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High-Resolution Rotational Analysis of Deuterated Hypochlorous Acid: Ground State, (100), and (020) Vibrational States

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The high-resolution Fourier transform spectra of the DOCl molecule were recorded and analyzed in the region of the ν_1 and $2\nu_2$ bands. Transitions belonging to the ν_1 and $2\nu_2$ bands were assigned up to $J^{max} = 55$ and 46, respectively. The sets of spectroscopic parameters of the (100) and (020) vibrational states obtained from the fit reproduce their energies derived from the experimental data with accuracies close to experimental uncertainties.

Key Words: rotation–vibration spectra; DOCl molecule; spectroscopic parameters.

1. INTRODUCTION

The study of hypochlorous acid is of great interest because of its probable important role in the balance of stratospheric ozone in polar regions (see, e.g., (*1–3*) and references therein). Therefore, laboratory spectroscopic investigations of this molecule are of interest too. As a consequence, HOCl spectra were studied extensively, (see, e.g., (*4–10*)) and its intramolecular force field was theoretically estimated (*11–15*). At the same time, there were only a few investigations devoted to analysis of the spectra of deuterated hypochlorous acid (*4, 16–18*). The infrared spectra of DOCl were recorded, for the first time, by Hedberg and Badger (*4*) at low resolution and later by Ashby (*16*) at medium resolution. In Ref. (*17*) Mirri *et al.* reported four microwave transitions. In 1987 Deeley (*18*) presented the results of the high-resolution analysis of all three fundamentals. In that case, the sets of spectroscopic parameters were determined both for the ground vibrational state and for the (100), (010), and (001) excited states.

At the beginning, the goal of this study was high-resolution spectroscopic analysis of the $2\nu_2$ band of the DOCl molecule. However, we found that the experimental opportunities allowed us not only to analyze the $2\nu_2$ band, but also to improve the spectroscopic information both on the ground vibrational state and on the (100) state. As a consequence, the results of the analysis of the rotational energies of the (000), (100), and (020) vibrational states, which were derived from the experimentally recorded high-resolution spectra of the ν_1 and $2\nu_2$ bands, are presented in this paper. Section 2 is devoted to experimental details. Assignment of the recorded transitions and determination of the ground state parameters is considered in Section 3. The rotational structure of the upper (100) and (020) vibrational states is discussed in Section 4.

2. EXPERIMENTAL DETAILS

The DOCl sample was prepared as described in Ref. (*19*) by substituting D_2O for H_2O. The spectra were recorded at room temperature with a Bruker IFS 120HR Fourier-transform interferometer (Hefei, China), which is equipped with a path length adjustable multipass gas cell. For the $2\nu_2$ band, a CaF_2 beam splitter and a Globar source were used. Two detectors, liquid-nitrogen-cooled MCT and InSb, were used for the ranges below and above 1800 cm^{-1}, respectively. The unapodized resolution was 0.01 cm^{-1}, and the Norton–Beer Medium apodization function was adopted in the Fourier transform. The mixed gas pressure 840 Pa and the absorption path length 69 m were used in the measurement. The line positions were calibrated with those of the H_2O in the HITRAN 96 database. The accuracy of the unblended not very weak and unsaturated lines was estimated to be 0.0006 cm^{-1}. For illustration, a small part of the spectrum is presented in Fig. 1. For the ν_1 band, a KBr beamsplitter, a Globar source, and a liquid-nitrogen-cooled InSb detector were used. The mixed gas pressure and absorption path length were 166 Pa and 51 m, respectively. The unapodized resolution was 0.005 cm^{-1}, and the Norton–Beer weak apodization function was used in the Fourier transform. Many HDO lines were observed in this spectral region, which enables us to calibrate the line positions by comparing them with those listed in the GEISA 97 database. The accuracy of the unblended lines for this band was estimated to be 0.0003 cm^{-1}, which is a little bit higher than the corresponding value (0.0005 cm^{-1}) in

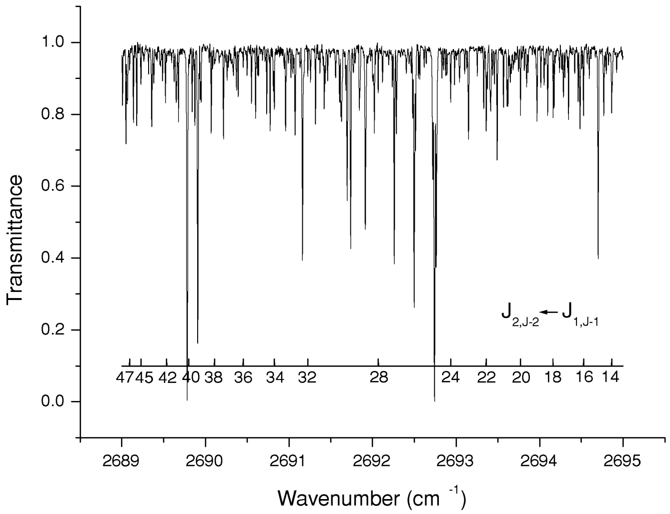

FIG. 1. A portion of the $2\nu_2$ spectrum: a section of the *b*-type structure and the $^rQ_2$ subbranch in the region 1855–1870 cm^{-1} are shown. See text for experimental details.

Ref. (*18*). It should be mentioned that in our measurements we found the half-life of DOCl to be longer than 4 h, while Ref. (*18*) gives a value of only 2 min. Thus we were able to easily carry out more scans (for instance, 180 scans for the ν_1 band) to record transitions with higher values of the quantum number J and to achieve higher accuracy in line positions than in Ref. (*18*). Three small pieces of the recorded spectra are shown in Figs. 1–3. The ^{35}Cl and ^{37}Cl isotopes are present in natural abundance in our DOCl samples. The signal to noise ratio of the DO^{37}Cl is not good enough, so we focus our study on the DO^{35}Cl molecule.

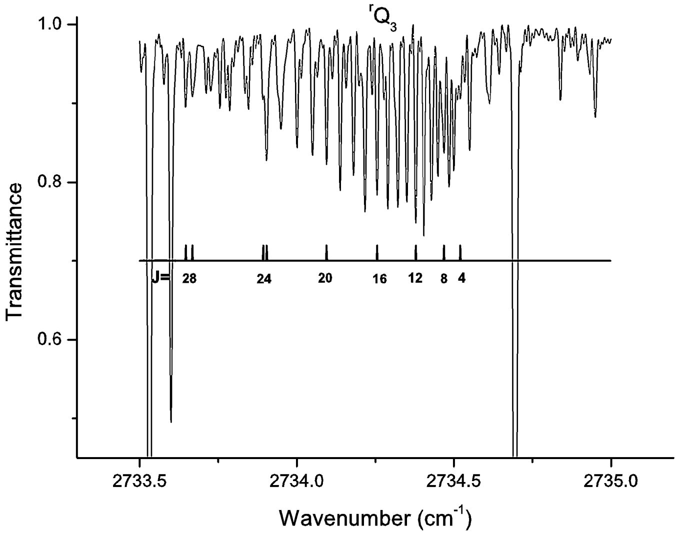

FIG. 2. A portion of the ν_1 fundamental spectrum: the $^rQ_3$ subbranch. It shows asymmetry splitting at J = 24. See text for experimental details.

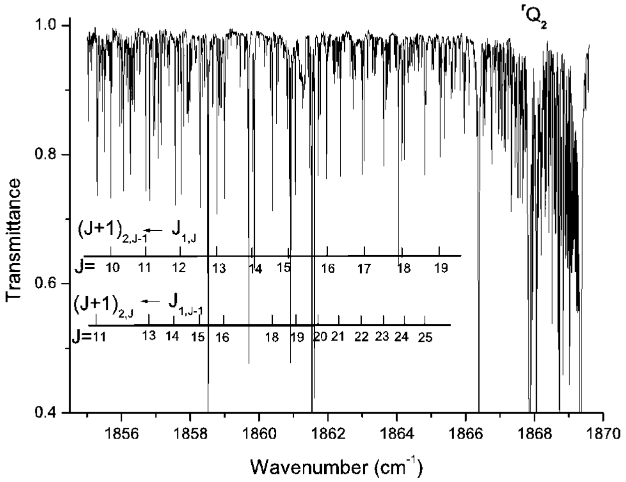

FIG. 3. A portion of the ν_1 fundamental spectrum: a *b*-type structure and high $J = 47$ lines are observed. See text for experimental details.

3. ASSIGNMENT OF TRANSITIONS AND GROUND STATE PARAMETERS

DOCl is a near-prolate asymmetric top molecule with the C_s symmetry, and any of its three vibrational coordinates is of the A' type. As a consequence, any of the vibrational–rotational bands contains absorption lines arising from transitions of two types, *a* and *b*. In fact, the bands analyzed in this work, ν_1 and $2\nu_2$, show both *a* and *b* structures with comparable linestrengths.

The first step of the study began with the assignment of transitions belonging to the $2\nu_2$ band. Transitions were assigned on the basis of the ground state combination differences method, and the ground state parameters (I^r representation, *A*-reduction) were taken from Table I of Ref. (*18*). In this case, we found that the transitions with considerably higher values of quantum number J can be assigned in our experimental spectra. So it was expected that ground state combination differences with higher values of quantum number J than those in Ref. (*18*) can be constructed on the basis of the assigned transitions, and as a consequence, the ground state parameters can be slightly improved in comparison with the parameters of Ref. (*18*). On this reason, the ground state combination differences were reanalyzed. To make the ground state combination differences obtained from the $2\nu_2$ band more correctly, we reanalyzed the ν_1 band as well.

As a result of the analysis, 2398 transitions with the quantum numbers $J^{max} = 55$, $K_a^{max} = 9$ and 2015 transitions with the quantum numbers $J^{max} = 46$, $K_a^{max} = 7$ were assigned to the ν_1 and $2\nu_2$ bands, respectively (statistical information concerning the studied bands is given in Table 1; Figs. 1–3 show small parts of the recorded spectra with the assignment of some sets of transitions). For comparison, it should be noted that in Ref. (*18*) transitions with $J^{max} = 40$ and $K_a^{max} = 8$ were assigned to the ν_1 band.

On the basis of transitions assigned from the bands ν_1 and $2\nu_2$, more than 4000 ground state combination differences

TABLE 1
Statistical Information Concerning Studied Bands of the DOCl Molecule

State	K_a	J_{max}	n_{tr}[a]	N_l[b]	m_1[c]	m_2[c]	m_3[c]
1	2	3	4	5	6	7	8
(100)	0	55	207	55	81.8	14.5	3.7
(100)	1	48	490	95	92.6	4.2	3.2
(100)	2	48	464	91	91.2	7.7	1.1
(100)	3	47	375	85	92.9	4.7	2.4
(100)	4	46	282	108	77.8	14.8	7.4
(100)	5	43	223	78	88.8	2.7	10.5
(100)	6	45	178	80	80.0	15.0	5.0
(100)	7	38	127	60	67.7	22.5	9.8
(100)	8	29	39	34	47.1	29.4	23.5
(100)	9	19	13	18	33.3	44.4	22.3
(020)	0	43	175	41	85.4	7.3	7.3
(020)	1	46	403	87	88.5	8.0	3.5
(020)	2	38	391	74	89.2	9.5	2.3
(020)	3	40	321	76	96.1	3.9	-
(020)	4	35	228	64	100.0	-	-
(020)	5	40	222	70	88.6	11.4	-
(020)	6	41	174	70	91.4	5.7	2.9
(020)	7	30	101	46	91.3	8.7	-

[a] n_{tr} is the number of assigned transitions.

[b] N_l is the number of obtained upper energies.

[c] Here $m_i = n_i/N_l \times 100\%$ $(i = 1, 2, 3)$, and n_1, n_2, and n_3 are the numbers of upper energies for which differences $\delta = E^{exp} - E^{calc}$ satisfy the conditions $\delta \leq 8 \times 10^{-4}$ cm^{-1}, 8×10^{-4} cm^{-1} $< \delta \leq 15 \times 10^{-4}$ cm^{-1}, and 15×10^{-4} cm^{-1} $< \delta$, respectively.

$\Delta_{E_{[J'K'_aK'_c]} - E_{[JK_aK_c]}}$ (for comparison, 1617 ones in the Ref. (*18*)) of the types $\Delta J = 0$, $\Delta K_a = +1$, $\Delta K_c = 0$; $\Delta J = 0$, $\Delta K_a = +1$, $\Delta K_c = -2$; $\Delta J = 0$, $\Delta K_a = +2$, $\Delta K_c = -2$; $\Delta J = +2$, $\Delta K_a = 0$, $\Delta K_c = +2$; $\Delta J = +2$, $\Delta K_a = -1$, $\Delta K_c = +2$; $\Delta J = +2$, $\Delta K_a = +1$, $\Delta K_c = +2$; $\Delta J = +2$, $\Delta K_a = +1$, $\Delta K_c = 0$; $\Delta J = +2$, $\Delta K_a = +2$, $\Delta K_c = 0$ were constructed and then used in the fitting procedure together with four microwave transitions from (*17*). Since the Q-branches in both of the analyzed bands are very dense, a lot of lines are blended, so we did not use the Q-branch transitions in the construction of combination differences. As a consequence, “experimental” ground state combination differences with $\Delta J = 1$ were not used in the fit. Moreover, to make the solution of the problem more suitable in physics, in the fit we used the mean values of combination differences instead of their real “experimental” values. In this case, the mean values of combination differences with lower values of the quantum numbers J and K_a ($J \leq 26 - 28$, $K_a \leq 5$) were determined from 4–6 individual values; for the combination differences with higher J and K_a—from 1 to 3 individual values. Finally, 732 “experimental” mean values with $J^{max} = 50$ and $K_a^{max} = 8$ were involved into the fit procedure.

The fit was made with the asymmetric-top Hamiltonian in the form [1] (I^r representation, A-reduction)

$$\begin{aligned} H = {} & E + \left[A - \frac{1}{2}(B+C)\right]J_z^2 + \frac{1}{2}(B+C)J^2 + \frac{1}{2}(B-C) \\ & \times J_{xy}^2 - \Delta_K J_z^4 - \Delta_{JK} J_z^2 J^2 - \Delta_J J^4 - \delta_K \left[J_z^2, J_{xy}^2\right]_+ \\ & - 2\delta_J J^2 J_{xy}^2 + H_K J_z^6 + H_{KJ} J_z^4 J^2 + H_{JK} J_z^2 J^4 + H_J J^6 \\ & + \left[J_{xy}^2, h_K J_z^4\right]_+ + L_K J_z^8 + L_{KKJ} J_z^6 J^2 \\ & + L_{KJ} J_z^4 J^4 + \cdots; \end{aligned} \qquad [1]$$

here $J_{xy}^2 = J_x^2 - J_y^2$, and $J^2 = \sum_\alpha J_\alpha^2$.

Parameters of the ground vibrational state derived from the fit are presented in column 2 of Table 2 together with their 1σ statistical confidence intervals. For comparison, earlier data from Ref. (*18*) are shown in column 3. It shows good correlation between our results and the data from Ref. (*18*).

We believe that our parameters are physically meaningful, because they reproduce the ground state combination differences, which correspond to high values of the quantum number J, with a mean accuracy of 0.0005–0.0006 cm^{-1}, which is close to experimental uncertainties. The four microwave transitions from (*17*) are reproduced with our parameters with experimental accuracy as well.

4. UPPER VIBRATIONAL STATES (100) AND (020)

At the second step of the study, rovibrational energies of the vibrational states (100) and (020) were obtained from the

TABLE 2
Rotational Parameters of the Ground Vibrational States of the DOCl Molecule (in cm^{-1})[a,b]

Parameter	Our	From (*18*)
1	2	3
A	11.05225700(247)	11.052315
B	0.476978130(270)	0.47697846
C	0.456129220(273)	0.45612955
$\Delta_K \times 10^4$	13.292947(858)	13.3292
$\Delta_{JK} \times 10^4$	0.2546159(310)	0.25592
$\Delta_J \times 10^4$	0.007472763(670)	0.0074683
$\delta_K \times 10^4$	0.15722(120)	0.1558
$\delta_J \times 10^4$	0.000302383(299)	0.0003039
$H_K \times 10^8$	73.1495(985)	77.6
$H_{KJ} \times 10^8$	-	0.494
$H_{JK} \times 10^8$	-	-
$H_J \times 10^8$	-	-
$h_K \times 10^8$	-9.356(297)	-
$h_{JK} \times 10^8$	-	-
$h_J \times 10^8$	-	-

[a] Values in parentheses are the 1σ statistical confidence intervals.

[b] *rms* deviation is 0.00053 cm^{-1}.

TABLE 3

Experimental Rovibrational Energy Levels for the (100) Vibrational State of the DOCl Molecule (in cm^{-1}) [a]

J	K_a	K_c	E	Δ	δ	J	K_a	K_c	E	Δ	δ	J	K_a	K_c	E	Δ	δ
	1		2	3	4		1		2	3	4		1		2	3	4
0	0	0	2665.5765		-17	7	1	7	2701.6320	5	-4	40	1	39	3445.1737	14	-1
1	0	1	2666.5092	1	-4	7	1	6	2702.2259	9	-3	41	1	41	3465.6056	2	-2
2	0	2	2668.3726	3	2	8	1	8	2708.9961	4	0	41	1	40	3483.4760	6	17
3	0	3	2671.1662	8	-1	8	1	7	2709.7594	5	0	42	1	42	3503.9826	7	-4
4	0	4	2674.8915	5	2	9	1	9	2717.2795	3	-1	42	1	41	3522.6912	6	-9
5	0	5	2679.5473	3	2	9	1	8	2718.2337	6	1	43	1	43	3543.2608	22	4
6	0	6	2685.1338	1	1	10	1	10	2726.4830	7	3	43	1	42	3562.8278		15
7	0	7	2691.6505	2	0	10	1	9	2727.6484	5	-1	44	1	44	3583.4364		-6
8	0	8	2699.0972	3	1	11	1	11	2736.6049	3	0	44	1	43	3603.8762		10
9	0	9	2707.4736	3	1	11	1	10	2738.0042	5	3	45	1	44	3645.8375	8	-2
10	0	10	2716.7791	3	2	12	1	12	2747.6466	3	0	46	1	46	3666.4842		-2
11	0	11	2727.0127	5	-2	12	1	11	2749.2996	4	1	46	1	45	3688.7111	7	-12
12	0	12	2738.1750	3	0	13	1	13	2759.6069	3	0	47	1	47	3709.3527	10	-5
13	0	13	2750.2640	7	-4	13	1	12	2761.5353	6	4	47	1	46	3732.4999	15	21
14	0	14	2763.2806	4	-2	14	1	14	2772.4852	6	-4	48	1	48	3753.1197		20
15	0	15	2777.2231	3	-1	14	1	13	2774.7096	4	-2	48	1	47	3777.1920	13	-6
16	0	16	2792.0909	1	0	15	1	15	2786.2825	4	1	2	2	1	2709.4648	2	0
17	0	17	2807.8835	2	2	15	1	14	2788.8236	2	-2	2	2	0	2709.4648	2	0
18	0	18	2824.5993	4	0	16	1	16	2800.9972	2	2	3	2	2	2712.2590	12	8
19	0	19	2842.2384	3	1	16	1	15	2803.8763	3	-1	3	2	1	2712.2590	12	6
20	0	20	2860.7989	3	-1	17	1	17	2816.6289	4	0	4	2	3	2715.9825	6	-2
21	0	21	2880.2810	3	1	17	1	16	2819.8672	3	-2	4	2	2	2715.9825	6	-7
22	0	22	2900.6825	4	-1	18	1	18	2833.1778	3	1	5	2	4	2720.6381	19	0
23	0	23	2922.0034	4	0	18	1	17	2836.7960	4	-1	5	2	3	2720.6381	19	-12
24	0	24	2944.2421	5	0	19	1	19	2850.6431	5	0	6	2	5	2726.2238	3	-6
25	0	25	2967.3979	4	4	19	1	18	2854.6622	4	0	6	2	4	2726.2265	3	-2
26	0	26	2991.4690	6	5	20	1	20	2869.0246	4	1	7	2	6	2732.7415	6	1
27	0	27	3016.4546	1	4	20	1	19	2873.4650	5	0	7	2	5	2732.7455	13	0
28	0	28	3042.3533	6	2	21	1	21	2888.3213	3	-1	8	2	7	2740.1892	15	3
29	0	29	3069.1645	5	3	21	1	20	2893.2040	5	-1	8	2	6	2740.1957	2	0
30	0	30	3096.8861	3	-1	22	1	22	2908.5333	2	-1	9	2	8	2748.5672	4	4
31	0	31	3125.5183	2	3	22	1	21	2913.8785	3	-3	9	2	7	2748.5778	4	2
32	0	32	3155.0590	6	7	23	1	23	2929.6600	3	1	10	2	9	2757.8752	5	4
33	0	33	3185.5065	9	6	23	1	22	2935.4884	4	-1	10	2	8	2757.8903	5	-6
34	0	34	3216.8600	8	4	24	1	24	2951.7001	4	-3	11	2	10	2768.1128	6	1
35	0	35	3249.1191	5	10	24	1	23	2958.0325	5	-1	11	2	9	2768.1362	6	2
36	0	36	3282.2802	8	-1	25	1	25	2974.6544	5	1	12	2	11	2779.2805	6	2
37	0	37	3316.3453	3	4	25	1	24	2981.5103	6	-2	12	2	10	2779.3131	5	2
38	0	38	3351.3108	3	2	26	1	26	2998.5210	8	0	13	2	12	2791.3772	3	0
39	0	39	3387.1763	4	-2	26	1	25	3005.9217	4	3	13	2	11	2791.4211	6	-5
40	0	40	3423.9404	6	-8	27	1	27	3023.3003	7	3	14	2	13	2804.4031	4	-1
41	0	41	3461.6037	7	1	27	1	26	3031.2645	3	-1	14	2	12	2804.4623	2	-2
42	0	42	3500.1621	6	-5	28	1	28	3048.9906	6	0	15	2	14	2818.3572	5	-8
43	0	43	3539.6168	6	-3	28	1	27	3057.5392	6	-1	15	2	13	2818.4357	4	3
44	0	44	3579.9640		-20	29	1	29	3075.5927	5	6	16	2	15	2833.2409	6	-3
45	0	45	3621.2074	8	-8	29	1	28	3084.7450	6	3	16	2	14	2833.3407	6	0
46	0	46	3663.3438		12	30	1	30	3103.1051	5	5	17	2	16	2849.0524	6	0
47	0	47	3706.3672		-10	30	1	29	3112.8800	7	-1	17	2	15	2849.1782	5	-1
48	0	48	3750.2841	11	2	31	1	31	3131.5258	10	5	18	2	17	2865.7910	4	-3
49	0	49	3795.0881		-8	31	1	30	3141.9451	5	6	18	2	16	2865.9486	8	1
50	0	50	3840.7836		16	32	1	32	3160.8556	4	-1	19	2	18	2883.4570	7	-5
52	0	52	3934.8298	13	9	32	1	31	3171.9374	9	3	19	2	17	2883.6511	5	-3
53	0	53	3983.1809	11	2	33	1	33	3191.0947	2	5	20	2	19	2902.0504	7	2
54	0	54	4032.4184		15	33	1	32	3202.8573	9	4	20	2	18	2902.2866	3	-5
55	0	55	4082.5417		53	34	1	34	3222.2415	7	13	21	2	20	2921.5697	4	1
1	1	1	2676.7760	4	-1	34	1	33	3234.7027	4	-3	21	2	19	2921.8562	5	4
1	1	0	2676.7975	6	2	35	1	35	3254.2927	6	5	22	2	21	2942.0148	4	1
2	1	2	2678.6179	3	4	35	1	34	3267.4737	5	-7	22	2	20	2942.3573	3	-2
2	1	1	2678.6812	7	1	36	1	36	3287.2513	3	-1	23	2	22	2963.3850	6	0
3	1	3	2681.3799	2	0	36	1	35	3301.1708	15	7	23	2	21	2963.7926	4	1
3	1	2	2681.5071	4	3	37	1	37	3321.1157	4	4	24	2	23	2985.6805	5	0
4	1	4	2685.0619	3	-3	37	1	36	3335.7894	8	5	24	2	22	2986.1606	4	-3
4	1	3	2685.2746	4	3	38	1	38	3355.8841	4	7	25	2	24	3008.9000	5	-1
5	1	5	2689.6652	3	-1	38	1	37	3371.3300	7	1	25	2	23	3009.4624	6	-3
5	1	4	2689.9839	4	5	39	1	39	3391.5552	8	1	26	2	25	3033.0430	6	-2
6	1	6	2695.1885	3	-3	39	1	38	3407.7918	1	-1	26	2	24	3033.6980	4	-2
6	1	5	2695.6342	5	1	40	1	40	3428.1295	6	0	27	2	26	3058.1100	5	3

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[a] Δ is the experimental uncertainty of the energy value, equal to one standard deviation in units of 10^{-4} cm^{-1}; δ is the difference $E^{exp} - E^{calc}$, also in units of 10^{-4} cm^{-1}; Δ is not quoted when the energy value was obtained from only one transition.

TABLE 3—*Continued*

J	K_a	K_c	E	Δ	δ	J	K_a	K_c	E	Δ	δ	J	K_a	K_c	E	Δ	δ
	1		2	3	4		1		2	3	4		1		2	3	4
27	2	25	3058.8671	2	-1	16	3	14	2884.5452	5	7	11	4	8	2891.1135	5	-4
28	2	27	3084.0986	2	0	16	3	13	2884.5452	5	-1	12	4	9	2902.2767	4	3
28	2	26	3084.9699	9	-1	17	3	15	2900.3591	4	1	13	4	10	2914.3678	6	-5
29	2	28	3111.0092	6	0	17	3	14	2900.3604	2	2	14	4	11	2927.3891	5	-2
29	2	27	3112.0062	6	-4	18	3	16	2917.1017	7	-6	15	4	12	2941.3394	6	1
30	2	29	3138.8417	6	6	18	3	15	2917.1036	6	-3	16	4	13	2956.2181	4	1
30	2	28	3139.9768	8	-2	19	3	17	2934.7741	9	1	17	4	14	2972.0255	4	4
31	2	30	3167.5931	12	-4	19	3	16	2934.7757	6	-7	18	4	15	2988.7603	11	-2
31	2	29	3168.8824	10	12	20	3	18	2953.3740	4	-1	19	4	16	3006.4233	5	-4
32	2	31	3197.2660	5	3	20	3	17	2953.3769	5	-3	20	4	17	3025.0151	6	5
32	2	30	3198.7195	5	5	21	3	19	2972.9021	4	0	21	4	18	3044.5329	3	0
33	2	32	3227.8577	8	7	21	3	18	2972.9060	7	-2	22	4	19	3064.9783	3	2
33	2	31	3229.4911	2	5	22	3	20	2993.3577	6	0	23	4	20	3086.3500	3	1
34	2	33	3259.3675	8	9	22	3	19	2993.3630	8	-2	24	4	21	3108.6482	4	1
34	2	32	3261.1960	4	3	23	3	21	3014.7411	7	5	25	4	22	3131.8725	3	5
35	2	34	3291.7942	3	5	23	3	20	3014.7475	7	-2	26	4	23	3156.0213	3	-3
35	2	33	3293.8350	5	8	24	3	22	3037.0507	6	2	27	4	24	3181.0961	7	-3
36	2	35	3325.1373	5	-3	24	3	21	3037.0600	9	4	28	4	25	3207.0960	8	3
36	2	34	3327.4064	7	5	25	3	23	3060.2871	8	1	29	4	26	3234.0197	5	3
37	2	36	3359.3971	3	-4	25	3	22	3060.2989	6	3	30	4	27	3261.8675	5	6
37	2	35	3361.9100	4	-4	26	3	24	3084.4500	10	2	31	4	28	3290.6376	1	-1
38	2	37	3394.5721	1	-4	26	3	23	3084.4645	5	1	32	4	29	3320.3316	4	6
38	2	36	3397.3483		8	27	3	25	3109.5384	6	1	32	4	28	3320.3316	4	-1
39	2	38	3430.6620	3	3	27	3	24	3109.5566	8	0	33	4	30	3350.9473	13	3
39	2	37	3433.7164		-5	28	3	26	3135.5525	6	2	33	4	29	3350.9473	13	-6
40	2	39	3467.6655	12	11	28	3	25	3135.5748	3	-1	34	4	31	3382.4852	11	5
40	2	38	3471.0179	7	-2	29	3	27	3162.4912	7	0	34	4	30	3382.4852	11	-8
41	2	40	3505.5795	15	0	29	3	26	3162.5190	9	0	35	4	32	3414.9443	14	4
41	2	39	3509.2497		-9	30	3	28	3190.3545	4	-2	35	4	31	3414.9443	14	-11
42	2	41	3544.4053	13	-8	30	3	27	3190.3886	8	0	36	4	33	3448.3243	12	6
42	2	40	3548.4146	6	5	31	3	29	3219.1420	5	-2	36	4	32	3448.3243	12	-13
43	2	42	3584.1411		-24	31	3	28	3219.1850	3	17	37	4	34	3482.6249	19	11
43	2	41	3588.5090	8	14	32	3	30	3248.8530	5	-3	37	4	33	3482.6249	19	-12
44	2	43	3624.7899	7	-6	32	3	29	3248.9029	14	2	38	4	35	3517.8447	20	12
44	2	42	3629.5280	13	-3	33	3	31	3279.4867	3	-6	38	4	34	3517.8447	20	-15
45	2	44	3666.3463	9	0	33	3	30	3279.5471	7	5	39	4	36	3553.9835	20	14
45	2	43	3671.4826	14	-2	34	3	32	3311.0433	2	-6	39	4	35	3553.9835	20	-20
46	2	44	3714.3613	7	-15	34	3	31	3311.1148	13	2	40	4	37	3591.0420	22	28
47	2	45	3758.1705	13	3	35	3	33	3343.5224	11	0	40	4	36	3591.0420	22	-13
48	2	46	3802.9036		-3	35	3	32	3343.6064	6	3	41	4	38	3629.0167	25	27
3	3	1	2763.5655	3	-2	36	3	34	3376.9214	3	-9	41	4	37	3629.0167	25	-24
3	3	0	2763.5655	3	-2	36	3	33	3377.0217	14	6	42	4	39	3667.9056	18	-3
4	3	2	2767.2897	7	4	37	3	34	3411.3596	9	7	42	4	38	3667.9117		-3
4	3	1	2767.2897	7	4	38	3	36	3446.4838	11	0	43	4	40	3707.7149		5
5	3	3	2771.9437	4	0	38	3	35	3446.6190	2	-3	43	4	39	3707.7203		-13
5	3	2	2771.9437	4	0	39	3	37	3482.6436		-5	44	4	40	3748.4475	2	2
6	3	4	2777.5285	6	-2	39	3	36	3482.8020	9	2	46	4	43	3832.6309		-5
6	3	3	2777.5285	6	-2	40	3	38	3519.7228	5	-4	5	5	1	2935.6990	2	1
7	3	5	2784.0448	8	3	40	3	37	3519.9072		10	6	5	2	2941.2785	3	-5
7	3	4	2784.0448	8	3	41	3	38	3557.9323	4	5	7	5	3	2947.7890	5	0
8	3	6	2791.4911	7	3	42	3	40	3596.6348		-5	8	5	4	2955.2286	6	-4
8	3	5	2791.4911	7	3	42	3	39	3596.8784	2	0	9	5	5	2963.5978	2	0
9	3	7	2799.8677	3	2	43	3	41	3636.4666	2	-2	10	5	6	2972.8960	3	-4
9	3	6	2799.8677	3	2	43	3	40	3636.7452	9	-3	11	5	7	2983.1242	2	0
10	3	8	2809.1747	4	1	44	3	42	3677.2143		1	12	5	8	2994.2808	4	-2
10	3	7	2809.1747	4	1	45	3	42	3719.2390	12	-8	13	5	9	3006.3666	4	-1
11	3	9	2819.4121	6	3	46	3	43	3761.8647	5	-13	14	5	10	3019.3811	5	0
11	3	8	2819.4121	6	2	47	3	45	3804.9422		-20	15	5	11	3033.3237	1	-1
12	3	10	2830.5789	6	-1	47	3	44	3805.4121		9	16	5	12	3048.1949	5	2
12	3	9	2830.5789	6	-2	4	4	1	2839.0125	5	1	17	5	13	3063.9936	2	0
13	3	11	2842.6761	4	0	5	4	2	2843.6650	4	0	18	5	14	3080.7199	5	-1
13	3	10	2842.6761	4	-2	6	4	3	2849.2479	5	0	19	5	15	3098.3733	3	-5
14	3	12	2855.7030	5	2	7	4	4	2855.7608	7	-3	20	5	16	3116.9545	2	-1
14	3	11	2855.7030	5	-2	8	4	5	2863.2043	3	-1	21	5	17	3136.4623	2	2
15	3	13	2869.6593	6	3	9	4	6	2871.5775	3	-3	22	5	18	3156.8960	2	1
15	3	12	2869.6593	6	-3	10	4	7	2880.8809	4	-1	23	5	19	3178.2555	5	-2

TABLE 3—*Continued*

J	K_a	K_c	E	Δ	δ	J	K_a	K_c	E	Δ	δ	J	K_a	K_c	E	Δ	δ
	1		2	3	4		1		2	3	4		1		2	3	4
24	5	20	3200.5410	5	-2	25	6	20	3335.7895	5	-1	25	7	19	3467.8267	8	0
25	5	21	3223.7514	4	-4	26	6	21	3359.9096	2	1	26	7	20	3491.9285	10	-4
26	5	22	3247.8877	6	3	27	6	22	3384.9532	7	0	27	7	21	3516.9550	2	8
27	5	23	3272.9475	6	2	28	6	23	3410.9200	7	0	28	7	22	3542.9030	5	10
28	5	24	3298.9311	4	0	29	6	24	3437.8101	2	4	30	7	24	3597.5640	3	9
29	5	25	3325.8380	2	-4	30	6	25	3465.6222	10	5	31	7	25	3626.2770	7	16
30	5	26	3353.6688	5	0	31	6	26	3494.3545	14	-9	32	7	26	3655.9075	8	-7
31	5	27	3382.4224	6	7	32	6	27	3524.0108	6	3	33	7	27	3686.4615	9	5
32	5	28	3412.0964	6	-2	33	6	28	3554.5877	4	15	34	7	28	3717.9351		19
33	5	29	3442.6930	9	0	34	6	29	3586.0817	4	-4	36	7	30	3783.6344	10	9
34	5	30	3474.2095	13	-9	35	6	30	3618.4950		-27	37	7	31	3817.8588	5	-15
35	5	31	3506.6480	4	-2	36	6	31	3651.8316	2	-7	38	7	32	3853.0025		-17
36	5	32	3540.0066	15	8	37	6	32	3638.0855	7	2	8	8	1	3351.7440	3	-2
37	5	33	3574.2832	6	5	38	6	33	3721.2566	9	4	9	8	2	3360.0916		-20
38	5	34	3609.4770		-12	39	6	34	3757.3437		-5	12	8	5	3390.7133	8	16
39	5	35	3645.5911	15	-7	40	6	35	3794.3489	1	1	13	8	6	3402.7722	7	5
40	5	36	3682.6225	8	-2	41	6	36	3437.8102		5	14	8	7	3415.7582		0
41	5	37	3720.5709	15	5	42	6	37	3465.6222	11	5	16	8	9	3444.5106	15	4
42	5	38	3759.4366		24	43	6	38	3494.3545		-9	17	8	10	3460.2748	5	-3
43	5	39	3799.2151		17	44	6	39	3524.0114	9	9	18	8	11	3476.9634		-20
6	6	1	3053.4925	3	7	45	6	40	3554.5877		15	19	8	12	3494.5800	3	-11
7	6	2	3059.9985	14	7	7	7	1	3192.2322	6	-7	20	8	13	3513.1214	14	-3
8	6	3	3067.4328	4	-2	8	7	2	3199.6614	6	-14	22	8	15	3552.9772	12	10
9	6	4	3075.7982	5	10	9	7	3	3208.0205	17	-7	23	8	16	3574.2881	10	-12
10	6	5	3085.0900	4	-1	10	7	4	3217.3069	5	-7	24	8	17	3596.5266		6
11	6	6	3095.3118	2	0	11	7	5	3227.5225	6	5	25	8	18	3619.6873		16
12	6	7	3106.4619	5	0	12	7	6	3238.6640	2	-2	26	8	19	3643.7665		-13
13	6	8	3118.5406	3	3	13	7	7	3250.7340	2	0	27	8	20	3668.7717	14	-5
14	6	9	3131.5468	9	1	14	7	8	3263.7327	18	16	29	8	22	3721.5447		-9
15	6	10	3145.4806	3	-3	15	7	9	3277.6550	1	-5	11	9	2	3551.2890		16
16	6	11	3160.3425	5	-2	16	7	10	3292.5066	8	-1	12	9	3	3562.4094	7	-8
17	6	12	3176.1319	7	1	17	7	11	3308.2830	12	-14	13	9	4	3574.4578	15	-12
18	6	13	3192.8482	5	3	18	7	12	3324.9885	4	-1	14	9	5	3587.4360		24
19	6	14	3210.4909	3	2	19	7	13	3342.6191	10	4	15	9	6	3601.3343		6
20	6	15	3229.0599	2	0	20	7	14	3361.1745	3	-1	16	9	7	3616.1604		14
21	6	16	3248.5550	4	-2	21	7	15	3380.6564	8	6	17	9	8	3631.9091	13	-2
22	6	17	3268.9759	5	-3	22	7	16	3401.0624	7	3	18	9	9	3648.5856		14
23	6	18	3290.3215	7	-9	23	7	17	3422.3922	4	-6	19	9	10	3666.1846		11
24	6	19	3312.5942	10	4	24	7	18	3444.6468	5	-10						

assigned experimental transitions and the set of the ground state rotational energies derived in the previous section. In this case, 668 energies with $J^{max} = 55$ and $K_a^{max} = 9$ were determined for the (100) vibrational state (in Ref. (*18*) $J^{max} = 40$ and $K_a^{max} = 8$) and 528 energies with $J^{max} = 46$ and $K_a^{max} = 7$ were obtained for the (020) state (see also statistical information in Table 1). The energies obtained are presented in column 2 of Tables 3 and 4. In this case, since the energies $E_{[J,K_a,K_c=J-K_a]}$ and $E_{[J,K_a,K_c=J-K_a+1]}$ (K_a = 4, 5, 6, 7, 8, and 9) of the states (100) and (020), which derived from the experimental data are equal in pairs, Tables 3 and 4 present only one energy from any pair.

Before the fitting of the obtained energies, analysis of possible resonance interactions may be interesting and useful. As can be seen from Table 3 of (*15*), the $2\nu_2$ band of the DOCl molecule is located far from any other vibrational band. As a consequence, the Hamiltonian in the form of Eq. [1] is suitable for description of its rovibrational structure. However, the ν_1 band (the band center is 2665.58 cm^{-1}) is located very close to the other band, namely, $3\nu_2$ (in accordance with (*15*), the band center is 2702.8 cm^{-1}). Rotational and centrifugal distortion parameters of the (030) state can be estimated very easily on the basis of the known information about the corresponding parameters of the (010) state from Ref. (*18*) and the ground state and (020) excited state from the present study with the simple equation

$$P^{0v0} = P^{000} + p_1 v + p_2 v^2, \qquad [2]$$

where P^{0v0} is any of the rotational parameters (A, B, C) or the centrifugal distortion parameter of the Watson-type Hamiltonian in Eq. [1] for the vibrational state ($0v0$); P^{000} is the corresponding parameter of the ground vibrational state; coefficients p_1 and p_2 describe the vibrational dependence of the rotational and centrifugal distortion parameters. In this case, in accordance with the general principles of the rotational–vibrational theory (see, e.g., Refs. (*20, 21*)), it must be fulfilled that $P^{000} \gg p_1 \gg p_2$.

TABLE 4

Experimental Rovibrational Energy Levels for the (020) Vibrational State of the DOCl Molecule (in cm^{-1})[a]

J	K_a	K_c	E	Δ	δ	J	K_a	K_c	E	Δ	δ	J	K_a	K_c	E	Δ	δ
	1		2	3	4		1		2	3	4		1		2	3	4
1	0	1	1811.6343		-5	14	1	13	1920.7920	10	2	5	2	4	1869.5613	10	-7
2	0	2	1813.4947	6	-5	15	1	15	1932.0836	3	1	5	2	3	1869.5613	10	6
3	0	3	1816.2858	4	0	15	1	14	1934.9046	8	-7	6	2	5	1875.1417	18	-9
4	0	4	1820.0059	2	-2	16	1	16	1946.7607	6	6	6	2	4	1875.1417	18	13
5	0	5	1824.6560	9	0	16	1	15	1949.9572	2	-1	7	2	6	1881.6493	8	3
6	0	6	1830.2355	9	-1	17	1	17	1962.3513	3	-2	7	2	5	1881.6433	10	-3
7	0	7	1836.7445	6	4	17	1	16	1965.9473	6	-1	8	2	7	1889.0875	9	3
8	0	8	1844.1808	3	-5	18	1	18	1978.8572	7	-2	8	2	6	1889.0949	9	0
9	0	9	1852.5466	2	-2	18	1	17	1982.8748	2	-3	9	2	8	1897.4557	3	11
10	0	10	1861.8399	16	-1	19	1	19	1996.2772	8	0	9	2	7	1897.4670	6	3
11	0	11	1872.0609	4	5	19	1	18	2000.7400	9	2	10	2	9	1906.7511	6	1
12	0	12	1883.2073	5	-1	20	1	20	2014.6100	4	-5	10	2	8	1906.7694	2	3
13	0	13	1895.2795	2	-9	20	1	19	2019.5410	8	-1	11	2	10	1916.9760	17	0
14	0	14	1908.2789	5	3	21	1	21	2033.8569	8	1	11	2	9	1917.0032	5	9
15	0	15	1922.2010	7	-3	21	1	20	2039.2782	6	0	12	2	11	1928.1300	9	5
16	0	16	1937.0481	10	4	22	1	22	2054.0150	5	-5	12	2	10	1928.1668	7	6
17	0	17	1952.8162	9	-6	22	1	21	2059.9505	8	-2	13	2	12	1940.2138		27
18	0	18	1969.5080	5	2	23	1	23	2075.0864	9	3	13	2	11	1940.2615	4	3
19	0	19	1987.1200	6	2	23	1	22	2081.5578	6	0	14	2	13	1953.2207	8	1
20	0	20	2005.6520	10	2	24	1	24	2097.0680	5	0	14	2	12	1953.2875	2	2
21	0	21	2025.1030	9	4	24	1	23	2104.0993	7	4	15	2	14	1967.1579	4	3
22	0	22	2045.4715	9	2	25	1	25	2119.9613	4	7	15	2	13	1967.2449	5	2
23	0	23	2066.7570	7	4	25	1	24	2127.5734	10	2	16	2	15	1982.0220	5	4
24	0	24	2088.9575	7	0	26	1	25	2143.7633	9	0	16	2	14	1982.1338	6	2
25	0	25	2112.0733	7	5	26	1	25	2151.9801	7	1	17	2	16	1997.8125	5	0
26	0	26	2136.1012	12	0	27	1	27	2168.4749	14	-6	17	2	15	1997.9550	10	8
27	0	27	2161.0423	7	8	27	1	26	2177.3183	5	-3	18	2	17	2014.5298	6	2
28	0	28	2186.8921	9	-2	28	1	28	2194.0971	10	5	18	2	16	2014.7063	2	-2
29	0	29	2213.6526	0	0	28	1	27	2203.5879	6	-2	19	2	18	2032.1726	4	-1
30	0	30	2241.3220	5	11	29	1	29	2220.6253	5	-4	19	2	17	2032.3912	4	2
31	0	31	2269.8962	8	3	29	1	28	2230.7876	3	0	20	2	19	2050.7411	4	0
32	0	32	2299.3762	6	-2	30	1	30	2248.0630	12	7	20	2	18	2051.0080	6	4
33	0	33	2329.7611	2	2	30	1	29	2258.9162	8	-2	21	2	20	2070.2349	6	3
34	0	34	2361.0479	7	-4	31	1	31	2276.4056	1	0	21	2	19	2070.5562	6	-5
35	0	35	2393.2371	10	0	31	1	30	2287.9737	11	3	22	2	21	2090.6529	6	4
36	0	36	2426.3260	2	-1	32	1	32	2305.6550	8	0	22	2	20	2091.0378	3	-5
37	0	37	2460.3139	12	-2	32	1	31	2317.9577	6	0	23	2	22	2111.9945	5	2
38	0	38	2495.1986	4	-10	33	1	33	2335.8096	4	1	23	2	21	2112.4530	5	2
39	0	39	2530.9786		-30	33	1	32	2348.8690	7	6	24	2	23	2134.2600	14	5
40	0	40	2567.6562		-25	34	1	34	2366.8690	8	5	24	2	22	2134.8003	4	1
43	0	43	2683.0440		-48	34	1	33	2380.7048	10	4	25	2	24	2157.4475	5	1
1	1	0	1822.8782	3	-12	35	1	35	2398.8313	3	1	25	2	23	2158.0807	3	0
2	1	2	1824.6928	2	1	35	1	34	2413.4657	11	10	26	2	25	2181.5575	6	0
2	1	1	1824.7630		-3	36	1	36	2431.6969	6	1	26	2	24	2182.2944	5	-1
3	1	3	1827.4477	11	-1	36	1	35	2447.1486	4	5	27	2	26	2206.5895	7	2
3	1	2	1827.5892	9	1	37	1	37	2465.4644		-1	27	2	25	2207.4415	8	-2
4	1	4	1831.1215	9	4	37	1	36	2481.7527		-9	28	2	27	2232.5414	5	-5
4	1	3	1831.3550	3	-16	38	1	38	2500.1335	3	1	28	2	26	2233.5227	4	2
5	1	5	1835.7125	6	-1	38	1	37	2517.2792	4	-7	29	2	28	2259.4144	10	-3
5	1	4	1836.0666	8	7	39	1	38	2553.7236		-23	29	2	27	2260.5358	8	-11
6	1	6	1841.2215	7	-7	40	1	40	2572.1733	6	19	30	2	29	2287.2075		3
6	1	5	1841.7166	9	-1	40	1	39	2591.0908	3	4	30	2	28	2288.4854	7	4
7	1	7	1847.6494	7	-1	41	1	40	2629.3718	2	-2	31	2	30	2315.9178	6	-6
7	1	6	1848.3090	2	2	42	1	42	2647.8052		14	31	2	29	2317.3665	6	-3
8	1	8	1854.9949	5	3	42	1	41	2668.5695	3	1	32	2	31	2345.5475	6	-2
8	1	7	1855.8421	11	0	43	1	43	2686.9650		-7	32	2	30	2347.1825	2	2
9	1	9	1863.2570	6	0	43	1	42	2708.6815		2	33	2	32	2376.0939	6	-5
9	1	8	1864.3165	8	1	44	1	44	2727.0248	6	13	33	2	31	2377.9312	13	-3
10	1	10	1872.4367	5	-1	44	1	43	2749.7048		-15	34	2	33	2407.5578		2
10	1	9	1873.7312	12	-1	45	1	44	2791.6429		-1	34	2	32	2409.6135	5	-8
11	1	11	1882.5335	5	1	46	1	45	2834.4894	6	-5	35	2	34	2439.9358	7	-7
11	1	10	1884.0865	10	-2	2	2	1	1858.4013	16	2	35	2	33	2442.2312	8	7
12	1	12	1893.5469	3	2	2	2	0	1858.4013	16	2	36	2	35	2473.2292	10	-11
12	1	11	1895.3830	5	9	3	2	2	1861.1912	14	-1	36	2	34	2475.7788	5	-11
13	1	13	1905.4763	8	-1	3	2	1	1861.1912	14	1	37	2	36	2507.4376	1	-6
13	1	12	1907.6172	9	-1	4	2	3	1864.9122	20	7	37	2	35	2510.2619	2	-6
14	1	14	1918.3223	11	2	4	2	2	1861.9122	20	12	38	2	37	2542.5584	4	-8

[a] Δ is the experimental uncertainty of the energy value, equal to one standard deviation is units of 10^{-4} cm^{-1}; δ is the difference $E^{exp} - E^{calc}$, also in units of 10^{-4} cm^{-1}; Δ is not quoted when the energy value was obtained from only one transition.

TABLE 4—*Continued*

J	K_a	K_c	E	Δ	δ	J	K_a	K_c	E	Δ	δ	J	K_a	K_c	E	Δ	δ
	1		2	3	4		1		2	3	4		1		2	3	4
38	2	36	2545.6776	11	0	36	3	33	2529.9300	13	8	31	5	27	2550.3831	5	0
3	3	2	1917.2298	17	3	37	3	35	2564.0929	3	4	32	5	28	2580.0195	2	9
3	3	1	1917.2298	17	3	37	3	34	2564.2251	9	-2	33	5	29	2610.5739	10	-3
4	3	2	1920.9489	8	4	38	3	36	2599.2875	8	-2	34	5	30	2642.0493	12	0
4	3	1	1920.9489	8	4	38	3	35	2599.4437		9	35	5	31	2674.4421		-12
5	3	3	1925.5973	7	2	39	3	37	2635.4011		2	36	5	32	2707.7570	9	13
5	3	2	1925.5973	7	2	39	3	36	2635.4017	5	-1	37	5	33	2741.9860	5	3
6	3	4	1931.1757	3	4	40	3	38	2672.4315	12	0	38	5	34	2777.1344		14
6	3	3	1931.1757	3	4	40	3	37	2672.6404	8	-5	40	5	36	2850.1767	6	6
7	3	5	1937.6830	5	0	4	4	1	1999.2286	5	-2	6	6	1	2232.0227	1	3
7	3	4	1937.6830	5	0	5	4	2	2003.8754	3	-2	7	6	2	2238.5208	2	-1
8	3	6	1945.1205	8	5	6	4	3	2009.4520	3	3	8	6	3	2245.9478	5	4
8	3	5	1945.1205	8	5	7	4	4	2015.9568	4	1	9	6	4	2254.3021	9	2
9	3	7	1953.4860	5	-4	8	4	5	2023.3911	7	3	10	6	5	2263.5840	3	0
9	3	6	1953.4860	5	-4	9	4	6	2031.7539	7	2	11	6	6	2273.7935	4	-2
10	3	8	1962.7819	9	0	10	4	7	2041.0451	5	-2	12	6	7	2284.9304	5	-3
10	3	7	1962.7819	9	-1	11	4	8	2051.2652	2	-3	13	6	8	2296.9950	4	2
11	3	9	1973.0066	4	1	12	4	9	2062.4140	6	-1	14	6	9	2309.9860	5	1
11	3	8	1973.0066	4	0	13	4	10	2074.4904	5	-4	15	6	10	2323.9036	6	0
12	3	10	1984.1602	6	3	14	4	11	2087.4957	5	2	16	6	11	2338.7480	3	3
12	3	9	1984.1602	6	2	15	4	12	2101.4279	5	-1	17	6	12	2354.5175	7	-4
13	3	11	1996.2420	8	1	16	4	13	2116.2876	7	-4	18	6	13	2371.2141	6	2
13	3	10	1996.2420	8	-1	17	4	14	2132.0754	8	1	19	6	14	2388.8357	4	2
14	3	12	2009.2531	5	-2	18	4	15	2148.7895	5	0	20	6	15	2407.3826	7	-3
14	3	11	2009.2531	5	1	19	4	16	2166.4307	10	2	21	6	16	2426.8538	7	1
15	3	13	2023.1917	9	2	20	4	17	2184.9979	6	0	22	6	17	2447.2501	2	4
15	3	12	2023.1917	9	-4	21	4	18	2204.4915	12	2	23	6	18	2468.5695	7	-2
16	3	14	2038.0584	5	-1	22	4	19	2224.9104	8	-2	24	6	19	2490.8141	5	7
16	3	13	2038.0596	5	2	23	4	20	2246.2554	7	2	25	6	20	2513.9806	4	3
17	3	15	2053.8532	6	-2	24	4	21	2268.5251	5	3	26	6	21	2538.0699	5	-1
17	3	14	2053.8547	7	0	25	4	22	2291.7191	1	0	27	6	22	2563.0821	15	0
18	3	16	2070.5756	8	-2	26	4	23	2315.8381	3	3	28	6	23	2589.0159	10	-1
18	3	15	2070.5780	4	2	27	4	24	2340.8801	3	1	29	6	24	2615.8714	1	1
19	3	17	2088.2260	5	3	28	4	25	2366.8464	4	6	30	6	25	2643.6476	5	1
19	3	16	2088.2285	5	2	29	4	26	2393.7350	3	5	31	6	26	2672.3431	4	-9
20	3	18	2106.8027	8	1	30	4	27	2421.5462	3	4	32	6	27	2701.9594	6	-9
20	3	17	2106.8063	8	1	31	4	28	2450.2795	7	5	33	6	28	2732.4958	5	0
21	3	19	2126.3062	15	-1	32	4	29	2479.9339	4	1	34	6	29	2763.9502	5	2
21	3	18	2126.3106	7	-5	33	4	30	2510.5098	8	3	35	6	30	2796.3220	3	-2
22	3	20	2146.7365	6	0	34	4	31	2542.0064	5	7	36	6	31	2829.6116	2	-3
22	3	19	2146.7427	8	0	35	4	32	2574.4215	6	-3	37	6	32	2863.8189	7	-1
23	3	21	2168.0928	6	1	5	5	1	2104.2294	6	-5	38	6	33	2898.9405	10	-5
23	3	20	2168.1007	7	-2	6	5	2	2109.8032	5	0	39	6	34	2934.9794	4	2
24	3	22	2190.3746	3	-2	7	5	3	2116.3047	4	-5	41	6	36	3009.8012	8	20
24	3	21	2190.3853	8	1	8	5	4	2123.7355	7	-2	7	7	0	2382.3613	1	1
25	3	23	2213.5825	10	2	9	5	5	2132.0944	5	-1	8	7	1	2389.7852		13
25	3	22	2213.5950	8	-5	10	5	6	2141.3818	5	2	9	7	2	2398.1341	12	1
26	3	24	2237.7150	5	3	11	5	7	2151.5966	5	-2	10	7	3	2407.4113	2	-1
26	3	23	2237.7313	7	-1	12	5	8	2162.7400	3	2	11	7	4	2417.6155	5	-2
27	3	25	2262.7722	8	4	13	5	9	2174.8107	5	2	12	7	5	2428.7471	5	2
27	3	24	2262.7930	4	3	14	5	10	2187.8088	5	1	13	7	6	2440.8050	10	3
28	3	26	2288.7533	8	2	15	5	11	2201.7336	4	-5	14	7	7	2453.7883	3	-5
28	3	25	2288.7791	8	2	16	5	12	2216.5868	5	4	15	7	8	2467.6986	9	-5
29	3	27	2315.6580	10	-1	17	5	13	2232.3654	4	0	16	7	9	2482.5355	11	3
29	3	26	2315.6881		-18	18	5	14	2249.0708	6	-1	17	7	10	2498.2965	12	-3
30	3	28	2343.4862	6	-2	19	5	15	2266.7021	9	-3	18	7	11	2514.9842	14	6
30	3	27	2343.5245	7	-7	20	5	16	2285.2600	4	3	19	7	12	2532.5949	6	-3
31	3	29	2372.2370	4	-5	21	5	17	2304.7426	4	1	20	7	13	2551.1313	9	-2
31	3	28	2372.2837	6	-8	22	5	18	2325.1510	3	7	21	7	14	2570.5915	8	-4
32	3	30	2401.9114	6	5	23	5	19	2346.4835	6	6	22	7	15	2590.9759	4	-2
32	3	29	2401.9671	8	-4	24	5	20	2368.7403	6	5	23	7	16	2612.2839	10	3
33	3	31	2432.5053		-7	25	5	21	2391.9206	8	0	24	7	17	2634.5149	7	8
33	3	30	2432.5735	3	-3	26	5	22	2416.0250	5	1	25	7	18	2657.6678	3	7
34	3	32	2464.0236	7	13	27	5	23	2441.0527	5	4	26	7	19	2681.7424	5	2
34	3	31	2464.1036	12	5	28	5	24	2467.0031	8	8	27	7	20	2706.7385	19	-3
35	3	33	2496.4592	2	0	29	5	25	2493.8745	8	1	29	7	22	2759.4950		3
35	3	32	2496.5549	1	-2	30	5	26	2521.6682	2	0	30	7	23	2787.2531		2
36	3	34	2529.8170	12	8												

It should be mentioned that the values of the P^{030} parameters were estimated in two different ways. On one hand, all three type parameters, P^{000}, p_1, and p_2, were estimated from the experimental values of the corresponding parameters of the (000), (010), and (020) vibrational states. On the other hand, the values of p_2 were omitted and pairs of the parameters P^{000} and p_1 were estimated from the fits of triads of corresponding parameters of the (000), (010), and (020) vibrational states. Then both sets of the estimated parameters were used to estimate the values of energies of the (030) vibrational states. It should be noted that calculations gave close results in both cases. In this case, it was found that for any set of energies $E_{[J,K_a,K_c=J-K_a]}$ or $E_{[J,K_a,K_c=J+1-K_a]}$ (with the fixed value of the quantum number K_a) the possibility of resonance interaction between the (100) and (030) vibrational states is very small except for the set $E_{[J,K_a=2,K_c=J-2]}(100)$, which is crossed with the set $E_{[J,K_a=1,K_c=J]}$ of the (030) vibrational state at a quantum number J close to 29–30 (see Table 5). As a conclusion, it is possible to expect the appearance of the Coriolis type resonance interaction in the experimentally recorded spectrum. And actually, if one will fit the only set of energies $E_{[J,K_a=2,K_c=J-2]}$ of the (100) state, minor peculiarities can be seen for the energies $E_{[30,2,28]}$, $E_{[31,2,29]}$. But these peculiarities (their values are about 0.0015–0.0020 cm^{-1}) are only a little bit larger than the experimental uncertainties, so we did not succeed in the attempt to assign the corresponding transitions belonging to the $3\nu_2$ band caused by the resonance interactions.

TABLE 5
Some Vibrational–Rotational Energies of the (100) and (030) States of the DOCl Molecule (in cm^{-1})

		(100)				(030)	
J	K_a	K_c	Energy	J	K_a	K_c	Energy
	1		2		3		4
25	2	23	3009.4624	25	1	25	3012.1090
26	2	24	3033.6980	26	1	26	3035.8486
27	2	25	3058.8671	27	1	27	3060.4950
28	2	26	3084.9699	28	1	28	3086.0476
29	2	27	3112.0062	29	1	29	3112.5056
30	2	28	3139.9768	30	1	30	3139.8683
31	2	29	3168.8824	31	1	31	3168.1351
32	2	30	3198.7195	32	1	32	3197.3050
33	2	31	3229.4911	33	1	33	3227.3774
34	2	32	3261.1960	34	1	34	3258.3515

Finally, rovibrational energies of both the (100) and (020) states were fitted with the Hamiltonian of an isolated vibrational state, Eq. [1]. Parameters obtained from the fit are presented in columns 3 and 6 of Table 6 together with their 1σ

TABLE 6
Spectroscopic Parameters of Some Vibrational States of the DOCl Molecule (in cm^{-1})[a]

Parameter	(000)	(100)	(100)	(010)	(020)
	our	our	from (*18*)	from (*18*)	our
1	2	3	4	5	6
E		2665.5782865(504)	2665.57866	909.62629	1810.7046161(844)
A	11.05225700	10.74404156(551)	10.74401	11.362635	11.7000617(184)
B	0.476978130	0.476325861(395)	0.47632516	0.47691746	0.476959877(831)
C	0.456129220	0.455052492(456)	0.45505155	0.45469115	0.453273933(919)
$\Delta_K \times 10^4$	13.292947	12.80924(208)	12.800	16.7783	20.90495(964)
$\Delta_{JK} \times 10^4$	0.2546159	0.2502911(324)	0.25073	0.26512	0.253297(648)
$\Delta_J \times 10^4$	0.007472763	0.00748398(231)	0.0074602	0.0075964	0.00767837(220)
$\delta_K \times 10^4$	0.15722	0.15147(139)	0.1521	0.1982	0.34592(404)
$\delta_J \times 10^4$	0.000302383	0.000310447(792)	0.0003158	0.0003058	0.00034536(131)
$H_K \times 10^7$	7.31495	7.0782(210)	6.86	12.56	15.460(133)
$H_{KJ} \times 10^7$	-	-	0.0216	0.3604	-0.3545(363)
$H_{JK} \times 10^7$	-	-	-	-	0.016076(368)
$H_J \times 10^7$	-	0.000007858(717)	-	-	-
$h_K \times 10^7$	-0.9356	-0.9356	-	-	16.011(436)
$h_{JK} \times 10^7$	-	-	-	-	-
$h_J \times 10^7$	-	-	-	-	-
$L_K \times 10^{10}$	-	-	-	-	-
$L_{KKJ} \times 10^{10}$	-	-	-	-	17.061(447)
$L_{KJ} \times 10^{10}$	-	-	-	-	0.2812(258)

[a] Values in parentheses are the 1σ statistical confidence intervals. The h_K parameter of the (100) state (column 3), which is presented without confidence interval, was fixed to the value of the h_K parameter of the ground vibrational state.

TABLE 7
Some Rovibrational Line Positions in the ν_1 Band of the DOCl Molecule

J'	K'_a	K'_c	J	K_a	K_c	Line position, exp., in cm^{-1}	δ^a, our, in $10^4\ \text{cm}^{-1}$	δ^a, Ref.(18), in $10^4\ \text{cm}^{-1}$
	1			2		3	4	5
34	7	27	33	7	26	2681.1623	18	64
36	7	29	35	6	30	2818.6483	20	33
37	7	30	36	8	29	2527.6210	-15	134
38	7	31	37	7	30	2684.5930	-17	41
25	8	18	26	8	19	2621.4326	18	103
26	8	19	25	8	18	2669.6374	-13	67
27	8	20	27	8	19	2645.4692	11	99
29	8	22	30	8	23	2617.5541	-9	88
11	9	2	11	9	3	2640.8798	16	154
12	9	3	11	10	2	2455.1651	-2	248
13	9	4	12	10	3	2456.0830	0	255
14	9	5	14	9	6	2640.8159	24	171
15	9	6	16	9	7	2625.9374	6	164
16	9	7	16	10	6	2443.9959	14	304
17	9	8	17	9	9	2640.7351	12	170
18	9	9	17	9	8	2657.4103	14	169
19	9	10	18	9	9	2658.3045	11	170

[a] $\delta = \nu_{exp.} - \nu_{calc.}$, where $\nu_{exp.}$ and $\nu_{calc.}$ is the experimental and calculated value of the line position, respectively.

statistical confidence intervals. For comparison, parameters of the (100) and (010) vibrational states from Ref. (*18*) are given in columns 4 and 5 of that table, respectively. Column 2 gives the parameters of the ground vibrational state from Table 2. One can see that our set of parameters of the (100) state correlates with the corresponding set of parameters from Ref. (*18*). At the same time, it should be mentioned that our parameters reproduce the experimental line positions, which correspond to higher values of quantum number J, with better accuracy. For an illustration, column 3 of Table 7 presents some experimental line positions of the ν_1 band. The column 4 of that table shows the differences $\Delta = \nu^{exp.} - \nu^{calc.}$, where $\nu^{calc.}$ are the values of corresponding line positions calculated on the basis of our parameters from columns 2 and 3 of Table 6. Results of calculations with the parameters from Ref. (*18*) are given in column 5 of Table 7.

We believe that the parameters of the states (100) and (020) obtained in the present paper are meaningful in physics because:

(1) Both the parameters of the (100) state and the parameters of the (020) state (with the exception of A, Δ_K, δ_K, H_K, and h_K) are close to the values of corresponding parameters of the ground vibrational state. At the same time, parameters A, Δ_K, δ_K, H_K, and h_K are increased anomaly strongly with the increasing vibrational quantum number v_2, *i.e.*, they show the behavior which is typical for bands belonging to a "soft" bending vibration, Ref. (*21*).

(2) The set of parameters derived from the fit reproduces the initial "experimental" upper energies with the accuracies close to experimental uncertainties (for illustration, see the statistical information in columns 6–8 of Table 1 and column 4 of Tables 3 and 4).

5. CONCLUSION

The high-resolution Fourier transform spectra of the DOCl molecule were recorded and analyzed in the region of the ν_1 and $2\nu_2$ bands. Transitions belonging to the ν_1 and $2\nu_2$ bands were assigned up to $J^{max} = 55$ and 46, respectively. On this basis, a set of the ground state rotational and centrifugal distortion parameters was determined. The sets of spectroscopic parameters of the (100) and (020) vibrational states obtained from the fit reproduce their rovibrational energies derived from the experimental data with the accuracies close to experimental uncertainties.

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