

Note

The millimeter-wave spectrum of chlorine nitrate (ClONO₂): The ν_6 vibrational state

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Abstract

The pure rotational spectrum of chlorine nitrate in its $\nu_6 = 1$ excited vibrational state has been studied. A total of 2901 lines, with K_a extending to 33 in the ³⁵Cl isotopologue and 30 in the ³⁷Cl isotopologue, respectively, have been recorded and assigned. This analysis, along with our recently reported study of the $\nu_5/\nu_6\nu_9$ dyad and the improved energy levels of ν_9 reported in this paper, should make possible accurate simulation of the corresponding ν_6 band and its complex hot band structure near 435 cm⁻¹.

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With the increase in spectral coverage of microwave spectroscopy and the growth in resolution of infrared spectroscopy, what were once separate disciplines studying separate subjects (rotational and vibrational spectroscopy, respectively) are now a single community studying the rotational–vibrational problem. ‘Infrared’ analyses of complex polyatomic molecules have long contained microwave data [1,2] and ‘microwave’ analyses are beginning to calculate the rotational structure of infrared bands [3,4].

Chlorine nitrate is a particularly good candidate for this latter approach because it is heavy enough that its rotational structure is at best partially resolved in the infrared. As a result, atmospheric retrievals have been based on some combination of laboratory derived band strengths and semi-empirical representations of the spectral contours and their temperature dependence [5,6].

Studies of chlorine nitrate in its unperturbed ground and $\nu_9 = 1$ state have been reported [7–9]. However, because the vibrational energy of the $\nu_9 = 1$ (120 cm⁻¹) is close to half that of $\nu_7 = 1$ (260 cm⁻¹), there are many polyads ($2\nu_9/\nu_7$, $3\nu_9/\nu_7\nu_9$, etc.) that are coupled by strong perturbations. We have reported analyses of several of these [10–13]. There is also a less systematic perturbation that leads to the $\nu_5/\nu_6\nu_9$ dyad [14].

In this note, we report the pure rotational spectrum of the essentially unperturbed $\nu_6 = 1$ state, which gives rise to the infrared spectrum around 435 cm⁻¹. This analysis, along with the recently reported $\nu_5/\nu_6\nu_9$ dyad [14] and the known ν_9 rotational energy level structure [9], provides a basis for an accurate simulation of the rotational structure in this region, including the strongest hot bands.

The experimental basis of the assignment and analyses reported here primarily differs from the work which we have previously reported on ClONO₂ in that the FASSST [15] data are based on a 400 scan average, rather than the single scan previously used. This increases the effective

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integration time to $\sim 10^{-3}$ s, and combined with an improved sample preparation, increases the S/N of the spectrum by ~ 100 . The frequencies of points in the spectrum have also been determined with greater precision due to several improvements in the frequency calibration

procedure, in which information from up- and down-frequency scans is averaged [16].

Because $v_6 = 1$ is about 50 cm^{-1} removed from any of the other vibrational states, it was expected that its rotational structure would be largely unperturbed. Accord-

Table 1
Comparison of S -reduction constants for the ground, $v_9 = 1$, and $v_6 = 1$ states of ClONO_2

Parameter	^{35}Cl			^{37}Cl		
	Ground state ^{a,b}	$v_9 = 1^b$	$v_6 = 1$	Ground state ^{a,b}	$v_9 = 1^b$	$v_6 = 1$
A	/MHz	12105.78277(23) ^c	12004.64061(28)	12116.7640(12)	12105.32502(32)	12117.821(11)
B	/MHz	2777.000768(39)	2776.814605(50)	2767.489285(86)	2700.973934(37)	2691.96268(24)
C	/MHz	2258.151163(37)	2262.133094(45)	2250.240091(76)	2207.604555(35)	2200.10340(21)
D_J	/kHz	0.500743(10)	0.508498(11)	0.508792(22)	0.4810004(97)	0.488293(10)
D_{JK}	/kHz	3.854253(83)	3.845749(92)	3.89561(22)	3.71562(11)	3.70850(11)
D_K	/kHz	9.4738(16)	8.10675(62)	9.796(14)	9.6419(34)	8.2395(25)
d_1	/kHz	-0.0957017(60)	-0.0958169(67)	-0.096306(14)	-0.0896618(57)	-0.0897908(89)
d_2	/kHz	-0.0177421(29)	-0.0169201(31)	-0.0179256(27)	-0.0161924(30)	-0.0154106(18)
H_J	/Hz	-0.0001361(10)	-0.0001365(10)	-0.0001524(24)	-0.00012483(92)	-0.0001285(10)
H_{JK}	/Hz	-0.005812(11)	-0.005697(10)	-0.005922(23)	-0.005504(12)	-0.005405(12)
H_{KJ}	/Hz	-0.015042(56)	-0.011281(55)	-0.01796(23)	-0.01488(10)	-0.01115(10)
H_K	/Hz	0.0391(25)	[0.0391] ^b	[0.0391]	0.0367(58)	[0.0367]
h_1	/Hz	-0.00002388(73)	-0.00002350(75)	-0.0000258(18)	-0.00002142(63)	-0.0000178(10)
h_2	/Hz	-0.00000446(43)	-0.00000247(45)	[-0.00000446]	-0.00000297(43)	[-0.00000297]
h_3	/Hz	0.00000472(25)	0.00000296(23)	[0.00000472]	0.00000457(23)	[0.00000457]
$3\chi_{aa}/2$	/MHz	-125.907(60)	[-125.907]	[-125.907]	-99.121(93)	[-99.121]
$(\chi_{bb} - \chi_{cc})/4$	/MHz	-11.130(13)	[-11.13]	[-11.13]	-8.699(14)	[-8.699]
χ_{ab}	/MHz	74.216(47)	[74.216]	[74.216]	58.539(80)	[58.539]
N_{lines}^d		2810	2523	1668	2119	2006
σ_{fit}	/kHz	44.9	47.9	56.7	40.7	42.5
σ_w^e		0.5677	0.5306	0.6178	0.5274	0.4536
$K_a \text{ max}$		43 (R + Q)	41 (R + Q)	33 (R + Q)	35 (R + Q)	36 (R + Q)

^a Ref. [14].

^b The new datasets comprise of new measurements complemented by those reported in Ref. [9].

^c Round parentheses enclose standard errors in the fitted values given in units of the last quoted digit. Square parentheses enclose assumed values fixed to those for the ground state.

^d The number of distinct frequency lines in the fit.

^e The weighted, root mean square deviation of the fit, in which synthesizer lines were assigned measurement error of 50 kHz, and FASSST lines an error of 100 kHz.

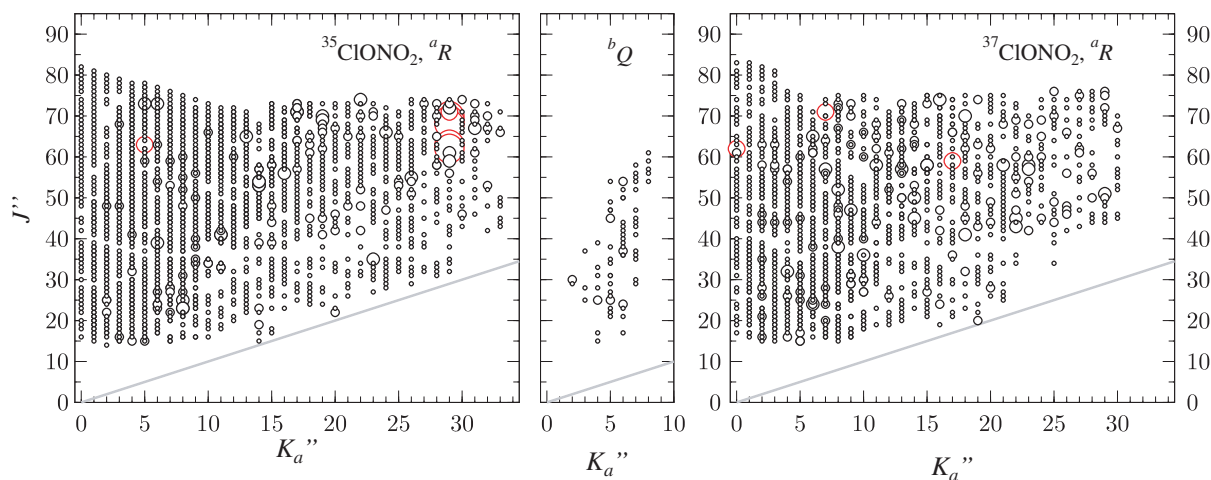


Fig. 1. Dataset distribution plots as a function of quantum numbers J'' and K_a'' for rotational transitions in the $v_6 = 1$ vibrational state in $^{35}\text{ClONO}_2$ and $^{37}\text{ClONO}_2$. Circle diameters are proportional to the magnitudes of the values of obs. – calc. and are such that the red circles are all for obs. – calc. < 0.3 MHz.

ingly, the analysis was based on Watson's unperturbed asymmetric rotor theory [17]. The fits and predictions were done with Pickett's SPFIT/SPCAT package [18,19]. There are six vibrational states for each isotopologue in the spectrum that are lower in energy than ν_6 , so rotational transitions in the lower states have to be considered. For this reason the assignment and construction of the datasets were carried out with the help of the AABS package for Assignment and Analysis of Broadband Spectra [20,21]. The package provides mechanisms for keeping track of transitions already assigned in various vibrational states and for rapid reduction of the spectrum to datasets for the fitting program.

Table 1 summarizes the results of our analysis of 1668 lines in the ^{35}Cl isotopologue and 1233 lines in the ^{37}Cl isotopologue of ν_6 . The table also includes expanded analyses of the ground state [14] and of the $\nu_9 = 1$ state of each isotopologue that were made possible by the improved experimental data. In ν_6 lines as high as $K_a = 33$ and $K_a = 30$ could be assigned with confidence for the ^{35}Cl and ^{37}Cl species, respectively. Fig. 1 shows the distributions in quantum number of the assigned lines for the two isotopologues. The majority are ^aR -type, although for the more abundant ^{35}Cl species several low K_a sequences of ^bQ -type lines could be assigned with confidence on the basis of characteristic hyperfine splitting patterns. The lack of Q-type transitions for $^{37}\text{ClONO}_2$ is the reason why some constants, such as A and D_K , are more poorly determined for this isotopologue. Close inspection of Fig. 1 indicates the existence of a small perturbation in the $K_a = 29$ R-branch sequence for $^{35}\text{ClONO}_2$ with a maximum near $J = 65$. Although the sensitivity of the FASSST spectrum was sufficient for assigning transitions in the ν_6 state, it was still necessary to exercise considerable care when dealing with weaker transition sequences. This is illustrated in Fig. 2, which shows that even in the relatively well visible $K_a = 20$ and 25 sequences there are a significant number of spurious overlaps that lead to anomalous intensities of several lines that would be acceptable if only correspondence between predicted and observed frequency was used. In the much weaker $K_a = 30$ sequence such overlaps become sufficiently serious to disqualify about half of the potentially measurable components, and the importance of careful consideration of the intensity information also increases. Fortunately, the lower- J high K_a lines exhibit doubling from chlorine nuclear quadrupole splitting and this can be used as additional information for assignment.

Inspection of the spectral constants in Table 1 shows that the analyses are well behaved, with only modest changes in the constants with changes in vibrational state or isotopologue and no evidence of the effects of a perturbation being absorbed into any of the spectral constants. Because of less extensive excited state datasets than for the ground state, some of the higher order constants of ν_6 and ν_9 have been constrained at their corresponding ground state values. The assignment of ν_6 is ultimately based on three factors: intensities of transitions in relation to those in excited states

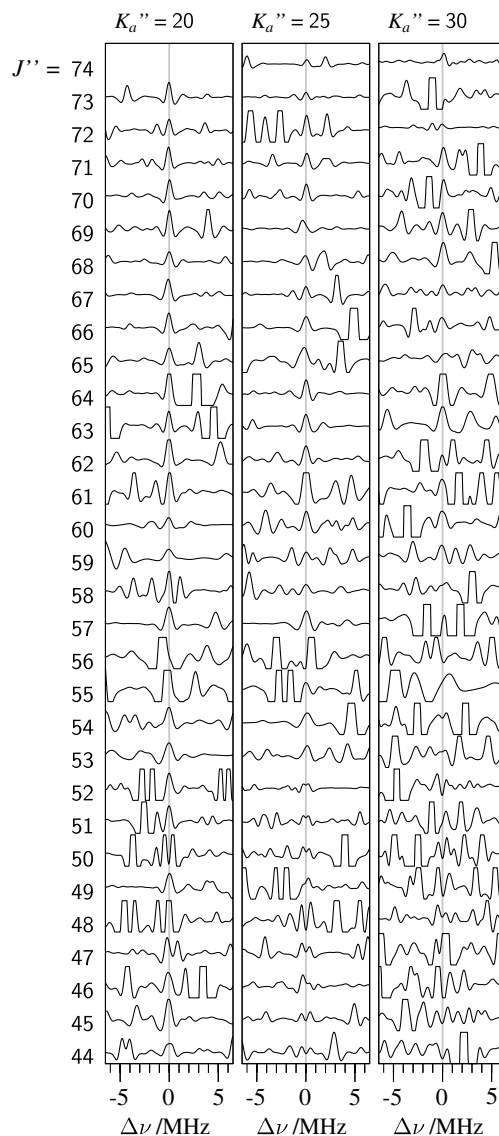


Fig. 2. Illustration of actual lineshapes and intensities for successive $\nu_6 = 1$ state R-type transitions in the FASSST spectrum of $^{35}\text{ClONO}_2$. In this Loomis-Wood type plot each spectral segment is centered on the relevant calculated transition frequency resulting from the final fit. The intensity axis in the $K_a'' = 30$ pane has been expanded by a factor of two relative to the two other panes.

of similar vibrational energy, on the isolated nature of this state, and on values of inertial defect, Δ_i , for the newly assigned state. The rotational constants in Table 1 correspond to $\Delta_i = 0.26704(1) \text{ u}\text{\AA}^2$ for $^{35}\text{ClONO}_2$ and $0.26524(5) \text{ u}\text{\AA}^2$ for $^{37}\text{ClONO}_2$, which are in very good agreement with values 0.26163 and $0.26045 \text{ u}\text{\AA}^2$ for the two isotopologues, respectively, calculated from the fitted harmonic force field [9]. The assigned line frequencies in a format that is convenient for use are often much more useful to the community than the spectral constants shown in Table 1. This is especially true for those who would like to do combined analyses in the future. These primary data files for ν_6 are included as Tables S1, S2 of the Supplementary Electronic Information, and for ν_9 in Tables S3, S4. The results of fits performed

with the A-reduced form of the Hamiltonian are also reported in Table S5.

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Appendix A. Supplementary data

Supplementary data for this article are available on ScienceDirect (www.sciencedirect.com) and as part of the Ohio State University Molecular Spectroscopy Archives (http://msa.lib.ohio-state.edu/jmsa_hp.htm).

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