off-axis relative to the b and c axes. The quartic centrifugal distortion constants are also highly similar; all those of phenyl isocyanide (except δ_J) are within 10% of those for benzonitrile. The purely K -dependent terms are most similar, whereas the purely J -dependent terms are most different. For both isomers, Φ_K was the only undetermined sextic centrifugal distortion constant. Of those that were determined, the Φ_J terms differ by an order of magnitude, while the other sextic constants are within 20% of one another. The three octic centrifugal distortion terms that were determined for both molecules are within 50% of one another. Altogether, the close agreement between the distortion constants supports the idea that the values are physically meaningful for both isomers.

The lowest-energy vibrational states ν_{22} and ν_{33}

Phenyl isocyanide exhibits a Coriolis-coupled dyad of low-lying excited vibrational states, similar to the vibrational manifold of

benzonitrile. The lower energy fundamental, ν_{22} (141 cm^{-1} , B_1 symmetry), is the out-of-plane bend of the isocyanide group ($\text{R}-\text{N}\equiv\text{C}$) relative to the aromatic ring and ν_{33} (155 cm^{-1} , B_2 symmetry) is the bend of the isocyanide in the plane of the ring. The vibrational energy levels are depicted in Fig. 4. A tetrad of states lies approximately 300 cm^{-1} above the ground vibrational state. The tetrad includes the first overtone and combination states of ν_{22} and ν_{33} , as well as the fundamental state ν_{21} . Higher in energy still, between 400 and 500 cm^{-1} above the ground vibrational state, lies a complex polyad of overtone, combination, and additional fundamental states. A table of all fundamental modes, their symmetries, harmonic frequencies, anharmonic frequencies, and corresponding infrared intensities at the B3LYP/6-311+G(2d,p) level of theory is provided in the [supplementary material](#).

Like the ground vibrational state, bands of “R transitions dominate the millimeter-wave spectra of the vibrational states. In our spectral region, both of the lowest-energy vibrational states follow the same degeneracy pattern as the ground state, where lines with low K_a^+ are degenerate with the K_a^- transition with the same value of K_c . They lose this degeneracy with increasing K_a and eventually become degenerate K_a^+ , K_a^- pairs with matching values of K_a . In ν_{22} , bands initially progress toward lower frequency moving away from the lead transition. The band undergoes two turnarounds and eventually progresses to lower frequency with increasing K_a and concurrently decreasing J'' . In the band depicted in Fig. 2, the first turnaround occurs after $J'' + 1 = 60$ and the initial loss of degeneracy occurs at $J'' + 1 = 59$.

In the lower-frequency portion of our spectral region, ν_{33} behaves like the ground state. Moving away from the bandhead, transitions within a band proceed toward higher frequency and then turn around and progress to lower frequency. This is the case for the band depicted in Fig. 2, although the loss of degeneracy

FIG. 4. The vibrational energy levels of phenyl isocyanide below 500 cm^{-1} , drawn from fundamental frequency values of the B3LYP/6-311+G(2d,p) calculation. The $\nu_{33} - \nu_{22}$ energy difference results from the perturbation analysis of the present work.

($J'' + 1 = 60$) and turnaround (after $J'' + 1 = 56$) occur at higher frequency than shown in the figure. At high frequencies, ν_{33} behaves similarly to ν_{22} , beginning to progress away from the band-head toward lower frequency, proceeding through two turnarounds, and eventually progressing to lower frequency. As the values of C_v for both of these vibrational states are about 2 MHz greater than those of C_0 , their bands are spaced only slightly more distantly than those of the ground state, with those of ν_{22} growing more distant from the ground state than those of ν_{33} with increasing J . Because the effective inertial defects of the fundamentals, ν_{22} and ν_{33} [$\Delta_i = -0.223\,933(25)$ and $0.378\,085(15)$, respectively], are substantially larger in magnitude than that of ground vibrational state [$\Delta_i = 0.073\,921(28)$], the transitions of the vibrational states spread out much more dramatically than those of the ground state.

Our initial approach to the assignment of ν_{22} and ν_{33} of phenyl isocyanide was the same as the one we employed to assign the analogous dyad of benzonitrile. Namely, we used as initial values the experimentally determined ground-state distortion constants. The initial values of the rotational constants were estimated by applying the B3LYP-predicted vibration-rotation interaction constants (α_i values) to the experimentally determined ground-state rotational constants. We found, however, that it was remarkably more challenging to obtain an initial fit of the low K_a series as a result of the broad spacing of proximal K_a series of phenyl isocyanide. Single-state models were only able to predict the $K_a = 0, 1$ series, so a coupled-state model was immediately implemented. The initial value of the energy separation of the coupled states (ν_{22} and ν_{33}), ΔE , was taken from the B3LYP anharmonic frequency calculation. As in the case of benzonitrile, phenyl isocyanide is of C_{2v} symmetry; ν_{22}

TABLE II. Experimentally determined parameters for ν_{22} and ν_{33} excited vibrational states of phenyl isocyanide (C_6H_5NC) compared to those for the ground state of phenyl isocyanide and the analogous excited states for benzonitrile (C_6H_5CN).

	Phenyl isocyanide ground state	Phenyl isocyanide ν_{22} (B_1 , 141 cm^{-1})	Phenyl isocyanide ν_{33} (B_2 , 155 cm^{-1})	Benzonitrile ³⁹ ν_{22} (B_1 , 141 cm^{-1})	Benzonitrile ³⁹ ν_{33} (B_2 , 163 cm^{-1})
A_v (MHz)	5659.337 4(13)	5 656.854 9(13)	[5 659.337 375 299]	5 654.5(20)	5 654.8(20)
B_v (MHz)	1639.771 667(59)	1 641.718 557(35)	1 643.302 423(35)	1 548.621 160(52)	1 549.725 942(47)
C_v (MHz)	1271.154 548(49)	1 273.153 282(41)	1 272.300 426(43)	1 216.238 170(44)	1 215.222 889(52)
Δ_J (kHz)	0.0494 489(40)	0.0502 869(36)	0.050 738 4(40)	0.045 995 0(27)	0.046 171 5(27)
Δ_{JK} (kHz)	0.912 873(36)	0.917 85(29)	0.867 29(29)	0.947 08(40)	0.907 14(40)
Δ_K (kHz)	0.260 5(17)	[0.260 5] ^a	[0.2605] ^a	[0.242 3] ^a	[0.242 3] ^a
δ_J (kHz)	0.012 465 0(22)	0.012 546 04(62)	0.012 953 94(58)	0.011 083 69(59)	0.011 367 62(49)
δ_K (kHz)	0.601 34(13)	0.594 57(11)	0.598 38(13)	0.607 315(93)	0.612 108(91)
Φ_J (Hz)	0.000 002 62(17)	0.000 002 82(12)	0.000 002 80(14)	0.000 001 166(86)	0.000 000 675(89)
Φ_{JK} (Hz)	0.001 813 4(85)	0.001 781 9(89)	0.001 715 0(89)	0.001 391 7(22)	0.001 654 5(22)
Φ_{KJ} (Hz)	−0.009 494(31)	−0.009 83(17)	−0.008 20(17)	−0.006 19(12)	−0.009 07(12)
ϕ_{JK} (Hz)	0.000 855 5(58)	0.000 778 4(51)	0.000 761 7(58)	0.000 749 3(41)	0.000 672 7(42)
ΔE (MHz)		290 266.50(10) ^b		572 848.96(20) ^b	
ΔE (cm^{-1})		9.682 248(3)		19.108 185(7)	
G_a (MHz)		9 718.593(13)		9 532.0(62)	
G_a^J (MHz)		−0.005 836 3(44)		−0.004 588(27)	
G_a^K (MHz)		−0.002 111 9(97)			
G_a^{JJ} (Hz)		0.008 58(12)			
G_a^{JK} (Hz)		−0.076 0(27)			
F_{bc} (MHz)		−0.480 985(59)		−0.411(39)	
F_{bc}^K (kHz)		−0.015 20(20)		−0.009 81(44)	
Δ_i (uA^2)	0.073 921(28)	−0.223 933(25)	0.378 085(15)	−0.191(32)	0.393(32)
N^c	4 723	3 727	3 627	3 001	2 933
σ (MHz) ^d	0.034	0.040	0.040	0.034	0.037

^a Δ_K , along with all sextic and octic centrifugal distortion constants not listed explicitly, were fixed at the ground state values of the corresponding molecule from Table I.

^b ΔE , G_a , G_a^J , G_a^K , G_a^{JJ} , G_a^{JK} , F_{bc} , and F_{bc}^K parameters are for coupling between the ν_{22} and ν_{33} vibrational states of the corresponding molecule.

^c Number of fitted transition frequencies.

^d Deviations for the two vibrational state subsets: the overall standard deviation of the coupled fit for phenyl isocyanide to 7354 lines is 0.040 MHz and for benzonitrile to 5934 lines is 0.036 MHz.

and ν_{33} belong to B_1 and B_2 irreducible representations, respectively. This situation precludes Fermi coupling but allows Coriolis coupling along the inertial axis whose angular momentum component transforms like the cross product of the irreducible representations of the vibrational states: $B_1 \otimes B_2 = A_2$. The A_2 irreducible representation corresponds to the P_a angular momentum operator so that the appropriate lead spectroscopic constant to represent the Coriolis coupling is G_a . This term was estimated using the Coriolis coupling constant, $\zeta_{22,33}^a$, predicted by the B3LYP calculation. This constant and the spectroscopic constant are directly related by the following equation:

$$G_a = \frac{\omega_{22} + \omega_{33}}{\sqrt{\omega_{22} \times \omega_{33}}} \zeta_{22,33}^a A, \quad (1)$$

where ω_{22} and ω_{33} are the harmonic vibrational frequencies for the normal modes and the ground state rotational constant, A_0 , is used for A .⁵⁶

Although assignments were made more challenging by the highly spread transitions of the vibrational states, the series were eventually identified and assigned based on the observation of near-continuous series in Loomis-Wood plots generated by the AABS software.⁴³ These K_a series were missing several transitions in the Loomis-Wood plot such that the “gap” moved to higher values of J'' in subsequent series, a tell-tale pattern of yet-to-be addressed resonances, similar to those observed previously in benzonitrile. After the initial identification of several K_a series, the data set was built up by including lines with increasing values of K_a in the region below 230 GHz, as for the benzonitrile dyad. Initially, only a single rotational constant, C_v , and the energy separation of the two vibrational states, ΔE , were allowed to vary; additional constants were allowed

to be fit with increasing data. The constants were monitored and only allowed to be fit if they remained close to (of the same sign and order of magnitude and not clearly diverging from) the corresponding ground-state value. In the end, the coupling terms G_a , G_a^I , G_a^K , G_a^{JK} , F_{bc} , and F_{bc}^K (in a previously described expansion of the coupling Hamiltonian),⁵⁷ along with ΔE , were necessary to fit the measured transitions, including resonances and nominal inter-state transitions (see below), to within experimental accuracy. The spectroscopic constants determined through this coupled-state analysis are provided in Table II. Data distribution plots for ν_{22} and ν_{33} are provided in Fig. 5 and demonstrate that lines with high error are scattered throughout the data set, quite like the appearance of the ground vibrational state data distribution plot, suggesting that a fair amount of error in the least-squares fit is due to underlying features. As with the ground vibrational state, there appear to be more high-error measurements along an upward right diagonal. Despite efforts to include additional distortion or coupling terms in the least-squares fit, however, we were unable to eliminate this pattern. The similarity with the ground vibrational state, however, suggests that the same issue may be responsible for the observed pattern in both ground and excited vibrational states.

The ν_{22} and ν_{33} vibrational states are reported here for the first time; each state contains over 3500 independent measurements. The data sets consist entirely of $^aR_{0,1}$ transitions with J'' ranging from 42 to 144 and K_a ranging from 0 to 48. While lines with higher values of K_a appeared to be visible, the intensities become low and transitions frequently overlap with others, introducing additional unnecessary error into the fit. Thus, these higher K_a series were excluded from the data set for least-squares fitting.

FIG. 5. Data distribution plots of values of $|(f_{\text{obs.}} - f_{\text{calc.}})/\delta f|$ for the coupled fit of measured transitions in the two lowest-energy excited vibrational states in phenyl isocyanide. Transitions with values of $|(f_{\text{obs.}} - f_{\text{calc.}})/\delta f| > 3$ are plotted in red. The similarity between the data distribution plots for ground and excited vibrational states suggests that any remaining issues apply to both the single-state and two-state least-squares fits.

In the final two-state least-squares fit of the dyad, we were unable to determine A_v for ν_{33} . All of the fitted rotational constants are within 0.3% of the corresponding ground state constant. As in the case of benzonitrile, we were unable to determine ΔK for either vibrational state due to the availability of only $R_{0,1}$ transitions. The other quartic distortion constants, however, are well determined and within 5% of those of the ground state, indicating that they are likely free of perturbation due to untreated coupling. The three sextic distortion constants that have been determined are within 11% of those of the ground state.

The inability to determine A_v for ν_{33} is somewhat perplexing and disappointing, as we were able to determine both values of A_v for the corresponding benzonitrile dyad. The values of A_{22} are approximately 2.4 MHz apart, slightly less than the difference in the A_0 values. The differences between the isomers' rotational constants for ν_{22} and ν_{33} are otherwise nearly the same as the differences between the ground states. This indicates that the isomers have very similar a_i values. The distortion constants that have been determined are also similar between phenyl isocyanide and benzonitrile. Of the quartic centrifugal distortion constants that were determined, the purely J -dependent terms are most dissimilar ($\sim 12\%$ difference) and values of the purely K -dependent term (δ_K) are most similar, in accordance with the pattern observed for the ground vibrational states of the isomers. The pattern of similarity between the sextic constants, however, is not quite as consistent between the vibrational states, possibly indicating an unresolved issue in the two-state fit of phenyl isocyanide.

The experimental energy separation determined between ν_{22} and ν_{33} [$\Delta E_{22,33} = 9.682\,248(3)\text{ cm}^{-1}$] is somewhat smaller than the energy difference predicted using either the B3LYP-predicted harmonic vibrational frequencies ($\Delta E_{22,33} = \sim 13.2\text{ cm}^{-1}$) or the B3LYP-predicted fundamental vibrational frequencies ($\Delta E_{22,33} = \sim 14.1\text{ cm}^{-1}$). The spectroscopically determined Coriolis coupling coefficient ($\zeta_{22,33}^a = 0.858(9)$), however, is very close (within 0.3%) to the corresponding value predicted by the vibrational frequency calculation at the B3LYP/6-311+G(2d,p) level of theory ($|\zeta_{22,33}^a| = 0.8556$).

Interpretation and analysis of the resonances

Once transitions furthest removed from the resonances had been assigned and fit, it became possible to assign lines closer and closer to the major resonances. By iteratively adding lines closer to the center of the resonance, refitting, and re-predicting, we were able to assign numerous resonances for this dyad. The resonances predominantly follow a $\Delta K_a = 2$ and 4 ($\Delta K_c = 3$) selection rule, as in benzonitrile. The resonance plots of a pair of corresponding resonances with $\Delta K_a = 2$ are provided in Fig. 6, showing the mirror image pattern that confirms their assignment. The magnitude of the resonances (the displacement of the furthest point on the resonance from its predicted frequency in the absence of local perturbation) can be gauged using the y -axis of the resonance plots [$(\nu - \nu_0)/(J'' + 1)$]. The largest resonances between ν_{22} and ν_{33} of phenyl isocyanide are notably larger than those of benzonitrile. A set of $\Delta K_a = 2$ resonances for each molecule is provided in Fig. 7. The axes are set to the same scale so that it is easy to compare the magnitude of the resonances. The resonances provided for benzonitrile in this figure are two of the largest in magnitude that we observed in the

FIG. 6. Resonance plots for phenyl isocyanide showing the $K_a = 9^+$ series for ν_{22} and $K_a = 7^-$ series for ν_{33} , an example of resonances conforming to the $\Delta K_a = 2$ selection rule. The plotted values are frequency differences between excited state transitions and their ground state counterparts, scaled by $(J'' + 1)$ in order to make the plots more horizontal. Measured transitions are represented by circles: ν_{22} (copper) and ν_{33} (green). There are no measured transitions with $|f_{\text{obs.}} - f_{\text{calc.}}|/\delta f > 3$. Predictions from the final coupled fit are represented by a solid, black line. The two resonances are mirror images of one another, confirming the K_a assignment of these resonance partners.

103–360 GHz spectral region, while those displayed for phenyl isocyanide are of medium magnitude relative to its largest resonances. It is evident from the y -axis in Fig. 7 that the most displaced point of the phenyl isocyanide resonance (at $J'' + 1 = 62$) appears approximately 19 units from its expected position absent local perturbation, which translates to $\sim 1200\text{ MHz}$ ($\nu - \nu_0$). The largest resonances of phenyl isocyanide appear up to $\sim 9400\text{ MHz}$ ($\nu - \nu_0$) away from where they would be expected based on the frequencies of other transitions in the corresponding K_a series. By comparison, the largest resonances we observed for benzonitrile between the analogous dyad of states were displaced from the expected frequency by less than 600 MHz ($\nu - \nu_0$). This trend of larger resonances in the dyad of phenyl isocyanide is

FIG. 7. Resonance plots showing $K_a = 8^+$ for ν_{22} and $K_a = 6^-$ for ν_{33} of phenyl isocyanide (left) and $K_a = 16^+$ for ν_{22} and $K_a = 14^-$ for ν_{33} of benzonitrile (right). The plotted values are frequency differences between excited state transitions and their ground state counterparts, scaled by $(J'' + 1)$ in order to make the plots more horizontal. Measured transitions are represented by circles: ν_{22} of phenyl isocyanide (copper), ν_{33} of phenyl isocyanide (green), ν_{22} of benzonitrile (blue), and ν_{33} of benzonitrile (purple). Measured transitions with $|f_{\text{obs}} - f_{\text{calc}}|/\delta f > 3$ are marked with red triangles. Predictions from the final coupled fit are represented by a solid, black line. The x- and y-axes are set to the same scale for each of the resonance plots.

illustrated globally in Fig. 8, which shows a set of superimposed resonance plots for K_a^+ series (even values of K_a between 2 and 30 are included for clarity); Fig. 8(a) is phenyl isocyanide and Fig. 8(b) is the corresponding set of resonance plots for benzonitrile. Whereas the reference state in Figs. 6 and 7 is the ground vibrational state, the reference state in Fig. 8 is a deperturbed prediction using the final coupled-state fit rotational and distortion constants, but with the perturbation parameters set to zero. These resonance plots thus show purely the effect of perturbation and not any effects due to differences between rotational and distortion constants between the vibrational and ground states. These resonance

plots do look highly similar to those using the ground state as a reference, validating such ground state-referenced plots. The resonance plots in Fig. 8 show two obvious features: the resonances already discussed and the broader undulation due to global perturbation. It can be seen that there is a regular progression of the resonance position and amplitude as K_a increases. Furthermore, it is evident that the resonance amplitudes for phenyl isocyanide are approximately 15 times larger than those in benzonitrile for matching values of K_a . Initially, this may seem surprising. Although the energy separation between vibrational states is smaller in the dyad of phenyl isocyanide than in benzonitrile, the energy separation

FIG. 8. Superimposed resonance plots of ν_{22} for K_a^+ series with even values of K_a between 2 and 30 for phenyl isocyanide (a) and benzonitrile (b). Measured transitions are omitted for clarity, but they are indistinguishable from the plotted values on this scale. The plotted values are frequency differences between excited state transitions and their deperturbed counterparts, scaled by $(J'' + 1)$, as for Figs. 6 and 7. The x- and y-axes are set to the same scale for each of the resonance plots.

between actual interacting rovibrational states is scattered in a not easily predictable pattern but with similar magnitudes. Figure 9(a) shows the $K_a = 14^+$ and 14^- energy level perturbations for ν_{22} and ν_{33} of phenyl isocyanide. Figure 9(b) shows the four corresponding resonance plots, which are essentially each a finite difference first derivative curve of the energy curves in Fig. 9(a). The resonance plots in Fig. 9(b) are like those in Fig. 8 but are not scaled by $J'' + 1$. In these plots, the mirroring of global perturbation ($\Delta K_a = 0$) is apparent, while the resonances are offset due to their differing selection rules. Three distinct regions are evident in these plots. The first is a low J region where the molecule behaves as a prolate top and the perturbation in Fig. 9(a) is fairly constant, approximately equal to the simple two-state model result shown in the following equation:

$$\sqrt{\left(\frac{\Delta E_{22,33}}{2}\right)^2 + G_a^2 K_a^2} - \frac{\Delta E_{22,33}}{2}. \quad (2)$$

The second region, where the molecule behaves asymmetrically, appears as an undulation at medium values of J . Since the undulations in Fig. 9(b) are the derivatives relative to the asymmetry curve, their position depends on the asymmetry parameter ($\kappa = \frac{2B-A-C}{A-C}$) and not on $\Delta E_{22,33}$. The values of κ are very similar between the two isomeric molecules. It is worth noting that the strongest resonances in Fig. 8 appear to track at least approximately with the undulation, indicating that the level of asymmetry also largely influences their positions. Finally, there is a high J region where the molecule behaves as an oblate top, where K_c becomes nearly a good quantum number and the perturbation magnitude increases approximately quadratically with J . The very strong scaling of the resonances with ΔE is evidently related to an interaction of the very large global ($\Delta K_a = 0$) perturbation with smaller, local perturbations ($\Delta K_a = 2$ or 4) in the matrix diagonalization. Contour plots of phenyl isocyanide and benzonitrile are depicted in Fig. 10. It is evident from these plots that

FIG. 9. Energy difference plots for $K_a = 14$ of phenyl isocyanide obtained by subtracting the deperturbed energies from the final coupled-fit energies (a) and corresponding frequency difference plots (b). Measured transitions are omitted for clarity in (b), but they are indistinguishable from the plotted values on this scale. The x-axis is set to the same scale for each of the plots and the same color scheme is used in (a) and (b).

resonances in phenyl isocyanide appear at lower values of J'' and K_a'' than in benzonitrile. Again, this behavior is reasonable based upon the smaller energy separation between ν_{22} and ν_{33} in phenyl isocyanide, allowing the energy levels of the lower state to intercept those of the upper state at lower K_a .

As in benzonitrile, the final least-squares fit allowed the prediction and measurement of several nominal interstate transitions. Such formally forbidden transitions are enabled by strong mixing between rotational levels of different vibrational states. All nominal interstate transitions included in the least-squares fit are provided in the [supplementary material](#), and a representative “matched pair” of nominal interstate transitions is illustrated in [Fig. 11](#).

A “matched pair” consists of nominal interstate transitions whose lower and upper rotational levels correspond to the lower and upper rotational levels of two standard, within-state “ $R_{0,1}$ ” transitions. Because phenyl isocyanide exhibits stronger resonances than does benzonitrile, there was a larger number of strong nominal interstate transitions predicted and measured for phenyl isocyanide. Initially, 42 matched pairs were identified as candidates for inclusion in the least-squares fit for phenyl isocyanide. To be included in the final least-squares fit, however, the measured nominal interstate transitions had to meet several criteria: (1) the transitions had to have similar intensities in the rotational spectrum, (2) all four transitions—the pair of nominal interstate transitions and the two

FIG. 10. Contour plots depicting the coupling landscape between rotational levels in ν_{22} and ν_{33} vibrational states of phenyl isocyanide (left: yellow and green, respectively) and benzonitrile (right: blue and purple, respectively). The mapped values are $(1 - P_{\text{mix}})$, where P_{mix} is the mixing coefficient of a given vibration-rotation energy level. Resonances between levels in the two vibrational states are apparent as matching, similarly shaped islands along the horizontal direction (same J) but differing in the values of K_a (see text). The horizontally elongated resonance islands appear to be resonances for $\Delta K_a = 3$ but are in fact sums of $\Delta K_a = 2$ and $\Delta K_a = 4$ resonances.

corresponding within-state transitions—had to be incorporated into the overall data set, and (3) the average of the frequencies of the nominal interstate matched pair had to be equal within their combined measurement errors (~ 0.07 MHz) to the average of the corresponding within-state frequencies. As a result, we included only 14 of the 42 matched pair candidates in the final least-squares fit. Using the same selection criteria, a total of 11 matched pairs were included in the final least-squares fit for benzonitrile. It is worth noting that nearly all of the nominal interstate transitions measured for benzonitrile are degenerate pairs of transitions, resulting in a roughly two-fold increase to the intensity of each of these transitions. All of the nominal interstate transitions measured for phenyl isocyanide are nondegenerate transitions. Thus, their intensity does not benefit from the intensity boost, and yet they are still sufficiently intense to be observed, again attesting to the stronger intensity of the individual nominal interstate transitions of the isocyanide isomer.

Comparison with computational estimates

Table III provides a comparison between experimentally determined values for the least-squares fit for ν_{22} and ν_{33} dyad with their B3LYP-estimated values. The experimentally determined b - and c -axis vibration-rotation interaction constants ($B_0 - B_v$ and $C_0 - C_v$) for both vibrational states are in excellent agreement with their B3LYP-predicted values. The errors in the computational predictions are remarkably small, 2% or less for each of these values. Unfortunately, $A_0 - A_{33}$ was unable to be determined in this work. The value of $A_0 - A_{22}$ has the greatest difference with the calculated value of any of the vibration-rotation interaction constants. While $A_0 - A_{22}$ was too low by about 80% of its value, the discrepancy of about 2 MHz is still quite small compared to the value of A_{22} , 5656.8549(13) MHz. It is not surprising that the A constant has the largest discrepancy with its calculated value as it is the largest constant and the constant most correlated with the K -dependent

FIG. 11. Energy diagram depicting a representative matched pair of nominal rotation-vibration transitions between ν_{22} (copper) and ν_{33} (green) vibrational states of phenyl isocyanide. Standard $R_{0,1}$ transitions within vibrational states are denoted by vertical arrows. The diagonal, dashed arrows indicate nominal inter-state transitions that are formally forbidden but observed as a result of rotational level mixing. The value printed on each arrow is the corresponding transition frequency (in MHz) with its observed–calculated value in parentheses. The marked energy separation is the energy separation between the two strongly interacting rotational energy levels.

distortion constants (Δ_K and Φ_K) and the Coriolis coupling terms. It is also expected to be strongly correlated with the undetermined value of A_{33} . As mentioned previously, the quartic and sextic distortion constants and the Coriolis coupling constants were very well predicted by the B3LYP calculation. Collectively, the predicted values from the B3LYP calculation provided excellent support to the experimental work.

TABLE III. Experimental and computed vibration-rotation interaction constants (α_i) for ν_{22} and ν_{33} excited vibrational states of phenyl isocyanide (C_6H_5NC).

	Experimental	B3LYP/6-311+(2d,p)
ν_{22}		
A_0-A_{22} (MHz)	2.482 5(18)	4.505
B_0-B_{22} (MHz)	−1.946 890(69)	−1.986
C_0-C_{22} (MHz)	−1.998 734(64)	−2.023
ν_{33}		
A_0-A_{33} (MHz)		−2.050
B_0-B_{33} (MHz)	−3.530 756(69)	−3.461
C_0-C_{33} (MHz)	−1.145 878(65)	−1.134

CONCLUSIONS

The present extensive data set and analysis of the ground vibrational state and two lowest-energy vibrational states of phenyl isocyanide have enabled a detailed comparison of its spectrum and behavior to those of benzonitrile. In particular, this is the first time a comparison of the Coriolis perturbation parameters for two such closely related isomers has been made. While the overall spectroscopic constants have proven to be very similar, there exist notable differences due to the smaller energy separation between ν_{22} and ν_{33} for phenyl isocyanide. This value is approximately half that for benzonitrile. As a result, the observed resonances are shifted to lower quantum number values. The magnitudes of the broad undulations are observed to scale roughly as the inverse of the energy separation, but those of the observed resonances vary by a much larger factor. While we were surprisingly unable to determine A_{33} , the perturbation analysis for phenyl isocyanide did permit determination of three additional higher-order coupling terms (G_a^K , G_a^J , and G_a^{JK}) that were not determined for benzonitrile, even though the data sets were comparable in size. The analysis of numerous resonances allowed for a precise determination of the energy difference of 9.682 248(3) cm^{-1} between the ν_{22} and ν_{33} fundamental states of phenyl isocyanide. This work supports the conclusion that B3LYP/6-311+(2d,p) anharmonic frequency calculations provide very useful estimates of the equilibrium rotational constants, fourth- and sixth-order centrifugal distortion constants, vibration-rotation interaction constants, and first-order Coriolis coupling constants. The expanded spectroscopic data set and the much more complete analysis of centrifugal distortion now permit prediction of all rotational transitions accessible to radioastronomy to sufficient precision for astronomical detection and identification.

SUPPLEMENTARY MATERIAL

See [supplementary material](#) for least-squares fitting files of phenyl isocyanide, output files from computations, computed vibration-rotation interaction constants, computed vibrational frequencies and infrared intensities, nominal inter-state transitions for the ν_{22} and ν_{33} dyad of phenyl isocyanide with their corresponding within-state transitions, and the NMR and mass spectra of phenyl isocyanide.

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