High Resolution Infrared Spectrum of Chlorine Dioxide: The ν_2 Fundamental Band

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Fourier transformed infrared absorption spectrum of gaseous ClO_2 has been obtained with the resolution of 0.06 cm^{-1}. The rotational structure of the bending fundamental band ($v_2=1\leftarrow0$) was analyzed. Rotational constants determined were in good agreement with previous microwave results. The band center was now fixed at 447.675 ± 0.030 cm^{-1}, and five centrifugal distortion constants for the $v_2=1$ state were also newly determined.

Extensive spectroscopic and kinetical studies have been started on photochemically produced molecules originating from chlorofluorocarbons, since it was disclosed that they are partially on charge of destruction of ozone in the upper atmosphere.[1] ClO_2 is one of the reaction products which appears in the final step in the Cl and O chain, and is considered to exist in the lower layer of the stratosphere, but has never been detected yet.[2]

It is thought to be important to study ClO_2 spectroscopically in the various regions of radiation in the laboratory system to give more detailed understanding of stratospheric reactions. Curl *et al.* have intensively studied the microwave spectrum, and determined a number of molecular parameters involving spin-rotation interaction constants.[3-8] Since infrared spectrum had first been observed by Bailey and Cassie,[9] some infrared works[10-12] were reported without any high resolution. The higher vibrational levels of the electronic ground state were mainly obtained by means of the electronic absorption spectrum[13] or fluorescence spectrum.[14]

We have recently observed the infrared spectrum by a Fourier transform spectrometer and partially by a diode laser spectrometer. This is a report of an analysis of the bending fundamental band ($v_2=1\leftarrow0$) in the 415—510 cm^{-1} region. 8 rotational transitions of $v_2=1$ state were observed in the microwave spectrum by Mariella and Curl.[8] The results of our infrared analysis will be compared with the microwave results.

Experimental

ClO_2 was prepared by the reaction of oxalic acid and potassium chlorate in dilute sulfuric acid at 60 °C.[15] The product was condensed in a dry ice bath, and then distilled in vacuum. The sample with the vapour pressure (about 1 mmHg) at dry ice temperature was introduced into a multiple reflection cell, whose optical path length was 10 m.

The spectrum was obtained by a Nicolet 7199 Fourier transform spectrometer. 128 scans of interferometer were accumulated (38 sec per scan) to construct an interferogram, and this was Fourier-transformed (it took about 30 min.) into an ordinary spectrum of 4000—400 cm^{-1} region. The maximum distance of the moving mirror is 8 cm, and by the use of Happ-Genzel apodization function to remove the ripple of the spectral curve the actual width (full width at half miximum) was found to reach 0.07 cm^{-1}. The peak separation of 0.05 cm^{-1} was found to be recognizable. To confirm the accuracy of the wavenumber scale, some of the atmospheric CO_2 and H_2O lines overlapped on the ClO_2 spectrum were compared with the standard spectral data.[16] The wavenumber precision was found to be better than ±0.02 cm^{-1}.

Analysis

Neglect of the Spin-Rotation Interaction. The spin-rotation constants for the $v_2=1$ state are known to be almost the same as those for the ground state.[8] In Fig. 1, the spin splitting patterns in the ground state are shown, on the basis of the following equations:

$$F_1 = \left\{\left[a-a_0\pm\frac{1}{2}b\delta_{1,K}\right]N(N+1)-3aK^2 + 9a^2K^2\left[1-\frac{K^2}{(N+1)^2}\right]\Big/4\bar{B}\right\}\Big/2(N+1), \quad (1)$$

$$F_2 = -\left\{\left[a-a_0\pm\frac{1}{2}b\delta_{1,K}\right]N(N+1)-3aK^2 + 9a^2K^2\left[1-\frac{K^2}{N^2}\right]\Big/4\bar{B}\right\}\Big/2N, \quad (2)$$

where

$$a_0 = -\frac{1}{3}(\varepsilon_{aa}+\varepsilon_{bb}+\varepsilon_{cc}),$$

$$a = -\frac{1}{6}(2\varepsilon_{aa}-\varepsilon_{bb}-\varepsilon_{cc}),$$

$$b = -\frac{1}{2}(\varepsilon_{bb}-\varepsilon_{cc}),$$

and

$$\bar{B} = \frac{1}{2}(B+C).$$

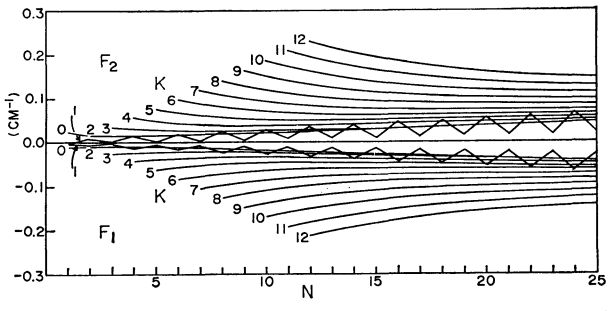

Fig. 1. Spin splitting pattern of $^{35}ClO_2$ in the ground state. Deviations, F_1 and F_2, caused by the spin rotation interaction, from pure rotational levels are shown. F_1 is for $N=J-S$, and F_2 for $N=J+S$, where N is the quantum number of rotational angular momentum, S is the quantum number of electron spin angular momentum, and J is the quantum number of total angular momentum. The calculations were made on Eqs. 1 and 2, where it was assumed that $a_0=0.017798$, $a=0.014262$, and $b=0.003679$ cm^{-1}.

ε's are spin-rotation interaction constants defined by

$$\mathcal{H}_{s.r.} = \varepsilon_{aa}N_aS_a + \varepsilon_{bb}N_bS_b + \varepsilon_{cc}N_cS_c, \quad (3)$$

where $\mathcal{H}_{s.r.}$ is the Hamiltonian for the spin-rotation interaction. As may easily be seen in Fig. 1, the spin-splitting should reach as much as 0.1 cm^{-1}, for lines of ^{P}R- and ^{R}P-branches if K is as high as 10 or so. These lines, however, have practically no intensity to be detected. The next largest spin-splitting is expected to occur in the lines of ^{R}Q- and ^{P}Q-branches, but these are so badly overlapped on one another. Absorption lines in the ^{R}R- and ^{P}P-branches are well separated from one another and intense enough. The spin-splittings for these lines are, however, always less than 0.05 cm^{-1} (our resolution). We, therefore, neglect the spin-rotation interaction in our present analysis.

Assignments of the Observed Peaks. The assignments were made on the basis of a comparison of the observed and calculated spectra. In the calculation, rotational matrices were trancated so as to include the elements with the K value which is higher by three than the maximum K we need. This makes the eigenvalues significant at least for 7 decimal digits. The ground state energy levels were calculated with the constants given by the microwave spectroscopy.[18] In an early stage of the analysis, the rotational constants A, B, and C of the $v_2=1$ state given by Mariella and Curl[8] were used to predict the J structures of low K sub-branches. Here essentially no single lines were detected, but most of the strong transitions were reasonably assigned to the observed peaks. In Fig. 2, part of the calculated spectrum is shown along with the observed spectrum.

At first sight, we can see ^{R}Q- and ^{P}Q-branches that make clusters: especially, $^{P}Q_K$ with $K\geqq 7$ give narrow and intense absorption peaks. These confirm the K-numbering. We can next recognize the strong absorptions formed by the turning head of the progressions in the $^{P}Q_2$, $^{P}Q_3$, $^{R}Q_1$, and $^{R}Q_2$ branches. The J-numbering for these progressions is of great merit for the following assignments in the low K region, because this allows us to fix the size of asymmetry, $B-C$. The absorption lines with $J=10$—30 in the $^{R}R_0$ and $^{P}R_1$ branches in the higher frequency region than the band center, and those in the $^{P}P_1$ and $^{R}P_0$ branches in the lower frequency region than the band center are the most intense ones in the whole band. They form progressions with nearly equal spacings.

Towards the high frequency end of the band, some of the ^{R}R branch lines are piled up to construct a progression with fairly regular spacing of about 0.6 cm^{-1}. From this we can determine the $\bar{B}'=1/2(B'+C')$ value. The J-numbering of this progression is rather straightforward, because we can use the ground state combination differences with the ^{P}P branch lines located in the other end of the band. The assignments are proceeded to reach reasonable intensity pattern.

We used the sample of ClO_2 with isotopes of natural abundance. This means that $^{35}ClO_2$ is mixed with $^{37}ClO_2$ with the ratio 3: 1. Hence difficulty was that not all absorption lines should necessarily be assigned to any transition of $^{35}ClO_2$. Also it happened that some fairly strong absorption was buried behind the $^{37}ClO_2$ absorption and made no apparent peak. No attempt was made to analyze $^{37}ClO_2$ spectrum in our present work.

Determination of the Molecular Constants. Upper state term values were calculated by adding the ground state rotational levels to the observed frequencies. The ground state rotational and centrifugal constants were fixed, as given in Table 1, in this work. Then, the term values were used for the least squares fitting to obtain the parameters of the following Hamiltonian:[17]

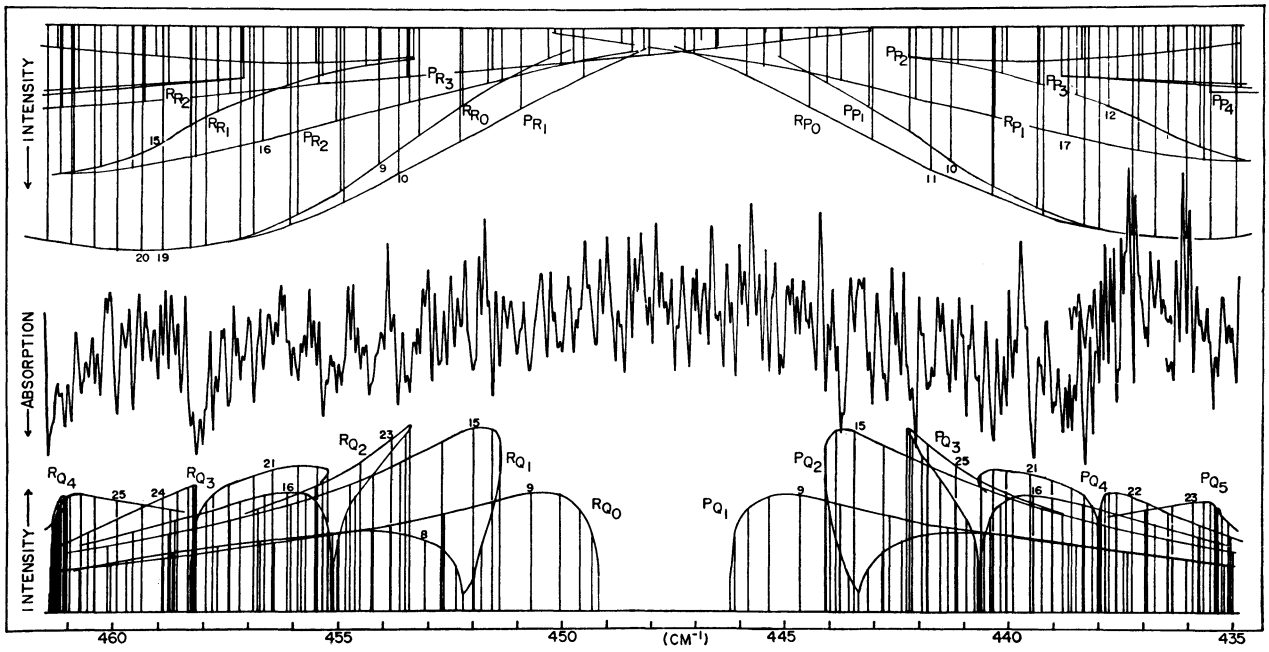

Fig. 2. The infrared absorption spectrum of ClO_2 in the 461—435 cm^{-1} region. Upper is the calculated pattern of R- and P- branches. Lower is the calculated pattern of Q-branches. The observed spectrum is shown in the middle.

Table 1. Molecular constants of $^{35}ClO_2$[a]

	(000)[b]	This work(010)	Previous data
ν_0		447.675(11)	447.3[c]/447.9[d]
A	1.737225(50)	1.77052(24)	1.77052(20)[e]
B	0.331982(7)	0.332021(59)	0.331682(60)
C	0.277993(6)	0.277215(46)	0.277202(60)
Δ_J	$2.335(334)\times10^{-7}$	$1.127(224)\times10^{-7}$	
Δ_{JK}	$-4.003(1000)\times10^{-6}$	$-2.714(222)\times10^{-6}$	
Δ_K	$6.905(300)\times10^{-5}$	$7.580(107)\times10^{-5}$	
δ_J	$7.67(100)\times10^{-8}$	$-2.714(222)\times10^{-9}$	
δ_K	$5.67(300)\times10^{-7}$	$-4.72(1365)\times10^{-6}$	

a) Units are in cm^{-1}. Uncertainties (3σ) in parentheses are in units of the last significant figure. b) The higher order centrifugal distortion constants $H_J=7\times10^{-7}$, $H_{JK}=2\times10^{-5}$, $H_{KJ}=-1\times10^{-4}$, $H_K=1\times10^{-3}$, $h_J=3\times10^{-7}$, $h_{JK}=-3\times10^{-4}$, in units of MHz, were used to calculate the ground state rotational energies, and the same values were assumed for $v_2=1$ state. c) Ref. 11 from IR spectrum. d) Ref. 11 from UV spectrum. e) Ref. 8.

$$\begin{aligned}\mathcal{H} = {} & \nu_0 + AP_a^2 + BP_b^2 + CP_c^2 - \Delta_J P^4 - \Delta_{JK}P^2P_a^2 \\ & - \Delta_K P_a^2 - 2\delta_J P^2(P_b^2-P_c^2) - \delta_K[P_a^2(P_b^2-P_c^2) \\ & + (P_b^2-P_c^2)P_a^2] + H_J P^6 + H_{JK}P^4P_a^2 + H_{KJ}P^2P_a^4 \\ & + H_K P_a^6 + 2h_J P^4(P_b^2-P_c^2) + h_{JK}P^2[P_a^2(P_b^2-P_c^2) \\ & + (P_b^2-P_c^2)P_a^2] + h_K[P_a^4(P_b^2-P_c^2) \\ & + (P_b^2-P_c^2)P_a^4]. \qquad (4)\end{aligned}$$

From totally 452 term values, ranging J up to 47, and K up to 15, first 9 parameters were determined. The parameters of P^6-term were fixed to the ground state values. There could not seen any systematic deviation in the residuals (observed-calculated) in the final least squares fit. Therefore, it has been concluded that the higher centrifugal distortion constants are not necessary to be included as variables.

Discussion

In Table 1, the final set of parameters are compared with the previous results. As described in the preceding chapter, the precision of the observed line position is better than ±0.02 cm^{-1}. Therefore, (in combination with the calculated error ±0.01 cm^{-1}), the standard error is estimated to be ±0.03 cm^{-1} for the band center.

The rotational constant B has a meaningful discrepancy between the microwave and our infrared analysis. This may be attributed to the fact that, in microwave analysis, Curl *et al.* assumed the same centrifugal distortion constants in $v_2=1$ state as in the ground state, and used only 4 rotational transitions of low J's of $K=0$ and 1 in their least squares fit.

As was pointed by Pliva and Telfair,[19] the term values of the upper state are strongly correlated with the ground state parameters. We should realize, therefore, that from an infrared term value analysis, such as what we have done in the present work, the differences ΔA, ΔB, ΔC, *etc.* of the parameters in the upper and ground states are determined rather than their absolute values of the parameters themselves. Even if the ground state parameters are revised in future, ΔA, ΔB, ΔC,···values fixed here will remain significant.

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