

Millimeter-wave spectroscopy of the chlorine isotopologues of 2-chloropyridine and twenty-three of their vibrationally excited states

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ABSTRACT

A combined total of 25 vibrational states of 2-chloropyridine (C_5H_4NCl , $\mu_a = 3.07$ D, $\mu_b = 1.70$ D), including states for both chlorine isotopologues, have been least-squares fit to sextic, A-reduced Hamiltonians with low error (<0.05 MHz). In total, over 22,500 transition frequencies were measured in the 135–375 GHz frequency region. The technique of fixing undeterminable distortion constants to the corresponding values of the ground vibrational state for fundamental states and to extrapolated values for overtone and combination states was employed. The experimentally determined rotational, centrifugal distortion, and vibration-rotation interaction constants are reasonably well-predicted by computational methods (B3LYP/6-311+G(2d,p)). For the chlorine isotopologues, the changes in rotational and quartic distortion constants upon vibrational excitation are quite similar, indicating that it is possible to estimate the constants of a lower-abundance isotopologue's excited vibrational state using the change in constant observed in the higher-abundance isotopologue. The changes in rotational and quartic distortion constants upon vibrational excitation are also quite similar between analogous vibrational states of 2-chloropyridine and chloropyrazine, despite their differences in molecular composition.

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1. Introduction

2-Chloropyridine, a C_s , near-prolate, asymmetric top (C_5H_4NCl , $\kappa = -0.85$, Fig. 1) has a large dipole moment ($\mu_a = 3.07$ D and $\mu_b = 1.70$ D, B3LYP/6-311+(2d,p)) resulting in strong a -type and weaker b -type rotational transitions. The rotational spectrum of pyridine, its parent aromatic heterocycle, has been studied extensively [1–12] with the most recent publication identifying several vibrationally excited states [12]. The rotational spectra of all mono-chlorinated derivatives of pyridine (Fig. 2) have been previously reported (2-chloropyridine [13–16], 3-chloropyridine [17,18], and 4-chloropyridine [19,20]) at frequencies less than 40 GHz. Dreizler and coworkers determined the nuclear quadrupole coupling constants for both the chlorine and nitrogen nuclei for each of the chloropyridines [16,19,21]. The current work extends the frequency range observed for 2-chloropyridine to 375 GHz. In addition to the chloropyridines, the rotational spectra of several other analogous chlorinated aromatic compounds have been previously reported (chlorobenzene [22,23], 2-chloropyrimidine [24], and chloropyrazine [25]; Fig. 2). Of the previous studies of the chloroarenes, those of chloropyrazine and

2-chloropyrimidine provide the most detailed analysis of the vibrationally excited states and provide meaningful comparisons to the vibrationally excited states observed in the current work.

The rotational spectrum of 2-chloropyridine was first reported in three nearly contemporaneous studies [13–15]. Independently, the ground state rotational constants and chlorine nuclear quadrupole coupling constants were determined from spectra collected from 12.4 to 18 GHz [13] and 8–40 GHz [14] for both chlorine isotopologues. Walden and Cook [15] reported the rotational constants and nuclear quadrupole coupling constants for [^{35}Cl]- and [^{37}Cl]-2-chloropyridine in their ground vibrational states using spectral data from 26.5 to 40 GHz. A vibrationally excited state (v_{27}) was also identified, measured, and least-squares fit for the [^{35}Cl]-isotopologue. Building upon that work, Meyer et al. [16] provided an improved, full quartic, A-reduction least-squares fit of each chlorine isotopologue in the ground vibrational state and an A-reduction least-squares fit of the first vibrationally excited state (v_{27}). The quadrupole coupling constants were refined for chlorine and determined for the first time for nitrogen. The spectroscopic constants of Meyer et al. [16] are summarized in Table 1. These constants provided useful initial predictions of the rotational spectra of the ground state and first vibrationally excited state (v_{27}) of each chlorine isotopologue in the 135–375 GHz range studied in this work. The low K_a series for the ground state of the [^{35}Cl]-

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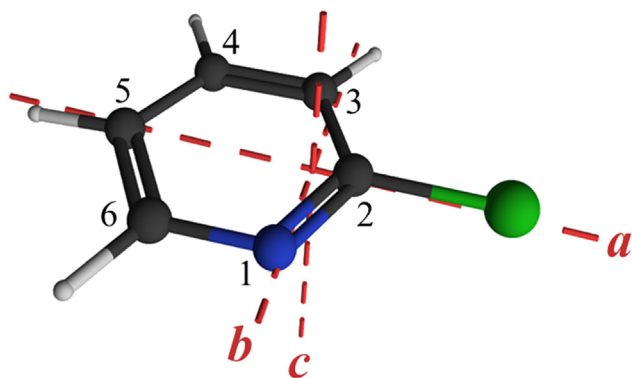


Fig. 1. [^{35}Cl]-2-Chloropyridine structure (B3LYP/6-311+G(2d,p)) with principal inertial axes and atom numbering. The dipole moment components are $\mu_a = 3.07$ D and $\mu_b = 1.70$ D.

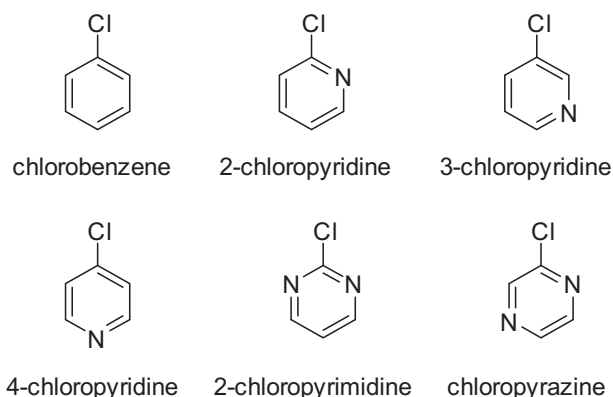


Fig. 2. Chlorobenzene and five mono- and di-nitrogen derivatives: 2-chloropyridine (*ortho*- $\text{C}_5\text{H}_4\text{NCl}$), 3-chloropyridine (*meta*- $\text{C}_5\text{H}_4\text{NCl}$), 4-chloropyridine (*para*- $\text{C}_5\text{H}_4\text{NCl}$), 2-chloropyrimidine ($\text{C}_4\text{H}_3\text{N}_2\text{Cl}$), and 2-chloropyrazine ($\text{C}_4\text{H}_3\text{N}_2\text{Cl}$).

isotopologue were predicted to an initial accuracy between 1 MHz (low J) and 16 MHz (high J).

The infrared and Raman vibrational spectra of 2-chloropyridine have been well-studied [26–37]. Several of these studies provide measurements of the low-energy vibrationally excited states [30–37] expected to be observable in a rotational spectrum collected at room temperature. Liquid-phase infrared measurements from the most recent study [37] and B3LYP/6-311+(2d,p) estimated vibration-rotation interaction constants are provided in Table 2. The experimental fundamental vibrational frequencies [37] were used to estimate the overtone and combination state vibrational frequencies below 800 cm^{-1} , presented in Fig. 3. The transition intensity is estimated based upon the population of the vibrational level at 298 K and the isotopic abundance. These previous measurements and current computational predictions provide the foundation for the current study of the rotational spectrum of 2-chloropyridine.

2. Experimental and theoretical methods

The rotational spectrum presented in this work from 135 to 375 GHz was obtained using the millimeter-wave and submillimeter-wave spectrometer, which has been previously described [25,38,39]. A commercial sample of 2-chloropyridine was used without further purification at a sample pressure of 5 or 15 mTorr in a continuous flow. The nearly continuous spectrum in combination with the AABS package [40,41], including ASFIT and ASROT [42], allowed for a very large number of rotational transitions to be measured and analyzed for most of the vibrational states and isotopologues studied in this work. For all least-squares fits reported in this work, a sixth-order, A-reduced, I' representation Hamiltonian was necessary to fit the observed spectrum. In an attempt to obtain spectroscopic constants that are fairly free of perturbation, we fixed distortion terms that could not be adequately determined from a particular least-squares fit as described below. For the ground state sextic constants that could not be satisfactorily fit, B3LYP/6-311+(2d,p) computed values were used. Ground state constant values were used for all least-squares fits of fundamental states where sextic or quartic terms could not be determined in their least-squares fits. For overtone or combination states, extrapolated distortion constants using polynomial fits were used when those terms could not be directly determined. Distortion constants that varied by more than an order of magnitude from the expected value or changed sign were fixed. When extrapolation of a distortion constant for an overtone or combination state resulted in a change of sign for that term, the distortion constant was set to zero. Measured transition frequencies that had *obs.* – *calc.* values greater than 0.1 MHz in their least-squares fits were excluded from the data set. All files associated with the least-squares fitting and prediction of these spectra are available in the [Supplementary Material](#).

The B3LYP/6-311+G(2d,p) optimizations and anharmonic frequency calculations were carried out in Gaussian 16 [43] with the WebMO interface [44]. Calculations were performed with very tight convergence criteria (opt = verytight int = grid = ultrafine), which afforded quartic and sextic distortion constants, fundamental vibrational frequencies, and vibration-rotation interaction constants. The output files of each theoretical calculation and analysis are provided in the [Supplementary Material](#).

3. Spectral and computational analysis

In total, frequencies of over 22,500 independent transitions were measured and least-squares fit in the current work. The rotational spectrum of 2-chloropyridine (Fig. 4) is dominated by intense degenerate *a*-type and *b*-type R-branch transitions ($^a\text{R}_{0,1}$, $^b\text{R}_{1,1}$, $^b\text{R}_{-1,1}$) arising from large μ_a and moderate μ_b . The difference in magnitude of the component dipole moments results in *a*-type transitions that are approximately 2.5 times more intense than the *b*-type transitions, which only becomes apparent when the degeneracy is broken. With the moderately large μ_b , many

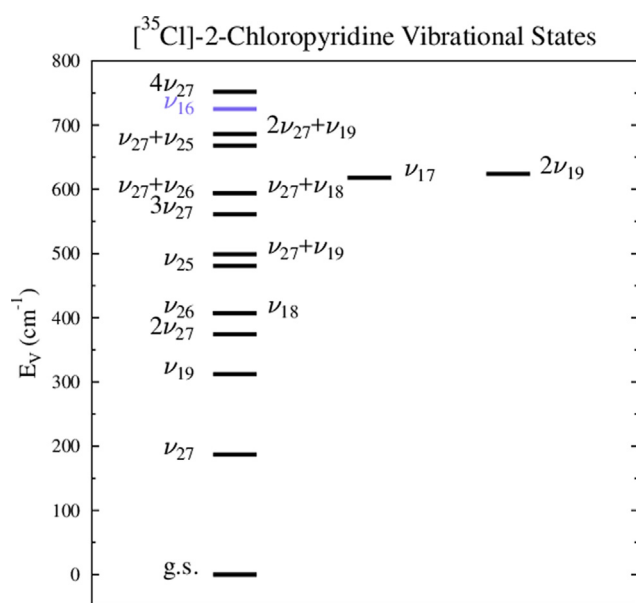
Table 1
Spectroscopic constants for [^{35}Cl]- and [^{37}Cl]-2-chloropyridine (A-reduced Hamiltonian, I' representation) from Ref. [16].

	[^{35}Cl] G.S.	[^{37}Cl] G.S.	[^{35}Cl] ν_{27}	[^{37}Cl] ν_{27}
A_0^{A} (MHz)	5872.0279 (6)	5872.16 (28)	5843.516 (2)	5843.277 (4)
B_0^{A} (MHz)	1637.8348 (1)	1591.76 (5)	1638.991 (1)	1592.926 (1)
C_0^{A} (MHz)	1280.5136 (1)	1252.17 (5)	1282.037 (1)	1253.675 (1)
Δ_J (kHz)	0.06528 (69)	0.063 (6)		
Δ_{JK} (kHz)	0.2794 (41)	0.245 (68)		
Δ_J (kHz)	0.966 (56)	[0.966]		
δ_J (kHz)	0.01507 (13)	0.015 (7)		
δ_K (kHz)	0.3323 (52)	[0.3323]		
N_{lines}	45	12	6	5

Table 2

Experimental and computed low-energy fundamental frequencies and vibration-rotation interaction constants for 2-chloropyridine.

Mode	Symmetry	Experimental ^a Frequency (cm ⁻¹)	Rotational Transition Intensities at 298 K ^b	B3LYP/6-311+(2d,p)			
				Fundamental Frequency (cm ⁻¹)	$A_0 - A_v$ (MHz)	$B_0 - B_v$ (MHz)	$C_0 - C_v$ (MHz)
[³⁵ Cl]	ν_{17}	618	0.05	624.1	2.07	0.056	0.99
	ν_{25}	481	0.09	487.4	1.22	0.31	-0.54
	ν_{18}	407	0.13	414.0	-0.34	1.816	0.90
	ν_{26}	407	0.13	412.7	5.20	-0.22	-0.73
	ν_{19}	312	0.22	307.3	-26.43	0.059	1.12
	ν_{27}	187	0.43	173.0	29.20	-1.10	-1.48
[³⁷ Cl]	ν_{26}	407	0.04	411.9	5.21	-0.23	-0.71
	ν_{18}	407	0.04	406.9	-0.33	1.78	0.88
	ν_{19}	312	0.07	304.8	-26.62	0.060	1.10
	ν_{27}	187	0.14	171.7	29.41	-1.08	-1.45

^a Experimental infrared or Raman fundamental frequencies measured from a mixture of natural abundance 2-chloropyridine isotopologues [37].^b Relative to [³⁵Cl]-2-chloropyridine ground vibrational state.**Fig. 3.** Vibrational energy levels of [³⁵Cl]-2-chloropyridine below 800 cm⁻¹. Fundamental ν_{16} is in slate blue as its rotational transitions were not measured and least-squares fit in this work. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

transitions of each type were included in the least-squares fits. With R-branches separated by approximately $2C$ (~ 2.6 GHz), 2-chloropyridine displays many thousands of R-branch transitions between 135 and 375 GHz at room temperature. For the ground vibrational state and some of the low-energy vibrationally excited states, Q-branch transitions were also observable and measured. The ${}^aR_{0,1}$ transitions show roughly the same pattern as that observed for chloropyrazine [25], but with the additional b -type transitions. These ${}^bR_{1,1}$ and ${}^bR_{-1,1}$ transitions are degenerate with a -type transitions that have the same values of J and K_c , but different values of K_a , and lose degeneracy as they progress away from the oblate-degenerate $K_a = 0, 1$ series. At high values of K_a and lower values of K_c , pairs of ${}^bR_{1,1}$, ${}^bR_{-1,1}$ transitions exhibit degeneracy as pairs of transitions with equal values of K_a .

Previously, only one vibrationally excited state had been reported for each of the chlorine isotopologues of 2-chloropyridine. In this work, we have assigned and least-squares fit transitions for fifteen vibrationally excited states of [³⁵Cl]-2-chloropyridine and eight vibrationally excited states for its [³⁷Cl]-isotopologue. At room temperature, the least intense of these states to be successfully measured, assigned, and least-

squares fit ($4\nu_{27}$) had transitions with intensities approximately 3.5% of their corresponding ground state transitions. We were unable to observe and assign transitions to states with intensities lower than those of [³⁵Cl] $4\nu_{27}$ given the spectral density. Thus, the assignment and least-squares fitting of the [¹³C]- and [¹⁵N]-isotopologues at natural abundance was not feasible using the current data, precluding a complete structure determination.

3.1. [³⁵Cl]-2-Chloropyridine, vibrational ground state

As shown in Fig. 5, the final data set of the vibrational ground state of [³⁵Cl]-2-chloropyridine consists of 5112 newly measured independent transitions and 61 independent transitions from previous microwave works [13–16]. In the 135–220 GHz range there were a moderate number of transitions that displayed nuclear quadrupole coupling due to the chlorine and nitrogen nuclei. These transitions were not included in the least-squares fit presented in Table 3. The data sets of 2-chloropyridine in its ground state and vibrationally excited states were fit to sextic, A-reduced, distorted-rotor Hamiltonian models. Despite the large number of independent transitions in the least-squares fit, Φ_J could not be determined and was fixed to its B3LYP/6-311+G(2d,p) estimated value. With all of the other experimentally determined sextic constants within 30% of their computationally predicted values, fixing this value to the computational prediction was more reasonable than fixing it to zero. There is quite good agreement between the computational predictions of the rotational constants (A_0 , B_0 , and C_0) and the experimental values determined by this least-squares fit; all three values are predicted within 1.5% of the experimental value. All of the quartic distortion constants show very good agreement between the predicted and experimental values, with the greatest discrepancy in ΔK , which is underpredicted by 2.7%. At the order of the sextic distortion constants, the discrepancies between predicted and experimental values are all between 5% and 30%. While the agreement of all centrifugal distortion constant values is imperfect, the values were certainly good enough for an *a priori* prediction of the spectrum to begin the iterative assignment of transitions and least-squares fitting processes.

3.2. [³⁵Cl]-2-Chloropyridine, ν_{27} ($v = 1, 2, 3, 4$)

The lowest-energy vibrational mode ν_{27} (A'' , 187 cm⁻¹) is the out-of-plane bending of the σ_{C-Cl} bond, and is observed with transitions approximately 0.40 times as intense as their ground state counterparts. This allowed the measurement and least-squares fitting of 3285 independent transitions and resulted in an excellent determination of its rotational constants and distortion constants with uncertainties comparable to those of the ground state

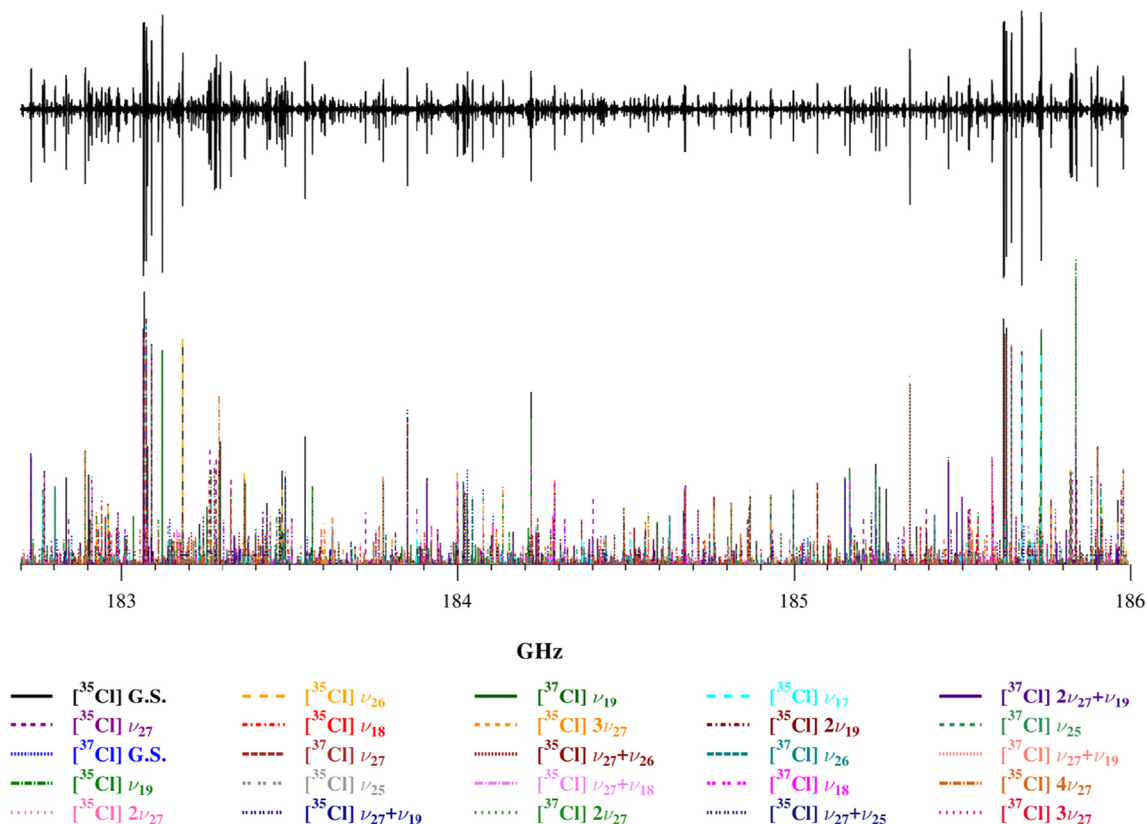


Fig. 4. Rotational spectrum of 2-chloropyridine from 182.7 to 186.0 GHz with predicted stick spectra for ^{35}Cl - and ^{37}Cl -2-chloropyridine ground and vibrationally excited states.

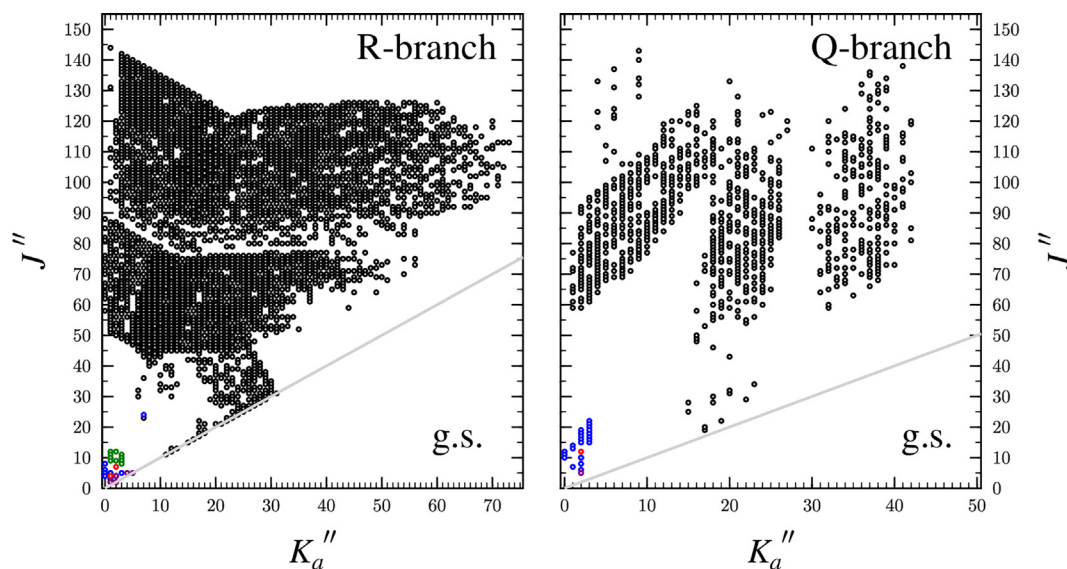


Fig. 5. Data distribution plots for the least-squares fit of spectroscopic data for ground state ^{35}Cl -2-chloropyridine from the current work (black circles) and the measurements from Doraiswamy and Sharma (red, [13]), Scappini and Guarnieri (purple, [14]), Walden and Cook (green, [15]), and Meyer et al. (blue, [16]). The size of the plotted circle is proportional to the value of $f_{\text{obs.}} - f_{\text{calc.}}$ and all values shown have errors smaller than twice the estimated experimental error of 50 kHz. Data distribution plots for all other states are available in the Supplementary Material. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

(Table 3). As with the ground state, Φ_J could not be determined, so it was fixed to the computationally predicted value for the ground state. It appears that this was a valid choice, as the remaining sextic distortion terms were quite similar in magnitude and of the same sign as those of the ground state. The experimentally determined vibration-rotation interaction constants are presented in Table 4. The close agreement between computed, extrapolated,

and experimental values of the vibration-rotation interaction constants conclusively supports the assignments of the vibrational states. The largest magnitude error is observed in $A_0 - A_{27}$ ($(A_0 - A_{27})_{\text{obs.}} - \text{calc.} = 0.73 \text{ MHz}$, 2.6%), which is reasonably small, allowing the constants predicted using the calculated vibration-rotation interaction constants to be effective initial predictions for vibrationally excited state spectra.

Table 3Spectroscopic constants for [³⁵Cl]-2-chloropyridine in its ground and its vibrationally excited states (A-reduced Hamiltonian, I^r representation). Vibrational frequencies from Ref. [37].

	B3LYP/6-311+G(2d,p)	[³⁵ Cl] G.S. ^a	ν_{27} A'', 187 cm ⁻¹	ν_{19} A', 312 cm ⁻¹	$2\nu_{27}$ A', 374 cm ⁻¹
$A_v^{(A)}$ (MHz)	5884.	5872.02795 (14)	5843.56038 (25)	5897.44618 (31)	5816.06771 (35)
$B_v^{(A)}$ (MHz)	1613.	1637.834265 (21)	1638.994890 (24)	1637.831898 (40)	1640.146563 (36)
$C_v^{(A)}$ (MHz)	1266.	1280.513036 (22)	1282.037575 (25)	1279.496795 (33)	1283.552035 (32)
Δ_J (kHz)	0.0654	0.06464424 (97)	0.0652322 (12)	0.0647703 (17)	0.0658406 (17)
Δ_{JK} (kHz)	0.283	0.281851 (13)	0.285780 (19)	0.277248 (44)	0.288228 (38)
Δ_K (kHz)	0.950	0.97677 (17)	0.78570 (30)	1.17663 (23)	0.62149 (25)
δ_J (kHz)	0.0155	0.0155563 (12)	0.0156341 (13)	0.0155855 (18)	0.0157104 (17)
δ_K (kHz)	0.320	0.319271 (31)	0.307000 (44)	0.334525 (86)	0.295184 (76)
Φ_J (Hz)	0.000000403	[0.000000403] ^b	[0.000000403] ^{b,c}	[0.000000403] ^{b,c}	[0.000000403] ^{b,c}
Φ_{JK} (Hz)	0.000115	0.0000909 (33)	0.0000745 (47)	0.0001311 (71)	0.0000520 (44)
Φ_{KJ} (Hz)	-0.000510	-0.000406 (11)	-0.000198 (18)	-0.000449 (35)	[0.0] ^d
Φ_K (Hz)	0.000994	0.001096 (58)	0.00113 (11)	[0.001096] ^c	[0.001168] ^e
φ_J (Hz)	0.000000754	0.000000704 (47)	0.000000657 (49)	0.000000898 (59)	0.000000654 (61)
φ_{JK} (Hz)	0.0000547	0.0000662 (20)	0.0000533 (25)	0.0000661 (42)	0.0000405 (34)
φ_K (Hz)	0.00164	0.001266 (55)	0.001003 (77)	0.00237 (11)	0.000760 (85)
N_{lines}		5112	3285	2017	1934
σ		0.046	0.043	0.044	0.044
Δ_i (uÅ ²)	0.00012	0.0382513 (83)	-0.631844 (10)	0.722217 (13)	-1.289260 (13)
κ	-0.850	-0.844	-0.843	-0.845	-0.843
	ν_{26} A'', 407 cm ⁻¹	ν_{18} A', 407 cm ⁻¹	ν_{25}^f A'', 481 cm ⁻¹	$\nu_{27} + \nu_{19}^f$ A', 499 cm ⁻¹	$3\nu_{27}$ A', 561 cm ⁻¹
$A_v^{(A)}$ (MHz)	5866.78741 (43)	5871.3924 (19)	5871.033 (23)	5870.18 (39)	5789.420 (22)
$B_v^{(A)}$ (MHz)	1638.095573 (59)	1636.483057 (87)	1637.6428 (22)	1638.728 (32)	1641.2938 (22)
$C_v^{(A)}$ (MHz)	1281.276445 (44)	1279.810807 (65)	1281.04317 (11)	1281.05264 (12)	1285.058299 (63)
Δ_J (kHz)	0.0648470 (30)	0.0651762 (64)	0.065628 (58)	0.06504 (12)	0.066375 (34)
Δ_{JK} (kHz)	0.28186 (10)	0.279334 (86)	[0.282] ^c	[0.281] ^e	[0.289] ^e
Δ_K (kHz)	0.97613 (30)	0.9763 (43)	[0.977] ^c	[0.986] ^e	[0.484] ^e
δ_J (kHz)	0.0155952 (27)	0.0157088 (37)	0.015894 (24)	0.015542 (59)	0.015739 (17)
δ_K (kHz)	0.31740 (11)	0.321469 (87)	0.3429 (13)	0.3130 (26)	0.28181 (57)
Φ_J (Hz)	[0.000000403] ^{b,c}	[0.000000403] ^{b,c}	[0.000000403] ^{b,c}	[0.000000403] ^{b,c}	[0.000000403] ^{b,c}
Φ_{JK} (Hz)	0.000112 (11)	0.0001000 (79)	[0.0000910] ^c	[0.000115] ^e	[0.0000236] ^e
Φ_{KJ} (Hz)	-0.000693 (95)	[-0.000406] ^c	[-0.000406] ^c	[-0.000241] ^e	[0.0] ^d
Φ_K (Hz)	[0.001096] ^c	[0.001096] ^c	[0.001096] ^c	[0.00114] ^e	[0.00120] ^e
φ_J (Hz)	0.000000801 (85)	0.000000526 (95)	[0.000000704] ^c	[0.000000852] ^e	[0.000000696] ^e
φ_{JK} (Hz)	0.0000782 (57)	[0.0000662] ^c	[0.0000662] ^c	[0.0000532] ^e	[0.0000277] ^e
φ_K (Hz)	0.00182 (18)	[0.00127] ^c	[0.00127] ^c	[0.00212] ^e	[0.000536] ^e
N_{lines}	1302	1052	201	213	340
σ	0.046	0.044	0.045	0.044	0.045
Δ_i (uÅ ²)	-0.224557 (19)	-0.009287 (38)	-0.17572 (55)	0.0132 (83)	-1.93535 (53)
κ	-0.844	-0.845	-0.845	-0.844	-0.842
	$\nu_{27} + \nu_{26}$ A', 594 cm ⁻¹	$\nu_{27} + \nu_{18}$ A'', 594 cm ⁻¹	ν_{17} A', 618 cm ⁻¹	$2\nu_{19}$ A', 624 cm ⁻¹	$\nu_{27} + \nu_{25}$ A', 668 cm ⁻¹
$A_v^{(A)}$ (MHz)	5838.750 (86)	5841.09 (41)	5870.32 (18)	[5923.] ^e	5841.62 (16)
$B_v^{(A)}$ (MHz)	1639.2653 (75)	1637.666 (33)	1637.758 (15)	1637.8206 (13)	1639.013 (13)
$C_v^{(A)}$ (MHz)	1282.778876 (90)	1281.35639 (11)	1279.599009 (79)	1278.511599 (93)	1282.53249 (12)
Δ_J (kHz)	0.065475 (59)	0.06525 (30)	0.065769 (72)	0.06423 (12)	0.06575 (17)
Δ_{JK} (kHz)	[0.286] ^e	[0.283] ^e	[0.282] ^c	[0.273] ^e	[0.286] ^e
Δ_K (kHz)	[0.785] ^e	[0.785] ^e	[0.977] ^c	[1.38] ^e	[0.786] ^e
δ_J (kHz)	0.015673 (29)	0.01554 (14)	0.015723 (61)	0.015614 (61)	0.015837 (86)
δ_K (kHz)	0.3066 (10)	0.2967 (50)	0.3559 (18)	0.3152 (18)	0.3184 (31)
Φ_J (Hz)	[0.000000403] ^{b,c}	[0.000000403] ^{b,c}	[0.000000403] ^{b,c}	[0.000000403] ^{b,c}	[0.000000403] ^{b,c}
Φ_{JK} (Hz)	[0.0000958] ^e	[0.0000836] ^e	[0.0000910] ^c	[0.000171] ^e	[0.0000745] ^e
Φ_{KJ} (Hz)	[-0.000485] ^e	[-0.000198] ^e	[-0.000406] ^c	[-0.000492] ^e	[-0.000198] ^e
Φ_K (Hz)	[0.00113] ^e	[0.00113] ^e	[0.001096] ^c	[0.001096] ^e	[0.00113] ^e
φ_J (Hz)	[0.000000754] ^e	[0.000000479] ^e	[0.000000705] ^c	[0.00000109] ^e	[0.000000658] ^e
φ_{JK} (Hz)	[0.0000654] ^e	[0.0000534] ^e	[0.0000663] ^c	[0.0000660] ^e	[0.0000534] ^e
φ_K (Hz)	[0.00156] ^e	[0.00100] ^e	[0.00127] ^c	[0.00349] ^e	[0.00100] ^e
N_{lines}	234	114	150	191	139
σ	0.052	0.043	0.041	0.048	0.048
Δ_i (uÅ ²)	-0.8800 (19)	-0.7089 (87)	0.2809 (39)	1.394 (14) ^g	-0.8093 (34)
κ	-0.844	-0.844	-0.844	-0.845	-0.844

(continued on next page)

Table 3 (continued)

	$2\nu_{27} + \nu_{19}$ A' , 686 cm^{-1}	$4\nu_{27}$ A' , 748 cm^{-1}
$A_v^{(A)}$ (MHz)	[5842.] ^e	5762.60 (30)
$B_v^{(A)}$ (MHz)	1639.7992 (18)	1642.513 (25)
$C_v^{(A)}$ (MHz)	1282.59607 (12)	1286.55741 (10)
Δ_J (kHz)	0.06514 (14)	0.066657 (24)
Δ_{JK} (kHz)	[0.284] ^e	[0.289] ^e
Δ_K (kHz)	[0.808] ^e	[0.374] ^e
δ_J (kHz)	0.015368 (74)	0.015631 (13)
δ_K (kHz)	0.2911 (22)	[0.265] ^e
Φ_J (Hz)	[0.000000403] ^{b,c}	[0.000000403] ^{b,c}
Φ_{JK} (Hz)	[0.0000953] ^e	[0.0] ^e
Φ_{KJ} (Hz)	[-0.0000381] ^e	[0.0] ^e
Φ_K (Hz)	[0.00117] ^e	[0.00124] ^e
ϕ_J (Hz)	[0.000000826] ^e	[0.000000782] ^e
ϕ_{JK} (Hz)	[0.0000404] ^e	[0.0000150] ^e
ϕ_K (Hz)	[0.00186] ^e	[0.000330] ^e
N_{lines}	108	162
σ	0.043	0.049
A_i ($\text{u}\text{\AA}^2$)	-0.675 (15) ^g	-2.5712 (67)
κ	-0.843	-0.841

^a Sextic least-squares fit including transitions of the previous works [15,16], without inclusion of any hyperfine resolved transitions.

^b Constant fixed to B3LYP/6-311+G(2d,p) value.

^c Constant fixed to ground state value.

^d Constant fixed to zero because value extrapolated from lower-energy states in corresponding series changed sign relative to corresponding values in lower-energy states.

^e Constant fixed to value extrapolated from lower-energy states in corresponding series using appropriate polynomial.

^f Tentative vibrational state assignments of $\nu_{27} + \nu_{19}$ and ν_{25} .

^g Inertial defect error calculated assuming error of 1 MHz in A_v .

The transitions of the two-, three-, and four-quanta overtone states of ν_{27} were easily predicted by extrapolation from the ground state and lower-energy members of the vibrational series. In the final least-squares fits of these states, 1934, 340, and 162 independent transitions were included for $2\nu_{27}$, $3\nu_{27}$, and $4\nu_{27}$, respectively. The number of transitions included in each of the least-squares fits decreased across this series because the intensity of transitions of the state decreases with increasing energy. With fewer transitions, more of the constants had to be fixed in

the fitting. Similar to the approach taken with chloropyrazine [25], when the reduced number of measured transitions caused a constant to become undeterminable by least-squares fitting, the constant was fixed to an extrapolated value based upon lower-energy states in the vibrational series. This was expected to provide values of the varied parameters that are closer to their true value compared to the alternative of fixing that constant to zero. This strategy is supported by the smoothness of the trends presented in Fig. 6.

Table 4

Vibration-rotation interaction constants of 2-chloropyridine (A-reduced Hamiltonian, I' representation).

	$[^{35}\text{Cl}]$ -2-chloropyridine		$[^{37}\text{Cl}]$ -2-chloropyridine	
	Experimental	B3LYP/6-311+(2d,p)	Experimental	B3LYP/6-311+(2d,p)
ν_{27}				
$A_0 - A_{27}$ (MHz)	28.46757 (29)	29.20	28.67310 (48)	29.41
$B_0 - B_{27}$ (MHz)	-1.160625 (32)	-1.10	-1.140913 (62)	-1.08
$C_0 - C_{27}$ (MHz)	-1.524539 (33)	-1.48	-1.488603 (59)	-1.45
ν_{19}				
$A_0 - A_{19}$ (MHz)	-25.41823 (34)	-26.43	-25.6246 (37)	-26.62
$B_0 - B_{19}$ (MHz)	0.002367 (45)	0.06	0.00347 (21)	0.06
$C_0 - C_{19}$ (MHz)	1.016241 (40)	1.12	0.996068 (66)	1.10
ν_{26}				
$A_0 - A_{26}$ (MHz)	5.24054 (45)	5.20	6.66 (24)	5.21
$B_0 - B_{26}$ (MHz)	-0.261308 (63)	-0.22	-0.375 (18)	-0.23
$C_0 - C_{26}$ (MHz)	-0.763409 (49)	-0.73	-0.73998 (10)	-0.71
ν_{18}				
$A_0 - A_{18}$ (MHz)	0.6355 (19)	-0.34	-1.60 (66)	-0.33
$B_0 - B_{18}$ (MHz)	1.351208 (89)	1.82	1.502 (49)	1.78
$C_0 - C_{18}$ (MHz)	0.702229 (69)	0.90	0.68355 (11)	0.88
ν_{25}				
$A_0 - A_{25}$ (MHz)	0.995 (23)	1.22	[1.25] ^a	1.25
$B_0 - B_{25}$ (MHz)	0.1915 (22)	0.31	-0.1642 (35)	0.29
$C_0 - C_{25}$ (MHz)	-0.53013 (11)	-0.54	-0.48160 (36)	-0.52
ν_{17}				
$A_0 - A_{17}$ (MHz)	1.71 (18)	2.07		
$B_0 - B_{17}$ (MHz)	0.076 (15)	0.06		
$C_0 - C_{17}$ (MHz)	0.914027 (82)	0.99		

^a A_{25} is fixed to the value predicted from the experimental A_0 value and the calculated vibration-rotation interaction constant.

As can be seen in Fig. 6, the spectroscopic constants for the entire ν_{27} series display smooth changes as a function of the vibrational quanta. All non-zero distortion constants are displayed; fixed constants are represented by open symbols. Trendlines were modeled from all determined constants in the series using an appropriate polynomial. Fig. 6a and b show the changes in the rotational constants relative to the corresponding ground state constants and the changes in the inertial defect as a function of vibrational excitation. Given that the sextic and quartic centrifugal distortion constants were fixed in the fit, the smoothness of these two plots provides important validation of the quality of the rotational constants determined by each least-squares fit. Fig. 6c and d display the centrifugal distortion constants relative to those of the ground state as a function of vibrational excitation. As with ν_{24} for [^{35}Cl]-chloropyrazine [25], the purely J -dependent terms (Δ_J and δ_J) show a smaller relative change upon vibrational excitation than the purely K -dependent terms (Δ_K and δ_K). The experimentally determined sextic centrifugal distortion constants show greater deviations as a function of vibrational excitation and were more

difficult to determine experimentally than the quartic centrifugal distortion terms. Four-quanta state $4\nu_{27}$ shows the greatest deviation from the trendline for the centrifugal distortion terms. This is partially due to the low number of transitions least-squares fit for $4\nu_{27}$, but could also be caused by untreated perturbations with its nearest vibrational neighbors. Lower-energy states ν_{27} , $2\nu_{27}$, and $3\nu_{27}$ are separated from their nearest vibrational neighbors by at least 30 cm^{-1} , whereas $4\nu_{27}$ is only 23 cm^{-1} and 17 cm^{-1} away from ν_{16} and ν_{23} , respectively. Although fixing some sextic and quartic centrifugal distortion terms could have a substantial impact on the other centrifugal distortion terms, the quality of the least-squares fits and smoothness of the plots in Fig. 6 suggest that these are reasonable estimates of their real values.

3.3. [^{35}Cl]-2-Chloropyridine, ν_{19} ($v = 1, 2$)

The second lowest-energy fundamental of [^{35}Cl]-2-chloropyridine, ν_{19} (A' , 312 cm^{-1}), is an in-plane bending mode of the $\sigma_{\text{C-Cl}}$ bond relative to the aryl ring. The final least-squares

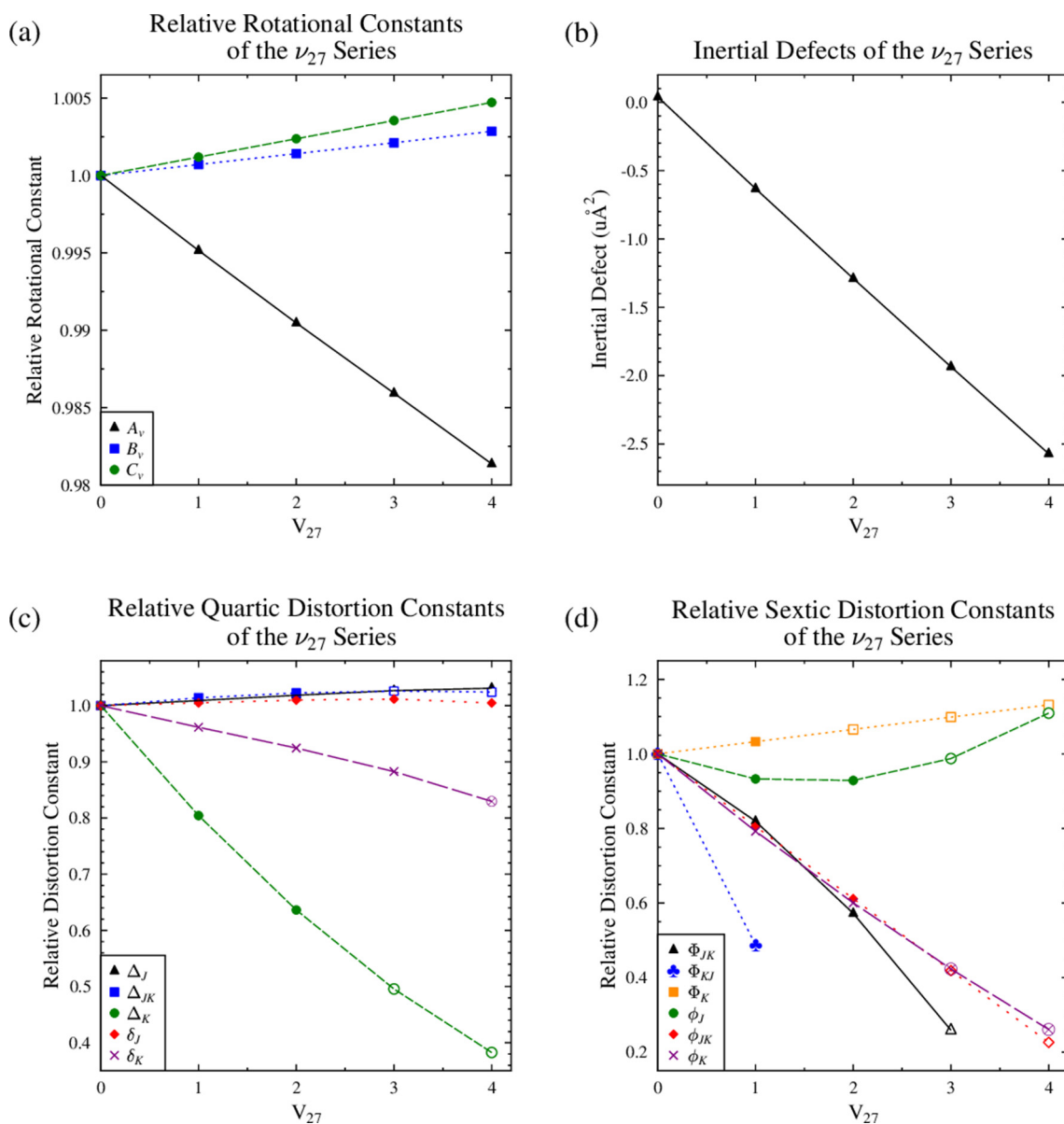


Fig. 6. (a) Relative rotational constants, (b) inertial defect, (c) relative quartic centrifugal distortion, and (d) relative sextic centrifugal distortion constants for the ν_{27} series of [^{35}Cl]-2-chloropyridine as a function of vibrational excitation ($\nu_{27} = 0, 1, 2, 3, 4$). The trendline for each series is a polynomial fit of all corresponding constants included in their least-squares fits. Open symbols represent points fixed to their extrapolated values in their least-squares fits.

fit of ν_{19} contained 2017 independent transitions and required that the sextic distortion terms Φ_J and Φ_K be fixed to their ground-state values. As with ν_{27} , the computed vibration-rotation interaction constants provided excellent initial predictions of the rotational constants; the largest magnitude discrepancy $((A_0 - A_{19})_{obs.-calc.} = 1.01 \text{ MHz, } 4.0\%)$ occurs again for the A rotational constant. Although its first overtone state, $2\nu_{19}$ (A' , 624 cm^{-1}), is only 6 cm^{-1} higher in energy than ν_{17} (A' , 618 cm^{-1}) and thus likely affected by perturbation, its low- K_a series were very well-predicted by constants extrapolated from the ground vibrational and corresponding fundamental states. Fig. 7 shows trends in the relative rotational constants (Fig. 7a), inertial defect (Fig. 7b), and relative distortion constants (Fig. 7c and d) for the ν_{19} series. The rotational constants and inertial defect trends demonstrate a linear progression upon excitation, so the determined constants are expected to be free of perturbation and very near their real values. While little can be said regarding the sextic distortion constants (Fig. 7d), all of which had to be fixed to the linearly extrapolated value for $2\nu_{19}$, the quartic distortion constants (Fig. 7c) are some-

what more informative. The purely J -dependent distortion terms that were fit show a near-linear progression with excitation. In contrast, δ_K for $2\nu_{19}$ exhibits a sharp decrease, indicating that this constant could be absorbing perturbation. When this constant is fixed to the extrapolated value, nearly 40 transitions had to be removed due to high error and the trends for both Δ_J and δ_J became non-linear, both apparently absorbing perturbation. As a result, the least-squares fit for $2\nu_{19}$ presented here includes δ_K , acknowledging that it has likely absorbed perturbation and deviates from its real value. A coupled-state least-squares fit was not attempted, because it is expected that the number of lines measurable at such low intensity would not be sufficient to complete the coupling analysis.

3.4. [^{35}Cl]-2-Chloropyridine, ν_{26} and ν_{18}

The fourth lowest-energy vibrationally excited state, ν_{26} (A'' , 407 cm^{-1}) is an asymmetric ring distortion vibration. The fifth lowest-energy vibrationally excited state, ν_{18} (A' , 407 cm^{-1}), is pre-

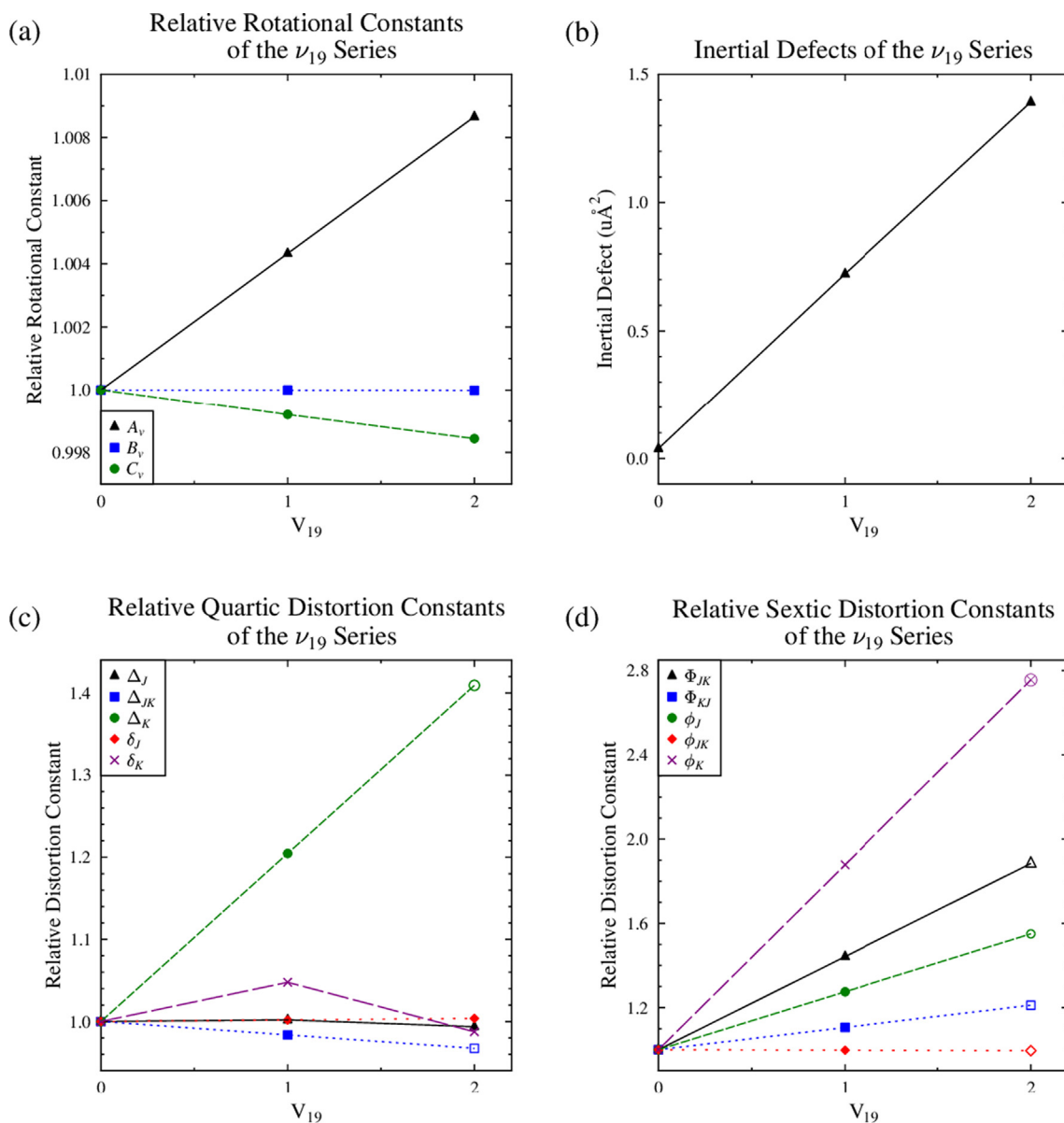


Fig. 7. (a) Relative rotational constants, (b) inertial defect, (c) relative quartic centrifugal distortion, and (d) relative sextic centrifugal distortion constants for the ν_{19} series of [^{35}Cl]-2-chloropyridine as a function of vibrational excitation ($\nu_{19} = 0, 1, 2$). The trendline for each series is a polynomial fit of all corresponding constants included in their least-squares fits. Open symbols represent points fixed to their extrapolated values in their least-squares fits.

dominantly a stretching of the σ_{C-Cl} bond with slight stretching of the ring along this same axis. Both of these fundamental states are higher in energy than the previously discussed overtone state, $2\nu_{27}$. These two states are expected to be very close in energy and thus coupled to one another. Indeed, some of the higher K_a series observed appeared to curve away from the predicted frequency in Loomis-Wood plots. Nevertheless, over 1000 transitions were measured and least-squares fit for each of the states. The vibration-rotation interaction values determined for these states are reasonably well-predicted with the exception of $A_0 - A_{18}$. The largest discrepancy between computationally predicted and observed vibration-rotation interaction constants of ν_{26} is that for $B_0 - B_{26}$ ($(B_0 - B_{26})_{obs.-calc.} = -0.04$ MHz, 15.8%), which is a reasonably small discrepancy compared to those for other vibrational states. As a result, it is expected that the rotational constants of ν_{26} are reasonably free of perturbation. The computationally predicted and observed $A_0 - A_{18}$ values, however, have different signs and a large discrepancy ($(A_0 - A_{18})_{obs.-calc.} = 0.98$ MHz, 153.5%). While this could be the result of unaddressed Coriolis coupling between ν_{26} and ν_{18} ($|G_a| = 351.9$ MHz and $|G_b| = 21.7$ MHz, B3LYP/6-311+G (2d,p)), the fact that their experimental $A_0 - A_v$ values do not exhibit an inverse relationship does not support such a conclusion. Moreover, a similar sign-change and large discrepancy between the computed and observed $A_0 - A_v$ values was observed for the analogous vibrational state, ν_{16} , in chloropyrazine [25]. There, as here, it appears most likely that the discrepancy is due to the very small B3LYP-calculated magnitude of $A_0 - A_v$. The distortion constants for both ν_{26} and ν_{18} are of the same sign and very close in magnitude to the corresponding values for the ground vibrational state, so it is not evident that any of them have absorbed perturbation.

3.5. [^{35}Cl]-2-Chloropyridine, ν_{25} and $\nu_{27} + \nu_{19}$

The sixth and seventh lowest-energy vibrationally excited states are the fundamental ν_{25} (A'' , 481 cm^{-1}) and the lowest-energy combination state, $\nu_{27} + \nu_{19}$ (A'' , 499 cm^{-1}). Fundamental ν_{25} is an out-of-plane, “butterfly” ring deformation mode in which the chlorine atom is nearly stationary. The number of transitions least-squares fit for each of these vibrationally excited states is just over 200 with their intensities less than one tenth that of the corresponding ground vibrational state transitions. This is a marked drop-off from the over-1000 transitions observed for each of ν_{26} and ν_{18} , and is very similar to the situation for the corresponding vibrational states of chloropyrazine [25]. Both of these states, while lower in energy than $3\nu_{27}$, have about two-thirds as many measured transitions. The vibration-rotation interaction constant with the largest magnitude discrepancy between observed and calculated values is again $A_0 - A_{25}$ ($(A_0 - A_{25})_{obs.-calc.} = -0.23$ MHz, 22.7%), while the largest percent error is for $B_0 - B_{25}$ ($(B_0 - B_{25})_{obs.-calc.} = -0.12$ MHz, 62.0%). Both constants, however, are reasonably close on an absolute basis to the small calculated values. The agreement between extrapolated and observed values of constants for combination states will be discussed in Section 4, Discussion and Conclusions. As was the case for the corresponding vibrational states of chloropyrazine [25], ν_{25} and $\nu_{27} + \nu_{19}$ are the first states whose quartic distortion constants Δ_{JK} and Δ_K had to be fixed to the ground or extrapolated values and for which all of the sextic centrifugal distortion constants are also fixed. While these states could potentially exhibit coupling, none of the fitted constants show clear evidence of perturbation.

3.6. [^{35}Cl]-2-Chloropyridine, $\nu_{27} + \nu_{26}$ and $\nu_{27} + \nu_{18}$

The combination states $\nu_{27} + \nu_{26}$ (A' , 594 cm^{-1}) and $\nu_{27} + \nu_{18}$ (A' , 594 cm^{-1}) are the ninth and tenth lowest-energy vibrationally

excited states of 2-chloropyridine. These states, like ν_{26} and ν_{18} , are expected to be coupled due to their close energies. Both of these states were least-squares fit to sextic, distorted-rotor Hamiltonians with Δ_{JK} , Δ_K , and all sextic constants fixed to their extrapolated values. The fact that 234 transitions were measured for $\nu_{27} + \nu_{26}$ and 150 were measured for the next higher-energy fundamental, ν_{17} , while only 114 transitions were measured for $\nu_{27} + \nu_{18}$, could indicate the existence of perturbation in the latter. At the same time, the smaller number of measured transitions could be coincidentally due to more overlap with transitions of other states. The observed constants do not exhibit large enough discrepancies from their extrapolated values (*vide infra*) to suggest coupling.

3.7. [^{35}Cl]-2-Chloropyridine, ν_{17} , $\nu_{27} + \nu_{25}$, and $2\nu_{27} + \nu_{19}$

Fundamental ν_{17} (A' , 618 cm^{-1}), an in-plane ring deformation mode, is the 11th lowest-energy vibrationally excited state and the highest-energy fundamental state observed in this work. As discussed previously, ν_{17} is only 6 cm^{-1} lower in energy than $2\nu_{19}$ and is expected to be coupled to the overtone, although the least-squares fits of these two states do not show clear evidence of such an effect, at least with the data set currently available. The 12th lowest-energy vibrationally excited state is $\nu_{27} + \nu_{25}$ (A' , 668 cm^{-1}) for which 139 transitions were measured. The 13th lowest-energy vibrationally excited state is $2\nu_{27} + \nu_{19}$ (A' , 686 cm^{-1}), for which only 108 transitions were measured and, unfortunately, the A rotational constant had to be fixed to the extrapolated value to obtain a converged least-squares fit.

3.8. [^{37}Cl]-2-Chloropyridine, vibrational ground state

As a result of the relative natural abundances of the chlorine isotopes (^{35}Cl : $^{37}\text{Cl} \sim 3:1$), transitions of the [^{37}Cl]-2-chloropyridine ground vibrational state are less intense than even the corresponding transitions of the [^{35}Cl]-isotopologue's first fundamental state. Just over 2700 transitions were nevertheless measured, resulting in a sixth-order Hamiltonian where only three sextic distortion terms (Φ_i , Φ_{KJ} , and Φ_K) had to be fixed to computationally predicted values (Table 5). The previous experimental work [13,14,16,45] provided a very useful starting prediction. Impressively, of the rotational constants and three quartic distortion constants determined using only 12 transitions by Meyer et al. [16], all but A_0 are within their quoted error limits of the constants determined in this work. The errors in calculated rotational constants and quartic distortion constants are nearly the same as those of the [^{35}Cl]-isotopologue, with somewhat greater error in the sextic centrifugal distortion constants. The estimate of ϕ_K shows the greatest discrepancy (45.6%), though it is reasonably good for this level of theory.

As expected, chlorine atom isotopic substitution results in a minute change (0.03 MHz) in the A_0 constant, because the chlorine atom is located very nearly on the a principal axis. The values of B_0 and C_0 are more drastically affected (46 MHz and 28 MHz, respectively) because the chlorine atom lies far off-axis relative to the b and c principal axes. The quartic centrifugal distortion constants are within 7% of one another between the isotopologues and the sextic distortion constants are within 90%, except for δ_K (136%). The discrepancies in the sextic distortion constants are likely affected to some extent by the necessity to fix three of these constants to computationally predicted values for the [^{37}Cl]-isotopologue.

3.9. [^{37}Cl]-2-Chloropyridine, ν_{27} ($v = 1, 2, 3$)

As a result of the lower isotopic abundance and concomitant transition intensity of [^{37}Cl]-2-chloropyridine relative to the

Table 5
Spectroscopic constants for [³⁷Cl]-2-chloropyridine in its ground and its vibrationally excited states (A-reduced Hamiltonian, I^r representation). Vibrational frequencies from Ref. [37].

	B3LYP/6-311+G(2d,p)	[³⁷ Cl] G.S. ^a	ν_{27} A'', 187 cm ⁻¹	ν_{19} A', 312 cm ⁻¹	$2\nu_{27}$ A', 374 cm ⁻¹
$A_v^{(A)}$ (MHz)	5927.	5871.99730 (21)	5843.32420 (43)	5897.6219 (37)	5815.7093 (45)
$B_v^{(A)}$ (MHz)	1576.	1591.787546 (28)	1592.928459 (55)	1591.78408 (21)	1594.05924 (21)
$C_v^{(A)}$ (MHz)	1245.	1252.189104 (27)	1253.677707 (52)	1251.193036 (60)	1255.153946 (59)
Δ_J (KHz)	0.06269	0.0619059 (13)	0.0624472 (22)	0.062150 (16)	0.063116 (19)
Δ_{JK} (KHz)	0.2739	0.273289 (26)	0.277174 (47)	0.26983 (30)	0.27896 (11)
Δ_K (KHz)	0.9620	0.98822 (16)	0.79387 (28)	1.151 (11)	0.619 (13)
δ_J (KHz)	0.01457	0.0145999 (15)	0.0146618 (23)	0.0147004 (85)	0.0147662 (96)
δ_K (KHz)	0.3115	0.310645 (55)	0.29815 (14)	0.32797 (43)	0.28771 (26)
Φ_J (Hz)	0.0000002773	[0.0000002773] ^b	[0.0000002773] ^{b,c}	[0.0000002773] ^{b,c}	[0.0000002773] ^{b,c}
Φ_{JK} (Hz)	0.0001090	0.0001716 (51)	0.0001409 (68)	0.000319 (32)	[0.0001102] ^d
Φ_{KJ} (Hz)	-0.0005001	[-0.0005001] ^b	[-0.0005001] ^{b,c}	[-0.0005001] ^{b,c}	[-0.0005001] ^{b,c}
Φ_K (Hz)	0.0009907	[0.0009907] ^b	[0.0009907] ^{b,c}	[0.0009907] ^{b,c}	[0.0009907] ^{b,c}
φ_J (Hz)	0.0000006784	0.000000994 (55)	0.000000614 (67)	0.000000994 ^c	[0.0000002342] ^d
φ_{JK} (Hz)	0.00005158	0.0000551 (27)	0.0000564 (54)	0.000175 (20)	[0.00005772] ^d
φ_K (Hz)	0.001630	0.00299 (10)	0.00226 (13)	[0.002994] ^c	[0.001543] ^d
N_{lines}		2705	1576	729	506
σ		0.040	0.045	0.047	0.047
A_I (uÅ ²)	0.00013	0.038953 (11)	-0.635199 (21)	0.733511 (71)	-1.294938 (81)
κ	-0.859	-0.853	-0.852	-0.853	-0.851
	ν_{26} A'', 407 cm ⁻¹	ν_{18} A', 407 cm ⁻¹	ν_{25} A'', 481 cm ⁻¹	$\nu_{27} + \nu_{19}$ A'', 499 cm ⁻¹	$3\nu_{27}$ A'', 561 cm ⁻¹
$A_v^{(A)}$ (MHz)	5865.34 (24)	5873.60 (66)	[5871.] ^e	[5869.] ^d	[5789.] ^d
$B_v^{(A)}$ (MHz)	1592.163 (18)	1590.286 (49)	1591.9517 (35)	1592.4464 (42)	1595.1699 (35)
$C_v^{(A)}$ (MHz)	1252.92908 (10)	1251.50555 (11)	1252.67070 (36)	1252.74247 (36)	1256.62019 (29)
Δ_J (KHz)	0.061408 (95)	0.06349 (34)	0.06410 (22)	0.06102 (28)	0.06430 (28)
Δ_{JK} (KHz)	[0.2733] ^c	[0.2733] ^c	[0.2733] ^c	[0.274] ^d	[0.2787] ^d
Δ_K (KHz)	[0.9882] ^c	[0.9882] ^c	[0.9882] ^c	[0.958] ^d	[0.4639] ^d
δ_J (KHz)	0.014310 (47)	0.01532 (17)	0.01558 (11)	0.01396 (14)	0.01510 (14)
δ_K (KHz)	0.2875 (18)	0.3358 (58)	0.3517 (44)	0.2848 (48)	0.2872 (45)
Φ_J (Hz)	[0.0000002773] ^{b,c}	[0.0000002773] ^{b,c}	[0.0000002773] ^{b,c}	[0.0000002773] ^{b,c}	[0.0000002773] ^{b,c}
Φ_{JK} (Hz)	[0.0001717] ^c	[0.0001717] ^c	[0.0001717] ^c	[0.0002883] ^d	[0.00007952] ^d
Φ_{KJ} (Hz)	[-0.0005001] ^{b,c}	[-0.0005001] ^{b,c}	[-0.0005001] ^{b,c}	[-0.0005001] ^{b,c}	[-0.0005001] ^{b,c}
Φ_K (Hz)	[0.0009907] ^{b,c}	[0.0009907] ^{b,c}	[0.0009907] ^{b,c}	[0.0009907] ^{b,c}	[0.0009907] ^{b,c}
φ_J (Hz)	[0.000000994] ^c	[0.000000994] ^c	[0.000000994] ^c	[0.0000006146] ^d	[0.0] ^f
φ_{JK} (Hz)	[0.00005511] ^c	[0.00005511] ^c	[0.00005511] ^c	[0.0001767] ^d	[0.00005903] ^d
φ_K (Hz)	[0.002994] ^c	[0.002994] ^c	[0.002994] ^c	[0.002269] ^d	[0.0008179] ^d
N_{lines}	141	117	82	60	72
σ	0.044	0.047	0.051	0.049	0.038
A_I (uÅ ²)	-0.2222 (50)	-0.017 (14)	-0.098 (15) ^g	-0.052 (15) ^g	-1.945 (15) ^g
κ	-0.853	-0.853	-0.853	-0.853	-0.851

^a Sextic least-squares fit including transitions of the previous works [15,16], without inclusion of any hyperfine resolved transitions.

^b Constant fixed to B3LYP/6-311+G(2d,p) value.

^c Constant fixed to ground vibrational state value.

^d Constant fixed to value extrapolated from lower-energy states in corresponding series using appropriate polynomial.

^e Constant fixed to value calculated using experimentally determined A_0 and calculated vibration-rotation interaction constant.

^f Constant fixed to zero because value extrapolated from lower-energy states in corresponding series changed sign relative to corresponding values in lower-energy states.

^g Inertial defect error calculated assuming error of 1 MHz in A_v .

[³⁵Cl]-isotopologue, only two of the former's ν_{27} overtone states were observed and measured (Table 5). Fig. 8 shows trends in the relative rotational constants (Fig. 8a), the inertial defects (Fig. 8b), and the relative distortion constants (Fig. 8c and 8d) for the [³⁷Cl]-2-chloropyridine ν_{27} series. Although the A rotational constant could not be fit for $3\nu_{27}$, the other rotational constants exhibit linear trends upon vibrational excitation (Fig. 8a). The quartic centrifugal distortion constants (Fig. 8c) also show the expected linear trends or slight curvature, while all of the sextic constants for overtone states of ν_{27} had to be fixed to linearly extrapolated values. The constants for ν_{27} ($v = 1, 2$, and 3) do not exhibit evidence of perturbation, like their [³⁵Cl] counterparts. The vibration-rotation interaction constants in Table 4 show that the largest magnitude discrepancy between the observed and calculated values is that for $A_0 - A_{27}$ ($(A_0 - A_{27})_{obs.-calc.} = -0.74$ MHz, 2.6%). It is worth noting that the discrepancies between observed and calculated vibration-rotation interaction constants are very nearly the same for both chlorine isotopologue ν_{27} fundamentals (-0.74 MHz for $(A_0 - A_{27})_{obs.-calc.}$, -0.06 MHz for $(B_0 - B_{27})_{obs.-calc.}$,

and -0.04 MHz for $(C_0 - C_{27})_{obs.-calc.}$). Since the constants of this fundamental are well-determined for both isotopologues and not affected by coupling, the consistency between calculation and experiment validates the use of this level of theory and basis set to model the structure and force constants.

3.10. [³⁷Cl]-2-Chloropyridine, ν_{19} , ν_{26} , ν_{18} , ν_{25} , and $\nu_{27} + \nu_{19}$

The other four fundamental vibrational states that were observed and analyzed for the [³⁷Cl]-isotopologue can be described similarly to their [³⁵Cl]-counterparts. For states where all three rotational constants were experimentally determined, the vibration-rotation interaction constants (Table 4) are very similar between the [³⁵Cl]- and [³⁷Cl]-isotopologues, with the exception of ν_{26} and ν_{18} . While the $C_0 - C_v$ values for the corresponding states of both isotopologues are very similar, the $A_0 - A_v$ and $B_0 - B_v$ values are markedly different. In the case of ν_{18} , this may be due to the relatively few lines measured and poor determination of A_{18} . The reader may also note, however, that the $A_0 - A_v$ values for

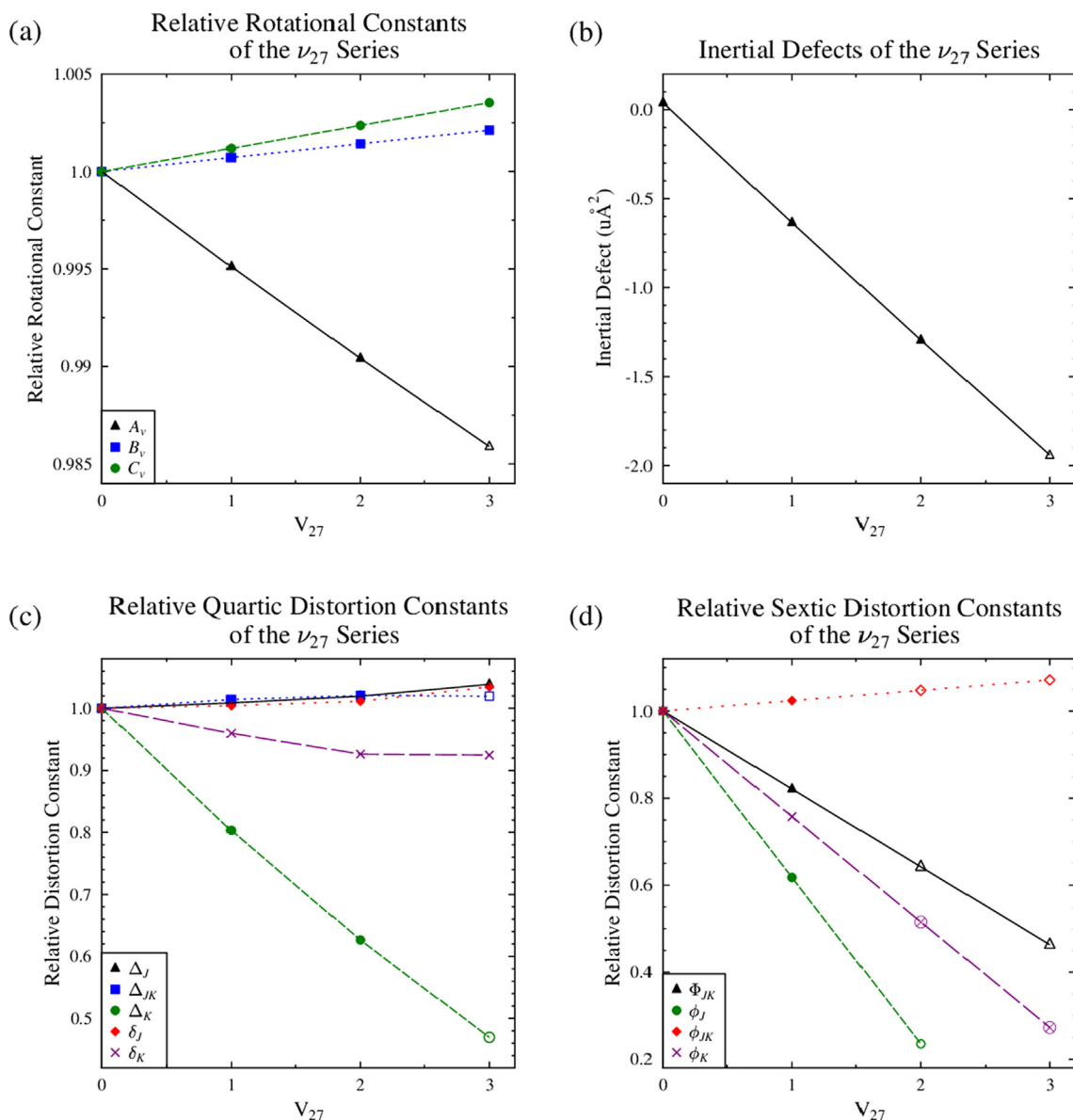


Fig. 8. (a) Relative rotational constants, (b) inertial defect, (c) relative quartic centrifugal distortion, and (d) relative sextic centrifugal distortion constants for the ν_{27} series of ^{37}Cl -2-chloropyridine as a function of vibrational excitation ($\nu_{27} = 0, 1, 2, 3$). The trendline for each series is a polynomial fit of all corresponding constants included in their least-squares fits. Open symbols represent points fixed to their extrapolated values in their least-squares fits.

ν_{26} and ν_{18} appear to be approximately equal and opposite in magnitude, an effect not observed in the corresponding states of the ^{35}Cl -isotopologue. Such a pattern may suggest that these states are exhibiting perturbation and, evidently, at lower values of K_a than in ^{35}Cl -2-chloropyridine. Since the B3LYP calculation predicts nearly the same Coriolis coupling constants for the ν_{26} and ν_{18} dyad of each isotopologue, this observation of perturbation would indicate that ν_{26} and ν_{18} are closer in energy in ^{37}Cl -2-chloropyridine than in ^{35}Cl -2-chloropyridine. The previous experimental work did not differentiate the energies between the two fundamental states and the B3LYP calculation estimates that the energy separation between them should be greater in the ^{37}Cl -isotopologue than in the ^{35}Cl -isotopologue, contrary to what appears to be the case experimentally. The computed isotopic shift from the ^{35}Cl -isotopologue to the ^{37}Cl -isotopologue for ν_{26} (-0.8 cm^{-1}) is much smaller than that for ν_{18} (-7.1 cm^{-1}). It is easily probable, considering the fact that the chlorine atom moves a great deal more in the ν_{18} normal mode than it does in the ν_{26} mode, that their isotopic shifts could bring their energies signifi-

cantly closer together. Further support for the possibility of observable coupling between ν_{26} and ν_{18} lies in the examination of the least-squares fitting of ν_{26} . Upon examination, while most of the distortion constants are fairly similar between the ^{37}Cl - and ^{35}Cl -isotopologues, δ_K is most different between isotopologues (Table S1). When this constant is fixed to the ground-state value, the $A_0 - A_v$ and $B_0 - B_v$ values match those of the corresponding ^{35}Cl -isotopologue much more closely, but several transitions become poorly predicted and must be removed from the data set. The poorly fitting transitions appear at the highest J and K_a values in the data set. The fact of a dissimilar δ_K value and that transitions with high quantum numbers were primarily affected suggests that those transitions may have been exhibiting substantial perturbation and that the spectroscopic constants may have been absorbing the effect of that untreated perturbation.

Unlike in the case of chloropyrazine [25], one combination state was possible to least-squares fit for ^{37}Cl -2-chloropyridine: $\nu_{27} + \nu_{19}$. As a result of the low intensity and few lines measured ($N_{\text{lines}} = 60$), the A rotational constant was not able to be fit and

had to be fixed to the linearly extrapolated value along with two quartic and all of the sextic centrifugal distortion constants.

4. Discussion and conclusions

The work herein described provides further evidence that B3LYP/6-311+(2d,p) optimization and anharmonic frequency calculations provide very good predictions of vibration-rotation interaction constants and centrifugal distortion constants for organic molecules of modest size. Although all of the predicted distortion constants fall outside the error bars of the experimentally determined constants, the quartic centrifugal distortion constants are predicted within 3% of their experimental values and most of the sextic distortion constants are within 46%. The quartic distortion constant prediction is thus quite impressive and errors in sextic constants are small enough to not obviously deter the computed values from greatly assisting in finding and least-squares fitting the ground or excited vibrational states. The vibration-rotation interaction constants, while also predominantly falling outside the error bars of the experimentally determined values, were clearly effective in locating a total of 11 fundamental states.

As in the recent study of chloropyrazine [25], spectroscopic constants for combination states were predicted using a linear extrapolation from the ground and corresponding vibrationally excited states. A comparison of these extrapolated values to their experimentally determined values is provided in Table 6. For states with all three rotational constants determined experimentally, the prediction of quartic centrifugal distortion constants is within 5% of those determined experimentally with many falling within 1%. For those with fixed A_v values, the largest discrepancy between experimentally determined and predicted quartic distortion constants is still within 11% (δ_K for ^{37}Cl $v_{27} + v_{19}$). The extrapolated rotational constants are all within 0.03% of their experimentally determined values, which is comparable to the precision of the

rotational constants of fundamental states predicted from computed vibration-rotation interaction constants. This level of agreement between the extrapolated and observed constants makes it easier to find combination states than fundamental states at high energies. Moreover, such agreement both validates the prediction method and the quality of the individual least-squares fits.

We suggested previously that using hyphenate distortion constants appears to be a better strategy for fixing undeterminable vibrational-state distortion constants than simply setting these constants to a value of zero [25]. For isotopologues that have the same symmetry and very similar orientation of the principal axes, it is worth considering the possibility of estimating the distortion constants of the lower-abundance isotopologue by using the change in the corresponding distortion constant upon the same vibrational excitation of the higher-abundance isotopologue. Table 7 shows the change in rotational and quartic centrifugal distortion constants upon vibrational excitation for each of the vibrational states that were least-squares fit for both chlorine isotopologues. It is evident for the three lowest vibrationally excited states, for which all quartic distortion constants were least-squares fit, that the change upon vibrational excitation is very nearly the same in both isotopologues, and the difference between isotopologues is smaller than the change upon excitation. The larger discrepancy between $A_0 - A_v$ values observed for v_{26} and v_{18} may be due to the aforementioned likelihood of coupling. Among the other constants, only the isotopic difference in the values of A_J and δ_J for v_{26} and A_J for $v_{27} + v_{19}$ are larger than the ^{37}Cl change upon vibrational excitation for the corresponding value. Such an observation is not surprising considering that the change in chlorine isotope has a very small effect on A_v and other primarily K -dependent constants. The sextic distortion constants (not listed due to the fact that most had to be fixed for the ^{37}Cl isotopologue and thus cannot be compared) are expected to exhibit relatively larger discrepancies due to their smaller magnitudes. Sextic con-

Table 6
Experimentally determined spectroscopic constants and differences from linearly extrapolated predictions for combination states of 2-chloropyridine (A -reduced Hamiltonian, I^r representation). Vibrational frequencies from Ref. [37].

	^{35}Cl $v_{27} + v_{19}$		^{35}Cl $v_{27} + v_{26}$		^{35}Cl $v_{27} + v_{18}$		^{35}Cl $v_{27} + v_{25}$	
	A'' , 499 cm^{-1}	obs. – calc.	A' , 594 cm^{-1}	obs. – calc.	A'' , 594 cm^{-1}	obs. – calc.	A' , 668 cm^{-1}	obs. – calc.
$A_v^{(A)}$ (MHz)	5870.18 (39)	1.20	5838.750 (86)	0.43	5841.09 (41)	–1.83	5841.62 (16)	–0.95
$B_v^{(A)}$ (MHz)	1638.728 (32)	–0.26	1639.2653 (75)	0.0092	1637.666 (33)	0.023	1639.013 (13)	0.21
$C_v^{(A)}$ (MHz)	1281.05264 (12)	0.031	1282.778876 (90)	–0.022	1281.35639 (11)	0.021	1282.53249 (12)	–0.035
A_J (kHz)	0.06504 (12)	–0.00032	0.065475 (59)	0.000041	0.06525 (30)	–0.00051	0.06575 (17)	–0.00047
A_{JK} (kHz)	[0.281] ^a		[0.286] ^a		[0.283] ^a		[0.286] ^a	
A_K (kHz)	[0.986] ^a		[0.785] ^a		[0.785] ^a		[0.786] ^a	
δ_J (kHz)	0.015542 (59)	–0.00012	0.015673 (29)	–0.000000031	0.01554 (14)	–0.00024	0.015837 (86)	–0.00013
δ_K (kHz)	0.3130 (26)	–0.0092	0.3066 (10)	0.0015	0.2967 (50)	–0.012	0.3184 (31)	–0.012
N_{lines}	213		234		114		139	
σ	0.044		0.052		0.043		0.048	
A_I ($\text{u}\text{\AA}^2$)	0.0132 (84)		–0.8800 (19)		–0.7089 (87)		–0.8093 (34)	
κ	–0.844		–0.844		–0.844		–0.844	
	^{35}Cl $2v_{27} + v_{19}$		^{37}Cl $2v_{27} + v_{19}$		^{37}Cl $v_{27} + v_{19}$		^{37}Cl $v_{27} + v_{19}$	
	A' , 686 cm^{-1}	obs. – calc.	A' , 686 cm^{-1}	obs. – calc.	A'' , 499 cm^{-1}	obs. – calc.	A'' , 499 cm^{-1}	obs. – calc.
$A_v^{(A)}$ (MHz)	[5842] ^a		[5842] ^a		[5869] ^a		[5869] ^a	
$B_v^{(A)}$ (MHz)	1639.7992 (18)	–0.22	1639.7992 (18)	–0.22	1592.4464 (42)	–0.48	1592.4464 (42)	–0.48
$C_v^{(A)}$ (MHz)	1282.59607 (12)	0.040	1282.59607 (12)	0.040	1252.74247 (36)	0.061	1252.74247 (36)	0.061
A_J (kHz)	0.06514 (14)	–0.00066	0.06514 (14)	–0.00066	0.06102 (28)	–0.0017	0.06102 (28)	–0.0017
A_{JK} (kHz)	[0.284] ^a		[0.284] ^a		[0.274] ^a		[0.274] ^a	
A_K (kHz)	[0.808] ^a		[0.808] ^a		[0.958] ^a		[0.958] ^a	
δ_J (kHz)	0.015368 (74)	–0.00031	0.015368 (74)	–0.00031	0.01396 (14)	–0.00080	0.01396 (14)	–0.00080
δ_K (kHz)	0.2911 (22)	–0.014	0.2911 (22)	–0.014	0.2848 (48)	–0.031	0.2848 (48)	–0.031
N_{lines}	108		108		60		60	
σ	0.043		0.043		0.049		0.049	
A_I ($\text{u}\text{\AA}^2$)	–0.675 (15) ^b		–0.675 (15) ^b		–0.052 (15) ^b		–0.052 (15) ^b	
κ	–0.843		–0.843		–0.853		–0.853	

^a Constant fixed to value extrapolated from ground and corresponding vibrational states.

^b Inertial defect error calculated assuming error of 1 MHz in A_v .

Table 7Change in spectroscopic constants upon vibrational excitation of 2-chloropyridine for both chlorine isotopologues (A-reduced Hamiltonian, I^r representation).

	V ₂₇		V ₁₉		2V ₂₇	
	[³⁵ Cl]	[³⁷ Cl]	[³⁵ Cl]	[³⁷ Cl]	[³⁵ Cl]	[³⁷ Cl]
A ₀ – A _v (MHz)	28.46757 (29)	28.67310 (48)	–25.41816 (67)	–25.6246 (37)	55.96024 (38)	56.2880 (45)
B ₀ – B _v (MHz)	–1.160625 (32)	–1.140913 (62)	0.002370 (47)	0.00347 (21)	–2.312298 (42)	–2.27169 (21)
C ₀ – C _v (MHz)	–1.524539 (33)	–1.488603 (59)	1.0162 (37)	0.996068 (66)	–3.038999 (39)	–2.964842 (65)
(A _J) ₀ – (A _J) _v (kHz)	–0.0005880 (15)	–0.0005413 (26)	–0.0001252 (20)	–0.000244 (16)	–0.0011964 (20)	–0.001210 (19)
(A _{JK}) ₀ – (A _{JK}) _v (kHz)	–0.003929 (23)	–0.003885 (54)	0.004572 (41)	0.00346 (30)	–0.006377 (40)	–0.00567 (11)
(A _K) ₀ – (A _K) _v (kHz)	0.19107 (34)	0.19435 (32)	–0.1998 (11)	–0.163 (11)	0.35528 (30)	0.369 (13)
(δ _J) ₀ – (δ _J) _v (kHz)	–0.0000778 (18)	–0.0000619 (27)	–0.0000286 (22)	–0.0001005 (86)	–0.0001541 (21)	–0.0001663 (97)
(δ _K) ₀ – (δ _K) _v (kHz)	0.012271 (54)	0.01250 (15)	–0.01525 (10)	–0.01733 (43)	0.024087 (82)	0.02294 (27)
N _{lines}	3285	1576	2021	729	1934	506
σ	0.043	0.045	0.044	0.047	0.044	0.047

	V ₂₆		V ₁₈		V ₂₅	
	[³⁵ Cl]	[³⁷ Cl]	[³⁵ Cl]	[³⁷ Cl]	[³⁵ Cl]	[³⁷ Cl]
A ₀ – A _v (MHz)	5.24054 (45)	6.66 (24)	0.6355 (19)	–1.60 (66)		
B ₀ – B _v (MHz)	–0.261308 (63)	–0.375 (18)	1.351208 (89)	1.502 (49)	0.1915 (22)	–0.1642 (35)
C ₀ – C _v (MHz)	–0.763409 (49)	–0.73998 (10)	0.702229 (69)	0.68355 (11)	–0.53013 (11)	–0.48160 (36)
(A _J) ₀ – (A _J) _v (kHz)	–0.0002028 (32)	0.000498 (95)	–0.0005320 (65)	–0.00158 (34)	–0.000984 (58)	–0.00219 (22)
(A _{JK}) ₀ – (A _{JK}) _v (kHz)	–0.00001 (10)		0.002517 (87)			
(A _K) ₀ – (A _K) _v (kHz)	0.00064 (34)		0.0005 (43)			
(δ _J) ₀ – (δ _J) _v (kHz)	–0.0000389 (30)	0.000290 (47)	–0.0001525 (39)	–0.00072 (17)	–0.000338 (24)	–0.00098 (11)
(δ _K) ₀ – (δ _K) _v (kHz)	0.00187 (11)	0.0230 (18)	–0.002198 (92)	–0.0252 (58)	–0.0236 (13)	–0.0411 (44)
N _{lines}	1302	141	1052	117	201	82
σ	0.046	0.044	0.044	0.047	0.045	0.051

	V ₂₇ + V ₁₉		3V ₂₇	
	[³⁵ Cl]	[³⁷ Cl]	[³⁵ Cl]	[³⁷ Cl]
A ₀ – A _v (MHz)				
B ₀ – B _v (MHz)	–0.894 (32)	–0.6589 (42)	–3.4595 (22)	–3.3824 (35)
C ₀ – C _v (MHz)	–0.53960 (12)	–0.55337 (36)	–4.545263 (67)	–4.43109 (29)
(A _J) ₀ – (A _J) _v (kHz)	–0.00040 (12)	0.00089 (28)	–0.001731 (34)	–0.00239 (28)
(A _{JK}) ₀ – (A _{JK}) _v (kHz)				
(A _K) ₀ – (A _K) _v (kHz)				
(δ _J) ₀ – (δ _J) _v (kHz)	0.000014 (59)	0.00064 (14)	–0.000183 (17)	–0.00050 (14)
(δ _K) ₀ – (δ _K) _v (kHz)	0.0063 (26)	0.0258 (48)	0.03746 (57)	0.0234 (45)
N _{lines}	213	60	340	72
σ	0.044	0.049	0.045	0.038

Table 8Change in spectroscopic constants upon analogous vibrational excitation of 2-chloropyridine and 2-chloropyrazine (A-reduced Hamiltonian, I^r representation).

	[³⁵ Cl]-2-chloropyridine V ₂₇	[³⁵ Cl]-2-chloropyrazine V ₂₄	[³⁵ Cl]-2-chloropyridine V ₁₉	[³⁵ Cl]-2-chloropyrazine V ₁₇	[³⁵ Cl]-2-chloropyridine 2V ₂₇	[³⁵ Cl]-2-chloropyrazine 2V ₂₄
A ₀ – A _v (MHz)	28.46757 (29)	28.6336 (14)	–25.41823 (34)	–25.1066 (21)	55.96024 (38)	56.5228 (19)
B ₀ – B _v (MHz)	–1.16062 (19)	–1.11717 (31)	0.0024 (52)	–0.11538 (29)	–2.3123 (17)	–2.233578 (70)
C ₀ – C _v (MHz)	–1.52454 (33)	–1.58301 (75)	1.0162 (97)	0.9543 (33)	–3.039 (88)	–3.161557 (61)
(A _J) ₀ – (A _J) _v (kHz)	–0.00059 (54)	–0.00061 (64)	–0.00013 (96)	–0.00017 (56)	–0.0012 (96)	–0.00124 (64)
(A _{JK}) ₀ – (A _{JK}) _v (kHz)	–0.00393 (30)	–0.003189 (27)	0.0046 (59)	0.00542 (29)	–0.006377 (16)	–0.005737 (41)
(A _K) ₀ – (A _K) _v (kHz)	0.19107 (34)	0.1938 (31)	–0.19986 (29)	–0.2163 (34)	0.35528 (30)	0.3682 (26)
(δ _J) ₀ – (δ _J) _v (kHz)	–0.00008 (77)	–0.00008 (98)	–0.00003 (16)	–0.00005 (49)	–0.000154 (81)	–0.000154 (25)
(δ _K) ₀ – (δ _K) _v (kHz)	0.0123 (38)	0.012942 (15)	–0.01525 (14)	–0.016598 (16)	0.0241 (21)	0.025179 (11)

	[³⁵ Cl]-2-chloropyridine V ₂₆	[³⁵ Cl]-2-chloropyrazine V ₂₃	[³⁵ Cl]-2-chloropyridine V ₁₈	[³⁵ Cl]-2-chloropyrazine V ₁₆	[³⁵ Cl]-2-chloropyridine V ₂₅	[³⁵ Cl]-2-chloropyrazine V ₂₂
A ₀ – A _v (MHz)	5.24054 (45)	4.5727 (21)	0.63555 (19)	0.3721 (23)	0.99495 (23)	1.5049 (55)
B ₀ – B _v (MHz)	–0.26131 (26)	–0.161208 (75)	1.3512 (95)	1.5308 (42)	0.191465 (22)	0.004305 (46)
C ₀ – C _v (MHz)	–0.76341 (92)	–0.7402 (39)	0.702229 (69)	0.8422 (59)	–0.530134 (11)	–0.68266 (38)
(A _J) ₀ – (A _J) _v (kHz)	–0.0002 (15)	–0.00018 (89)	–0.00053 (47)	–0.00056 (89)	–0.00098 (80)	0.0017483 (25)
(A _{JK}) ₀ – (A _{JK}) _v (kHz)	–0.000009 (10)	0.0003 (48)	0.0025 (70)	0.0013 (35)		–0.077153 (11)
(A _K) ₀ – (A _K) _v (kHz)	0.00064 (34)	–0.0037 (28)	0.00047 (43)	0.0274 (31)		
(δ _J) ₀ – (δ _J) _v (kHz)	–0.00004 (95)	–0.000029 (81)	–0.00015 (89)	–0.000166 (86)	–0.00034 (40)	0.0009818 (12)
(δ _K) ₀ – (δ _K) _v (kHz)	0.001871 (11)	0.000976 (11)	–0.0022 (24)	0.000784 (12)	–0.023629 (13)	–0.009588 (22)

(continued on next page)

Table 8 (continued)

	³⁵ Cl]-2-chloropyridine v ₂₇ + v ₁₉	³⁵ Cl]-2-chloropyrazine v ₂₄ + v ₁₇	³⁵ Cl]-2-chloropyridine 3v ₂₇	³⁵ Cl]-2-chloropyrazine 3v ₂₄	³⁵ Cl]-2-chloropyridine v ₂₇ + v ₂₆	³⁵ Cl]-2-chloropyrazine v ₂₄ + v ₂₃
A ₀ – A _v (MHz)	1.8479 (39)	3.2319 (58)	82.60795 (22)	83.6742 (94)	33.27795 (8 6 0)	35.4219 (58)
B ₀ – B _v (MHz)	–0.893735 (32)	–1.057295 (48)	–3.459535 (22)	–3.345185 (91)	–1.431035 (7 5 0)	–2.451995 (46)
C ₀ – C _v (MHz)	–0.539604 (12)	–0.63697 (30)	–4.54526 (67)	–4.73564 (79)	–2.26584 (2 6 4)	–2.218275 (11)
(Δ _J) ₀ – (Δ _J) _v (kHz)	–0.00039576 (12)	–0.0014517 (37)	–0.00173 (40)	–0.00162 (50)	–0.00083 (9 0 0)	–0.0010917 (61)
(Δ _{JK}) ₀ – (Δ _{JK}) _v (kHz)		0.02685 (15)		–0.014653 (19)		0.01685 (18)
(Δ _K) ₀ – (Δ _K) _v (kHz)						
(δ _J) ₀ – (δ _J) _v (kHz)	0.000014 (59)	–0.0004982 (18)	–0.00018 (70)	–0.0001 (21)	–0.00012 (9 0 2)	–0.0000882 (30)
(δ _K) ₀ – (δ _K) _v (kHz)	0.006271 (26)	–0.004688 (28)	0.037451 (57)	0.036892 (45)	0.012671 (1 0 0)	
	³⁵ Cl]-2-chloropyridine v ₁₇	³⁵ Cl]-2-chloropyrazine v ₁₅	³⁵ Cl]-2-chloropyridine 2v ₁₉	³⁵ Cl]-2-chloropyrazine 2v ₁₇	³⁵ Cl]-2-chloropyridine v ₂₇ + v ₁₈	³⁵ Cl]-2-chloropyrazine v ₂₄ + v ₁₆
A ₀ – A _v (MHz)	1.7079 (18)	–0.6481 (23)		–50.1481 (18)	30.93795 (41)	31.0719 (13)
B ₀ – B _v (MHz)	0.07626 (15)	0.343 (19)	0.013665 (13)	–0.232995 (14)	0.16827 (33)	0.345 (11)
C ₀ – C _v (MHz)	0.914 (20)	0.827235 (12)	2.0014 (56)	1.9316 (46)	–0.843354 (11)	–0.753315 (14)
(Δ _J) ₀ – (Δ _J) _v (kHz)	–0.00112 (20)	–0.0010417 (10)	0.0004142 (12)	–0.0007517 (24)	–0.00060576 (30)	0.0009783 (42)
(Δ _{JK}) ₀ – (Δ _{JK}) _v (kHz)				0.018947 (74)		–0.070153 (13)
(Δ _K) ₀ – (Δ _K) _v (kHz)						
(δ _J) ₀ – (δ _J) _v (kHz)	–0.00017 (10)	–0.0005272 (36)	–0.00006 (10)	–0.0003182 (12)	0.0000163 (14)	0.0008418 (20)
(δ _K) ₀ – (δ _K) _v (kHz)	–0.036629 (18)	–0.018288 (20)	0.004071 (18)		0.022571 (50)	
	³⁵ Cl]-2-chloropyridine v ₂₇ + v ₂₅	³⁵ Cl]-2-chloropyrazine v ₂₄ + v ₂₂	³⁵ Cl]-2-chloropyridine 2v ₂₇ + v ₁₉	³⁵ Cl]-2-chloropyrazine 2v ₂₄ + v ₁₇	³⁵ Cl]-2-chloropyridine 4v ₂₇	³⁵ Cl]-2-chloropyrazine 4v ₂₄
A ₀ – A _v (MHz)	30.40795 (16)	30.3419 (40)		32.294 (29)	109.42795 (30)	111.1119 (21)
B ₀ – B _v (MHz)	–1.178735 (13)	–1.130995 (32)	–1.964935 (18)	–1.253076 (10)	–4.678735 (25)	–4.535995 (17)
C ₀ – C _v (MHz)	–2.019454 (12)	–2.261765 (12)	–2.083034 (12)	–2.27007 (82)	–6.044374 (10)	–6.30385 (47)
(Δ _J) ₀ – (Δ _J) _v (kHz)	–0.00110576 (17)	0.0025183 (49)	–0.00049576 (14)	–0.00088 (89)	–0.00201276 (24)	–0.00148 (35)
(Δ _{JK}) ₀ – (Δ _{JK}) _v (kHz)		–0.126153 (15)		0.0008 (52)		–0.039833 (77)
(Δ _K) ₀ – (Δ _K) _v (kHz)				0.1162 (69)		0.6299 (77)
(δ _J) ₀ – (δ _J) _v (kHz)	–0.00028 (60)	0.0016118 (24)	0.0002 (40)	–0.00008 (55)	–0.00007 (31)	
(δ _K) ₀ – (δ _K) _v (kHz)	0.000871 (31)		0.028171 (22)	0.011382 (18)		
	³⁷ Cl]-2-chloropyridine v ₂₇	³⁷ Cl]-2-chloropyrazine v ₂₄	³⁷ Cl]-2-chloropyridine v ₁₉	³⁷ Cl]-2-chloropyrazine v ₁₇	³⁷ Cl]-2-chloropyridine 2v ₂₇	³⁷ Cl]-2-chloropyrazine 2v ₂₄
A ₀ – A _v (MHz)	28.6731 (48)	28.8588 (29)	–25.6246 (37)	–25.3281 (38)	56.288 (45)	56.9136 (27)
B ₀ – B _v (MHz)	–1.14091 (17)	–1.098982 (10)	0.003466 (21)	–0.108224 (11)	–2.271694 (21)	–2.19621 (34)
C ₀ – C _v (MHz)	–1.488603 (59)	–1.54311 (17)	0.9961 (58)	0.9322 (48)	–2.96484 (49)	–3.08039 (34)
(Δ _J) ₀ – (Δ _J) _v (kHz)	–0.00054 (56)	–0.00058 (14)	–0.00024 (61)	–0.000171 (87)	–0.00121 (90)	–0.00119 (73)
(Δ _{JK}) ₀ – (Δ _{JK}) _v (kHz)	–0.00388 (37)	–0.00319 (62)	0.003459 (30)	0.004435 (10)	–0.005671 (11)	–0.00553 (18)
(Δ _K) ₀ – (Δ _K) _v (kHz)	0.19435 (32)	0.2014 (50)	–0.16278 (11)	–0.2124 (54)	0.36922 (13)	0.3681 (40)
(δ _J) ₀ – (δ _J) _v (kHz)	–0.00006 (75)	–0.00007 (42)	–0.0001 (63)	–0.00004 (66)	–0.00017 (72)	–0.00015 (37)
(δ _K) ₀ – (δ _K) _v (kHz)	0.012495 (15)	0.01253 (0)	–0.017325 (43)	–0.01682 (23)	0.022935 (27)	0.024096 (15)
			³⁷ Cl]-2-chloropyridine v ₂₆	³⁷ Cl]-2-chloropyrazine v ₂₃	³⁷ Cl]-2-chloropyridine v ₁₈	³⁷ Cl]-2-chloropyrazine v ₁₆
A ₀ – A _v (MHz)			6.6573 (24)	4.5837 (65)	–1.6027 (66)	0.3445 (31)
B ₀ – B _v (MHz)			–0.375454 (18)	–0.16328 (26)	1.50155 (49)	1.50922 (23)
C ₀ – C _v (MHz)			–0.739976 (10)	–0.71561 (17)	0.683554 (11)	0.822875 (96)
(Δ _J) ₀ – (Δ _J) _v (kHz)			0.0005 (50)	–0.0001921 (42)	–0.0015841 (34)	–0.0001361 (21)
(Δ _{JK}) ₀ – (Δ _{JK}) _v (kHz)				0.000582 (30)		–0.016888 (11)
(Δ _K) ₀ – (Δ _K) _v (kHz)				–0.0146 (16)		
(δ _J) ₀ – (δ _J) _v (kHz)			0.0003 (70)	–0.000035 (22)	–0.0007201 (17)	0.0000432 (11)
(δ _K) ₀ – (δ _K) _v (kHz)			0.023145 (18)	0.00116 (40)	–0.025155 (58)	–0.00513 (33)

stants estimated by this method should thus be treated with caution. The analysis and examples just discussed, however, demonstrate that estimating the quartic distortion constants using the lower-abundance isotopologue's ground vibrational state constant, adjusted by the change in that constant upon vibrational excitation of the higher-abundance isotopologue, is indeed a highly effective technique.

The current study of the vibrationally excited states of 2-chloropyridine, in combination with a similar study of 2-chloropyrazine [25], permits a revealing extension of the analysis provided above. Table 8 provides a comparison of the changes in rotational and quartic centrifugal distortion constants between

analogous vibrational states of 2-chloropyridine and 2-chloropyrazine. The correspondence of the changes in spectroscopic constants – in terms of both sign and magnitude – for these two different molecules, across 20 vibrationally excited states, is quite remarkable. The similarity of the changes – including those for the quartic centrifugal distortion constants – reflects the underlying structural and spectroscopic characteristics shared by these molecules. These molecules are not isomers: one species containing two nitrogen atoms and four carbon atoms in the ring and the other having only one nitrogen atom and five carbon atoms (with an additional hydrogen atom). Despite a nontrivial difference in molecular composition, the ground state structures, rotations,

and vibrations of these two C₅ molecules share fundamental similarities. We are unaware of other systems for which so substantial a body of experimental data is of sufficiently high accuracy to provide these insights.

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Declaration of competing interest

None.

Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jms.2019.111206>.

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