Note

The millimeter-wave spectrum of chlorine nitrate (ClONO$_2$): the $3v_9$ and v_7v_9 interacting dyad[☆]

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There is a growing interplay between infrared observations of rotation–vibration transitions and microwave measurements of the rotational structure of the vibrational states. This interplay has perhaps been most extensive in HNO$_3$ (e.g., [1–3]). ClONO$_2$ is a similar, but more challenging case for both infrared and microwave analysis. In the infrared, the closely spaced transitions make the resolution of individual lines difficult. In the microwave, the large number of thermally populated vibrational states makes assignment of the rotational spectrum of higher lying vibrational states challenging.

The pure rotational spectra of the lowest lying states have been studied in the millimeter and submillimeter regions: the ground and v_9 states [4–6], and the $2v_9/v_7$ dyad [7]. Because of the dense rotational structure of ClONO$_2$, the analysis of the $2v_9/v_7$ dyad involved several different level crossings, numerous couplings, and extensive perturbations, especially when modeled at microwave accuracy. This is also the case for the coupled dyad of $3v_9$ and v_7v_9, which is the next step in our goal of analyzing the thermally populated states.

The chlorine nitrate was synthesized using the reaction between chlorine monofluoride and lead nitrate [8]. Data were taken with a FASSST system [9] between 122 and 356 GHz, and with a phase-locked BWO between 78 and 118 GHz. Pickett's SPFIT program suite [10] was used to fit the data and to generate predictions.

For the ^{35}ClONO$_2$ isotope, 3559 lines were fit for an rms of 110 kHz. The ^{37}ClONO$_2$ isotope had 3259 lines assigned for an rms of 107 kHz. It is of interest to compare these fits with the fits for the $2v_9$ and v_7 dyad [7]. For example, for $2v_9$ and v_7, $\Delta E_v = 16.793476(24)$ and $15.214766(42)$ cm^{-1} for ^{35}Cl and ^{37}Cl, respectively. For $3v_9$ and v_7v_9, $\Delta E_v = 24.321668(18)$ and $22.76589(13)$ cm^{-1}. This larger ΔE_v shifts the perturbations higher in K_a; for ^{35}Cl, the $\Delta K_a = 2$ perturbation that was between $K_a = 15$ and 13 for $2v_9$ and v_7 is now between $K_a = 22$ and 20 for $3v_9$ and v_7v_9. Similarly the main $\Delta K_a = 3$ perturbation that was between $K_a = 11$ and 8 is shifted to $K_a = 15$ and 12. The shifts in ^{37}Cl are from 14 and 12 to 20 and 18, and from 10 and 7 to 14 and 11. Another change is that the sharp (few J affected) perturbations in low K_a were previously $\Delta K_a = 2$ and $\Delta K_a = 3$ interactions in $2v_9$ and v_7, now they are $\Delta K_a = 4$ and $\Delta K_a = 5$ interactions for $3v_9$ and v_7v_9.

The transitions at the peak of these sharp perturbations also have a change in the quadrupole pattern; usually four degenerate transitions become a doublet of two degenerate transitions. For the ^{37}Cl isotope, with a third less intensity than the ^{35}Cl, this additional decrease in line intensity resulted in these highly perturbed lines not being assigned with any accuracy, and they were not used in the fit. Perturbed lines on either side of the peak were included. A separate analysis was done for each isotopomer with a Watson's S reduction Hamiltonian in the I^r representation. A complete list of measured transitions and the details of the fit can be found in the journal's on-line supplemental material. The constants used in the fits are listed in Table 1.

Because of the fitting indetermancy between the vibrational energy separation and the first order Fermi and Coriolis constants, these constants have been set to zero, as in our earlier analysis of the $v_7/2v_9$ [11]. This choice impacts the definitions of these mixed states and the derived constants. Additionally, as we have shown

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Table 1
Rotational, centrifugal distortion, and perturbation constants (MHz)

Parameter	ClNO$_3$		^{37}ClNO$_3$	
	v_7v_9	$3v_9$	v_7v_9	$3v_9$
A	11998.2681(138)	11851.6172(41)	11993.0950(236)	11853.6515(229)
B	2771.22763(43)	2776.033420(301)	2695.54060(43)	2700.13364(39)
C	2256.86549(33)	2267.908567(252)	2206.60557(40)	2216.81612(36)
$D_J \times 10^4$	4.92048(79)	5.39778(64)	4.69246(75)	5.20900(72)
$D_{JK} \times 10^3$	4.71417(155)	3.02386(129)	4.68506(140)	2.76974(135)
$D_K \times 10^2$	−0.3013(114)	1.7344(59)	−0.3082(161)	1.8774(122)
$d_1 \times 10^4$	−1.06375(87)	−0.85811(73)	−1.01044(85)	−0.78900(80)
$d_2 \times 10^5$	−1.43332(677)[a]	−1.94529(394)	−1.28558(875)	−1.80364(795)
$H_J \times 10^{10}$	−0.7625(999)	−2.5717(895)	−1.1553(971)	−2.488(102)
$H_{JJK} \times 10^8$	−0.9583(239)	0.2366(161)	−1.1432(214)	0.1771(207)
$H_{JJK} \times 10^7$	2.4658(179)	2.7687(153)	3.5277(309)	−3.7906(312)
$H_K \times 10^6$	−4.472(181)	–	–	–
$h_1 \times 10^{10}$	−1.594(118)	1.220(99)	−1.803(119)	1.127(113)
$h_2 \times 10^{11}$	7.53(117)	−4.25(73)	7.19(128)	−6.22(117)
$h_3 \times 10^{11}$	−0.893(353)	2.02(32)	–	–
Interaction constants				
$F_{400vv'}$		0.4229(42)		0.3857(78)
$F_{410vv'} \times 10^5$		−9.263(969)		−6.92(218)
$F_{500vv'} \times 10^7$		3.37(120)		4.83(221)
$F_{6100vv'}$		−2.097(99)		−0.775(95)
$F_{6101vv'} \times 10^4$		−1.252(29)		1.643(46)
$F_{6200vv'} \times 10^2$		0.720(15)		−1.196(15)
$F_{6400vv'} \times 10^8$		−1.357(135)		7.124(204)
$E_{v7v9} - E_{3v9}$		729650.03(53) MHz		682976.6(40) MHz
		24.321668(18) cm^{-1}		22.76589(13) cm^{-1}
rms		110.4 kHz		107.4 kHz

Note. The quadrupole constants were fixed at the values of [6] for this analysis.

[a] The corresponding constant in v_7 of [7] should also be negative.

Table 2
Off-diagonal terms used for perturbations in the I^r representation

SPFIT parameter	ΔK_a	Hamiltonian term
$(3+q)nmvv' \quad q=1,2,\ldots$	$2q$	$\frac{1}{4}\left[\left[J_+^{2q}+J_-^{2q},J_a^{2n}\right]_+,J^{2m}\right]_+$
$6qnmvv' \quad q=0,2,4,\ldots$	$q+1$	$\frac{1}{8}\left[\left[(J_+^{q+1}-J_-^{q+1}),J_a^{2n}\right]_+,J^{2m}\right]_+$
$6qnmvv' \quad q=1,3,5,\ldots$	q	$\frac{1}{8}\sqrt{\frac{q+1}{2}}\left[\left[\left[J_a,(J_+^q+J_-^q)\right]_+,J_a^{2n}\right]_+,J^{2m}\right]_+$

$J_+ = J_b + \mathrm{i}J_c, J_- = J_b - \mathrm{i}J_c, [A,B]_+ = AB + BA$.

I^r representation $(x=b, y=c, z=a)$.

for the rotational constants of the mixed $v_5/2v_9$ dyad in HNO$_3$ [11], while the values of the constants in the individual states can vary significantly as a function of this choice, their averages are quite constant. For example, for the dyad discussed here the averaged values of the P4 distortion parameters are very similar to the values obtained for the ground and unperturbed v_9.

The off-diagonal interaction terms are labeled according to their parameter identification values in SPFIT. To assist going between the SPFIT code and the interaction terms in the Hamiltonian, the parameters for the I^r representation are listed in Table 2. The first item is for anharmonic perturbations, with $\Delta K_a = \pm 2, \pm 4, \ldots$ and the second and third are for Coriolis-type perturbations with $\Delta K_a = \pm 1, \pm 3, \ldots$.

While the general form of the interaction operators is quite clear from the on-line documentation for SPFIT (found at spec.jpl.nasa.gov), the specific combination of operators and multipliers is less clear. For future reference we have provided Table 2 as a reference. These operators were verified by checking the energy levels from hand calculations against the output of SPCAT. To make earlier constants consistent with these publications, the following parameters should be divided by a factor of 2: [12] parameters W_K and W_J, [13] parameters $F_{j^2,\pm}, F_{k^2,\pm}$, [11] parameters $D_{ab}, E_{\rho\pm J}$ and the group of parameters in Eq. (5) that are anti-commutated with J_{bc}^2, the group of parameters in [7] in Eq. (1) that are anti-commutated with J_{bc}^2, and the parameter C_{abK} corresponds to the operator $\frac{1}{2}[J_a^2,[J_a,J_b]_+]_+$.

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