

The Millimeter-Wave Spectrum of Chlorine Nitrate (ClONO₂): The 2ν₉ and ν₇ Vibrational States

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Chlorine nitrate is a molecule of interest in atmospheric studies because of its role as a reservoir species, removing both chlorine and nitrogen species from catalytic cycles of ozone destruction. The ground and ν₉ vibrational states have been previously studied in the millimeter and submillimeter spectral regions. We have now recorded and analyzed the next states that are lowest in energy, the coupled 2ν₉/ν₇ dyad, from 128 through 355 GHz using a fast scan submillimeter spectroscopic technique system. © 2002 Elsevier Science (USA)

Key Words: chlorine nitrate; ν₇; 2ν₉; ClONO₂; millimeter; spectra; spectroscopy.

I. INTRODUCTION

Chlorine nitrate (ClONO₂) is a planar, near-prolate molecule with several low-lying vibrational states and thus a dense spectrum. It is an important molecule for atmospheric spectroscopists because of its role in stratospheric chemistry, removing both nitrogen and chlorine species from catalytic cycles of ozone destruction and holding them in a reservoir.

The character of the vibrational fundamentals has been established by Miller *et al.* (1). More recently Orphal *et al.* (2) have reported a detailed analysis of the harmonic force field as derived from measured vibrational fundamentals. At longer wavelength, the torsional spectrum has been investigated by Chance and Traub (3).

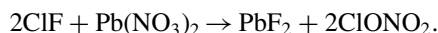
High-resolution spectra of the ν₄ band near 780 cm⁻¹ have been obtained by Bell *et al.* (4) and the observed band contours related to spectroscopic constants. This band has also been investigated by Xu *et al.* (5) in a cooled jet with a diode laser spectrometer, which allowed the assignment of the lower *J* transitions populated in the jet. A similar technique has been applied to the ν₂ band near 1293 cm⁻¹ by Domenech *et al.* (6).

Microwave (7, 8) and millimeter-wave (9, 10) techniques have been used to study the ground and first excited torsional state (ν₉, with an energy of 121.9 cm⁻¹ (2, 3)). The next step in analyzing the thermally populated states is study of the funda-

mental band that is next lowest in energy, ν₇ (ClON in-plane bend) at 262.1 cm⁻¹ (10). This is near enough to 2ν₉ and of the correct symmetry to produce perturbations as energy levels cross. Our analysis studies these states for both the ³⁵Cl and ³⁷Cl isotopes.

II. EXPERIMENT

The chlorine nitrate was synthesized using the reaction (11)



The presence of water in the lead nitrate caused nitric acid to be produced as well, but due to its higher vapor pressure, most of it could be distilled from the sample. The remainder was used as an aid in calibrating the spectra. The measurements were done using the FASSST (fast scan submillimeter spectroscopic technique) system, which uses a backward wave oscillator (BWO) as a source, a 20-foot-long glass cell, and a liquid-helium-cooled InSb bolometer as a detector (12, 13). Three different BWOs were used to acquire data from 128 to 355 GHz. The experimental accuracy of the FASSST is typically 100 kHz.

III. OBSERVED SPECTRA

Chlorine nitrate has dipole components along both the *a* and *b* axes, with the μ_{*a*} being significantly larger (μ_{*a*} = .72(7) D and μ_{*b*} = .24(2) D) (8). Over the frequency range measured,

Supplementary data for this article are available on IDEAL (<http://www.idealibrary.com>) and as part of the Ohio State University Molecular Spectroscopy Archives (<http://msa.lib.ohio-state.edu/jmsa.hp.htm>).

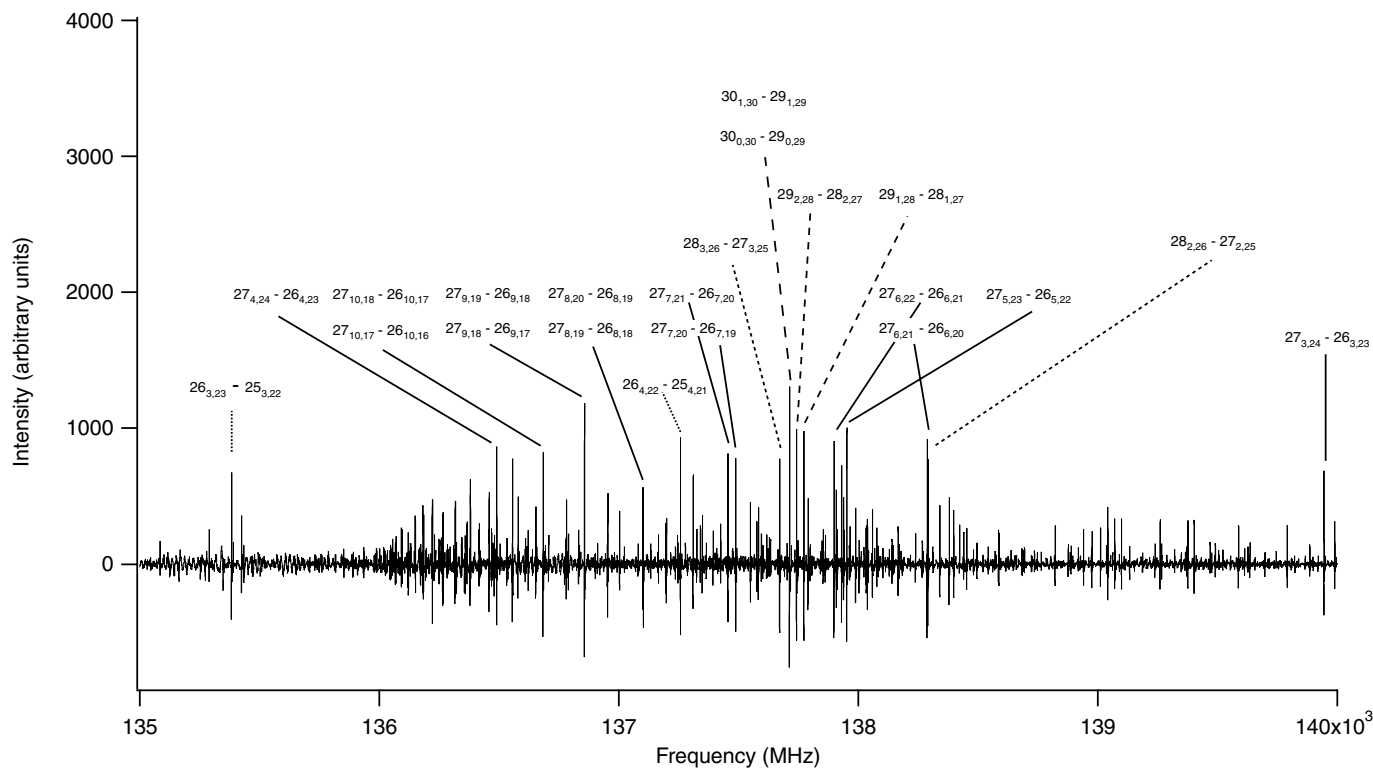


FIG. 1. Compressed spectrum of chlorine nitrate taken with the FASSST system. Ground state lines for the ^{35}Cl isotope are marked up through $K_a = 10$, higher K_a lines for $J = 27-26$ may be seen to the left of the $K_a = 10$ transition. Dotted lines are used to distinguish transitions between J other than $27-26$. The pattern is very similar for the vibrational states; ν_9 lines are the easiest to see, half the intensity of the ground state lines and offset slightly higher in frequency.

the a -type R -branches are by far the strongest transitions. The strongest Q -branch lines, which are b -type, are of intensity similar to that of the weakest observed R -branch lines, and the P -branch lines are an order of magnitude weaker than the Q -branch. Therefore the majority of lines measured are a -type R -branch, with a few b -type R - and Q -branch transitions. A portion of the $J = 27-26$ R -branch is shown in Fig. 1. The high- K_a transitions are symmetric-top-like, but starting at $K_a = 8$ a splitting due to asymmetry becomes visible. This splitting increases rapidly as K_a decreases, resulting in transitions belonging to another R -branch appearing in this one (e.g., the $30_{1,30}-29_{1,29}$ transition). Each vibrational state follows this pattern, but the ground state is easier to pick out to use as an example.

The small energy difference between ν_7 and $2\nu_9$ results in significant $\Delta K_a = 2$ and $\Delta K_a = 3$ interactions between the vibrational states. One of the effects of this is occasional large frequency shifts, up to 2400 MHz, as shown in Fig. 2. This was calculated by comparing predictions from a fit of only the unperturbed lines and with no perturbation constants to the full fit. Most of the perturbations are fairly sharp, since energy levels cross rapidly, as can be seen in the two diagonal bands cutting across the lower right corner. A more grad-

ual crossing occurs between the $K_a = 15$ of $2\nu_9$ and the $K_a = 13$ of ν_7 ; in fact it crosses twice, as seen in Fig. 3. Due to the nearly complete mixing of states at the heights of some of these perturbations, transitions between vibrational states are observed; an example of this is shown in Fig. 4. Some of those measured are listed in Table 1. Also, due to the mixing of states, a few b -type transitions switch intensities with their a -type counterparts. Some selected transitions of this type are listed in Table 2. Another perturbation-induced effect is a modification of the quadrupole pattern, as shown in Fig. 5. The lower trace shows two transitions in ν_7 , each having four near-degenerate components, and the upper trace shows them in $2\nu_9$ where they have split, leaving two components in each transition.

The two most abundant isotopomers of chlorine nitrate are $^{35}\text{ClONO}_2$ and $^{37}\text{ClONO}_2$, with the ^{37}Cl isotope being one-third the abundance of the ^{35}Cl isotope. Transitions from $J = 25$ to 75 were measured, from $K_a = 0$ to 35 for the ^{35}Cl and from $K_a = 0$ to 20 for the ^{37}Cl . The ^{37}Cl isotope lines are shifted lower in frequency, starting on the order of 3 GHz at the beginning of the measured range and increasing steadily to on the order of 10 GHz at the end. The pattern of transitions is the same, except in the perturbed areas. Due to the difference in vibrational

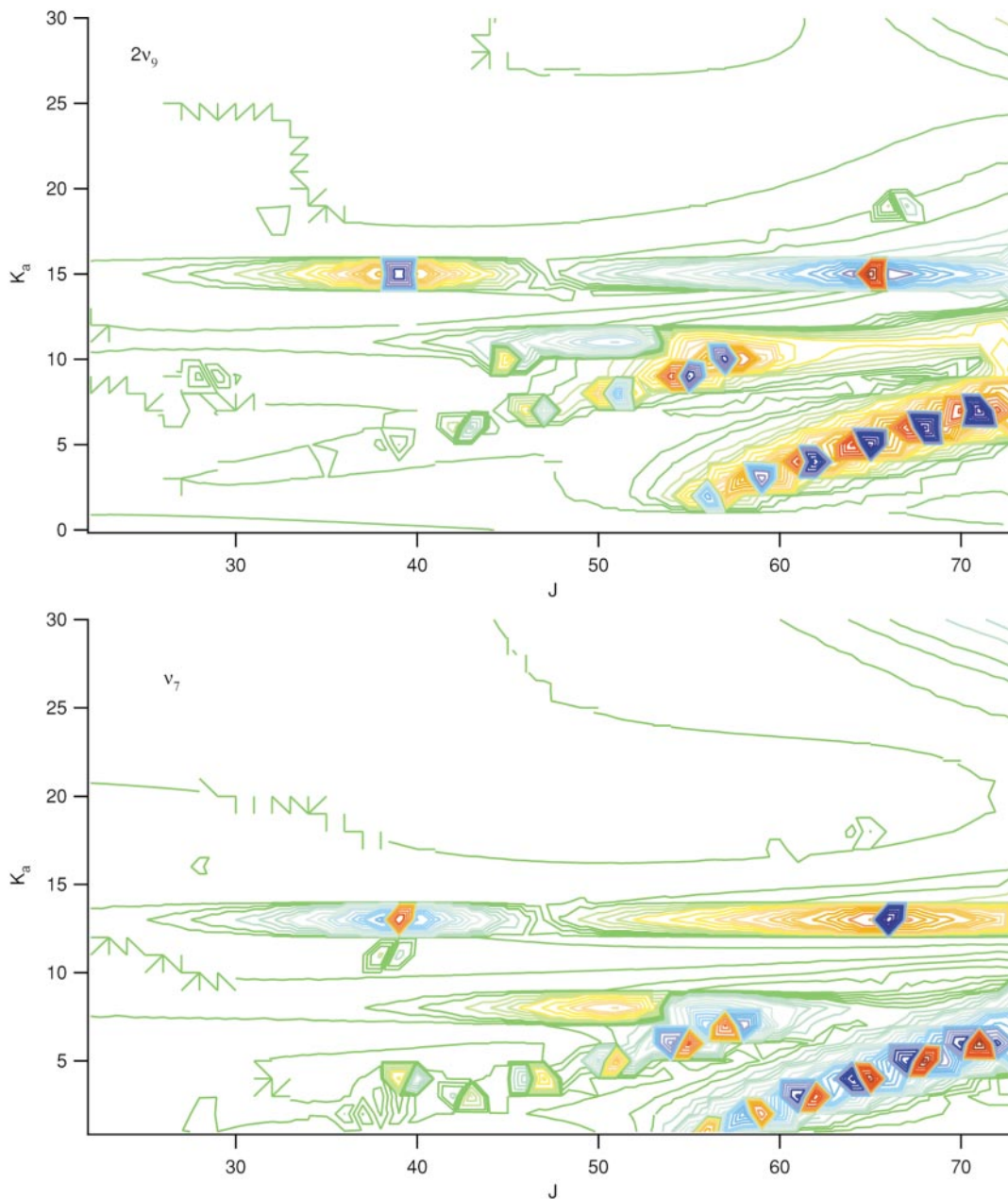


FIG. 2. The J and K_a dependence of the frequency shifts in R -branch a -type lines due to $\Delta K_a = 2$ and 3 interactions for $2\nu_9$ ($K_c = J - K_a$) in the upper graph and for ν_7 ($K_c = J - K_a + 1$) in the lower graph. The contours go from -2500 MHz (dark red) to 2500 MHz (dark blue). The progression of contours is 0, 1, 2, 4, 6, 8, 10, 15, 20, 25, 30, 40, 50, 60, 70, 100, 130, 160, 200, 300, 400, 500, 700, 900, 1200, 1500, 1900, 2500.

energy between the isotopes (calculated to be 2.69 cm^{-1} for ν_7 (10)), the perturbations are centered on different J and K_a values. The most significant difference between the isotopes is the perturbation between $K_a = 15$ of $2\nu_9$ and $K_a = 13$ of ν_7 in the ^{35}Cl isotope. This perturbation is shifted in K_a by 1 for the ^{37}Cl isotope, so that it is between $K_a = 14$ of $2\nu_9$ and $K_a = 12$ of ν_7 and does not begin until J is in the 50s, as opposed to being

observable across the entire range of measured frequencies as in the ^{35}Cl isotope.

IV. ANALYSIS

A separate analysis was done for each isotopomer using Pickett's SPFIT and SPCAT programs (14), with a Watson's S

TABLE 1
Selected Interstate Transition Frequencies (MHz); $2\nu_9$ Is $v = 0$, ν_7 Is $v = 1$

J''	K''_a	K''_c	v''	F''	J'	K'_a	K'_c	v'	F'	obs. freq.	$o - c$
39	13	26	1	39	38	15	23	0	38	197285.0561	0.1094
39	13	27	1	38	38	15	24	0	38	197285.9419	0.1631
39	15	25	0	38	38	13	26	1	37	167296.3357	-0.0879
65	4	62	1	65	64	5	59	0	64	309972.3936	0.0270
65	4	62	1	64	64	5	59	0	63	309974.3777	0.1200
65	5	60	0	64	64	4	61	1	63	316993.9591	-0.1471
65	6	60	0	64	64	3	61	1	63	317001.1698	-0.1368
65	6	60	0	66	64	3	61	1	65	317003.0183	0.0219
65	15	50	0	67	64	13	51	1	66	331944.7491	0.0879
65	13	52	1	54	64	15	49	0	63	331972.4324	-0.0370
68	6	62	0	67	67	5	63	1	66	334321.3615	-0.0630
68	6	62	0	69	67	5	63	1	68	334323.3939	0.1496
68	7	62	0	70	67	4	63	1	69	334368.3417	-0.0909
66	15	52	0	67	65	13	53	1	66	337122.2103	0.1186
66	13	54	1	68	65	15	51	0	67	337277.8073	0.0016

TABLE 2
Selected b -Type Transitions with Strong Intensity Due to Mixing of States

J''	K''_a	K''_c	v''	F''	J'	K'_a	K'_c	v'	F'	obs. freq.	$o - c$
37	1	36	1	39	36	2	35	1	38	173377.8155	-0.07855
59	2	57	1	61	58	3	56	1	60	276809.5619	-0.06310
62	3	59	1	64	61	4	58	1	63	294853.3329	-0.11525
64	2	62	1	66	63	3	61	1	65	299251.8489	-0.13759
65	2	63	1	67	64	3	62	1	66	303721.5466	0.04704
67	3	64	1	69	66	4	63	1	68	317272.9238	-0.06911
68	3	65	1	70	67	4	64	1	69	321728.6917	0.01750
70	5	66	1	70	69	4	65	1	69	335331.7698	-0.02011
70	4	66	1	70	69	5	65	1	69	335332.4026	0.07846
69	5	64	1	71	68	6	63	1	70	335624.5627	-0.03636

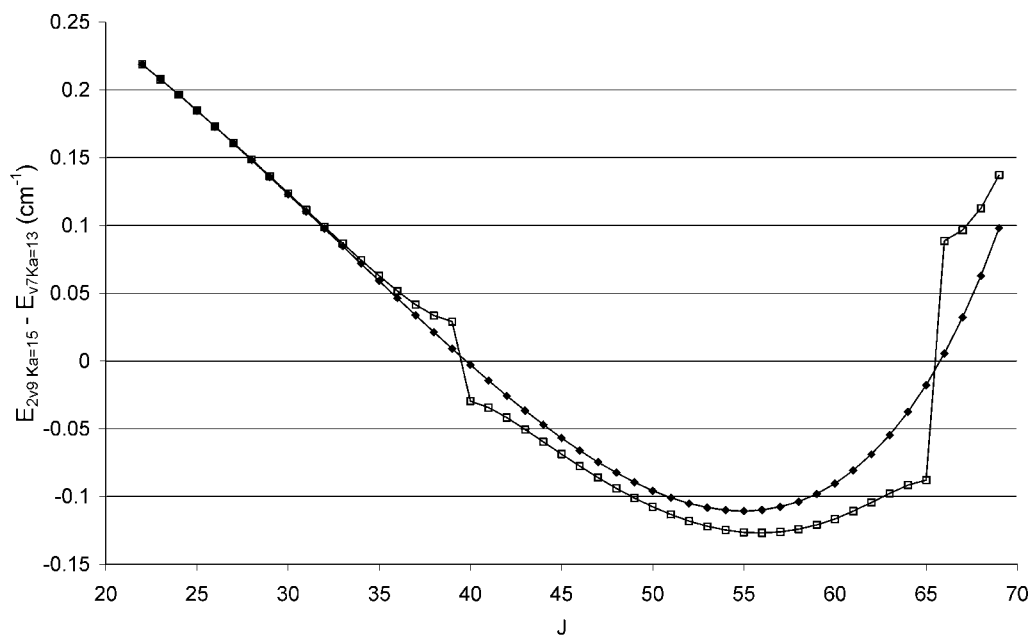


FIG. 3. The J dependence of the difference in energies between the ν_7 $K_a = 13$ and the $2\nu_9$ $K_a = 15$ perturbed energy levels (\square) and theoretical unperturbed energy levels (\blacklozenge). As the unperturbed energy difference approaches zero, the perturbed levels shift to avoid that crossing, causing large mirror image frequency shifts in both vibrational states.

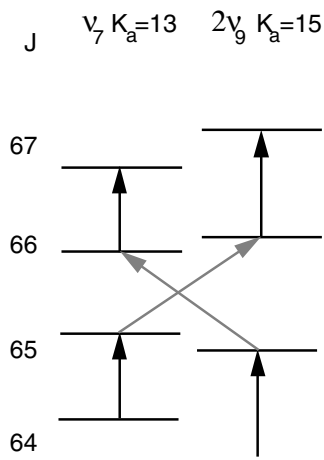


FIG. 4. Example transitions between vibrational states due to mixing of states, $66_{15,52}(2\nu_9) \leftarrow 65_{13,53}(\nu_7)$ and $66_{13,54}(2\nu_9) \leftarrow 65_{15,52}(\nu_7)$.

reduction as chlorine nitrate is near-prolate ($\kappa = -0.9$ (10)). For the ^{35}Cl isotope, 3180 transitions were included in the fit, while the ^{37}Cl isotope included 1953 transitions (not counting quadrupole degeneracies as separate transitions). A complete

list of measured transitions is available as supplementary data (see footnote on title page).

The constants obtained are shown in Table 3. Each analysis used the quadrupole constants previously determined for the ground state (10), and included $\Delta K_a = 1, 2,$ and 3 interaction terms. These off-diagonal terms can be expressed as

$$H_{vv'} = 2F_{\pm}J_{bc}^2 + 2[F_{\pm J}J^2 + F_{\pm K}J_a^2 + F_{\pm JK}J^2J_a^2, J_{bc}^2]_{+} \\ + (C_{ab} + C_{abJ}J^2 + C_{abK}J_a^2)[J_a, J_b]_{+} + C_3(J_{+}^3 - J_{-}^3)/2 \\ + C_{3a}[J_a, (J_{+}^3 + J_{-}^3)]_{+}/\sqrt{2}, \quad [1]$$

where

$$[A, B]_{+} = AB + BA \quad [2]$$

$$J_{bc}^2 = J_b^2 - J_c^2. \quad [3]$$

Centrifugal distortion constants including all the P^6 s and two P^8 s were used for both isotopes. Because of the

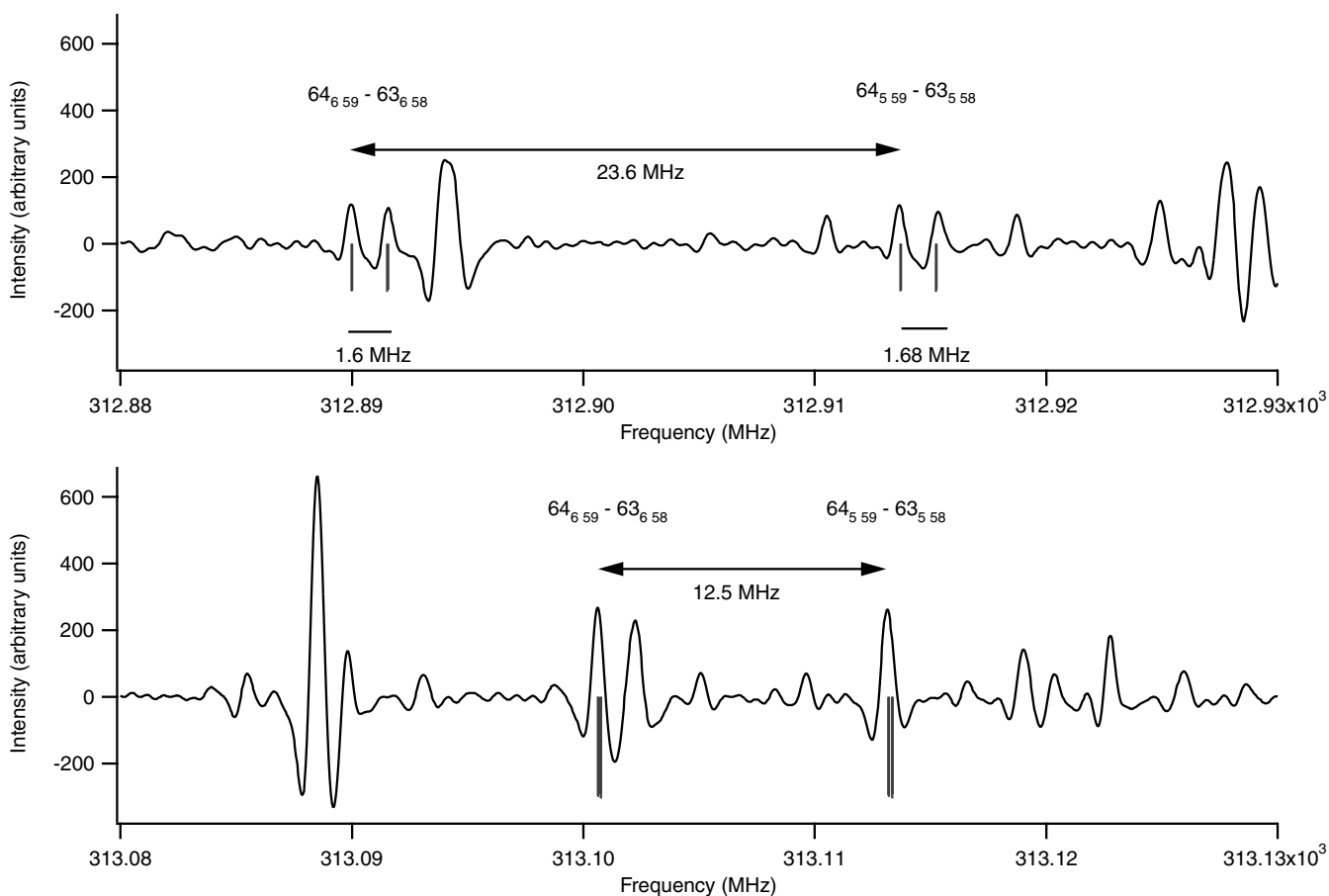


FIG. 5. The $64_{6,59} \leftarrow 63_{6,58}$ and $64_{5,59} \leftarrow 63_{5,58}$ transitions in the $2\nu_9$ state (upper graph) and the ν_7 state (lower graph). The $2\nu_9$ transitions are shifted -1321 and -1309 MHz, respectively, due to a $\Delta K_a = 2$ perturbation, with a visible change in the quadrupole pattern, while the ν_7 transitions are not split.

TABLE 3
Rotational, Centrifugal Distortion, and Perturbation Constants (MHz)

Parameter	³⁵ ClONO ₂		³⁷ ClONO ₂	
	ν_7	$2\nu_9$	ν_7	$2\nu_9$
A	12116.8725(164)	11932.9734(175)	12111.797(41)	11936.193(55)
B	2771.27229(73)	2776.26133(67)	2695.50329(107)	2700.28761(103)
C	2251.95469(52)	2264.61104(50)	2201.8618(11)	2213.58979(122)
D _J · 10 ⁴	4.82412(119)	5.32509(115)	4.4603(40)	5.2628(42)
D _{JK} · 10 ³	4.8580(38)	2.9153(32)	7.0903(178)	0.6408(155)
D _K · 10 ²	-0.2786(142)	1.8529(130)	0.825(64)	2.433(82)
d ₁ · 10 ⁴	-1.25823(121)	-0.85895(114)	-1.02805(152)	-0.78454(179)
d ₂ · 10 ⁵	1.6066(56)	-1.9282(56)	-2.0962(93)	-1.2064(95)
H _J · 10 ¹⁰	—	-4.545(133)	—	-9.79(92)
H _{JK} · 10 ⁷	-0.1995(47)	-0.1538(518)	.1221(255)	-0.235(32)
H _{JKK} · 10 ⁶	0.5135(48)	-0.5288(41)	1.638(2)	-1.405(37)
H _K · 10 ⁶	-9.24(43)	0.99(32)	24.587(293)	9.8(44)
h ₁ · 10 ¹⁰	-3.334(150)	-2.449(140)	-1.037(184)	1.116(234)
h ₂ · 10 ¹⁰	1.904(102)	-1.693(103)	—	0.588(156)
h ₃ · 10 ¹¹	2.499(313)	3.937(303)	7.41(66)	—
L _J · 10 ¹⁴	—	—	1.74(78)	2.69(78)
L _{JK} · 10 ¹²	7.53(60)	-7.76(50)	—	114.8(106)
L _{KKJ} · 10 ⁹	-0.1351(53)	0.1188(47)	1.432(89)	-1.277(59)
L _K · 10 ⁸	—	—	-6.691(272)	-1.86(65)
Interaction Constants				
F _±	-0.34604(260)	—	-0.5117(43)	—
F _{±J} · 10 ⁶	-5.45(80)	—	3.0(8)	—
F _{±K} · 10 ⁴	1.328(141)	—	1.304(42)	—
F _{±JK} · 10 ⁸	1.83(43)	—	3.50(67)	—
C _{ab}	5.458(91)	—	21.801(72)	—
C _{abJ} · 10 ⁵	7.18(34)	—	-64.08(36)	—
C _{abK} · 10 ²	-0.1736(85)	—	-1.8467(102)	—
C ₃ · 10 ²	-0.1423(164)	—	1.9752(144)	—
C _{3a} · 10 ⁴	—	—	-4.448(65)	—
E _{v7} -E _{2v9}	503805.07(79) MHz	—	456440.92(138) MHz	—
rms	16.793502(26) cm ⁻¹	—	15.214697(46) cm ⁻¹	—
	113.5 kHz	—	137.4 kHz	—

interactions, ΔE_v could also be fit, and with good accuracy, 16.793476(24) cm⁻¹ for ³⁵Cl and 15.214766(42) for ³⁷Cl. With E_{ν_7} measured at 262.1 cm⁻¹ (12), $E_{2\nu_9}$ can be calculated as 245.3 cm⁻¹ for ³⁵ClONO₂. These constants allow predictions of lines within 1 MHz for both lower and higher J than measured, and for higher K_a with the ³⁷Cl isotope, but not much higher K_a for the ³⁵Cl isotope because another perturbed range is predicted with K_a in the low to mid 40s.

V. CONCLUSION

The pure rotational spectrum of the $2\nu_9$ and ν_7 vibrational states of chlorine nitrate have been measured and analyzed, allowing predictions of transitions in the millimeter and sub-millimeter region for both ³⁵Cl and ³⁷Cl isotopes and modeling of the thermally populated rotational structure. The interactions

between the two states have been studied and fit within experimental error.

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