

# High-Resolution Rotational Analysis of the Lowest D–O Overtone Bands of Deuterated Hypochlorous Acid: $2\nu_1$ and $3\nu_1$

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The high-resolution Fourier transform spectrum of the DO<sup>35</sup>Cl molecule was recorded and analyzed in the region of the two lowest D–O overtone bands,  $2\nu_1$  and  $3\nu_1$ . Because of the presence of strong resonance interactions, the influence of the (130) state on the (200) state, and also that of the (221), (230) states on the (300) state, was taken into account. Transitions belonging to the  $2\nu_1$  and  $3\nu_1$  bands were assigned up to  $J^{\max} = 35$  in both cases. The sets of spectroscopic parameters and resonance coefficients obtained from the fit reproduce the “experimental” rovibrational energies of the (200) and (300) vibrational states with accuracies close to experimental uncertainties. © 2001 Academic Press

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

## 1. INTRODUCTION

In this work we continue our study, Ref. (1), of the high-resolution vibration–rotational spectra of the deuterated species of the HOCl molecule, which is of direct interest because of its important role in the balance of stratospheric ozone in polar regions (see, e.g., (2–4 and references therein)). The subject of the present analysis is the two unstudied overtone bands of the D–O stretching vibration  $2\nu_1$  and  $3\nu_1$ . Section 2 presents the experimental conditions of our study. Model of the Hamiltonian which was used in the theoretical analysis of experimental data is presented in Section 3. Sections 4 and 5 are devoted to the analysis and discussion of the spectra of the  $2\nu_1$  and  $3\nu_1$  bands, respectively.

## 2. EXPERIMENTAL DETAILS

The DOCl sample was prepared as described in Ref. (5) by substituting D<sub>2</sub>O for H<sub>2</sub>O. 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. A CaF<sub>2</sub> beam splitter, a Globar source, and a liquid-nitrogen-cooled InSb detector were used. For the  $2\nu_1$  band, the mixed sample gas pressure and absorption path length were 840 Pa and 87 m, respectively. The unapodized resolution was 0.01 cm<sup>-1</sup>, and the Norton–Beer weak apodization function was used in the Fourier transform. The

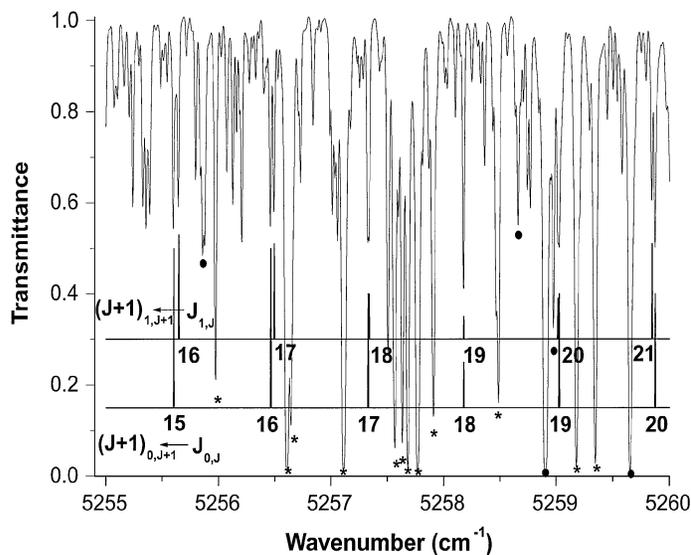
line positions were calibrated with those of the H<sub>2</sub>O in the HITRAN 96 database. The accuracy of the unblended lines was estimated to be 0.001 cm<sup>-1</sup>. For illustration, a part of the spectrum is presented in Fig. 1. For the  $3\nu_1$  band, the unapodized resolution was 0.015 cm<sup>-1</sup> and the same apodization function as for the  $2\nu_1$  band was also adopted. The mixed sample gas pressure 993 Pa and the absorption path length 69 m were used in the measurement. The line positions were calibrated with those of the H<sub>2</sub>O in the GEISA 97 database. The accuracy of the unblended not very weak lines was estimated to be 0.002 cm<sup>-1</sup>. An overview and a small portion of the spectra of the  $3\nu_1$  band are shown in Fig. 2 and Fig. 3, respectively.

## 3. THEORETICAL BACKGROUND

Since the DOCl is a near prolate asymmetric top molecule with the  $C_s$  type symmetry, all of its three vibrational coordinate are of the  $A'$  type. So all the vibrational–rotational bands contain absorption lines arising from transitions of two types,  $a$  and  $b$ . However, as our further analysis will show, transitions of the  $a$  type are considerably stronger than those of the  $b$  type in the  $2\nu_1$  and  $3\nu_1$  bands. In this work, we were able to assign transitions of the  $a$  type in both bands.

To the contrary of the fundamental band  $\nu_1$ , Ref. (1), which was exactly isolated from the other vibrational bands, both the  $2\nu_1$ , and, especially,  $3\nu_1$  bands show strongly perturbed rotational structures. For this reason, we used a Hamiltonian model which takes into account the resonance interactions in

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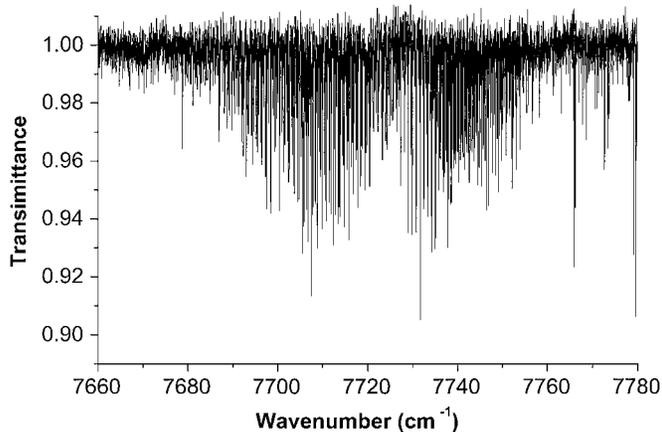
**FIG. 1.** Portion of the R-branch of the  $2\nu_1$  first overtone band of the DOCl. Two sets of transitions are shown. The  $D_2O$  and HDO lines are indicated by the dots and stars, respectively.

the analysis:

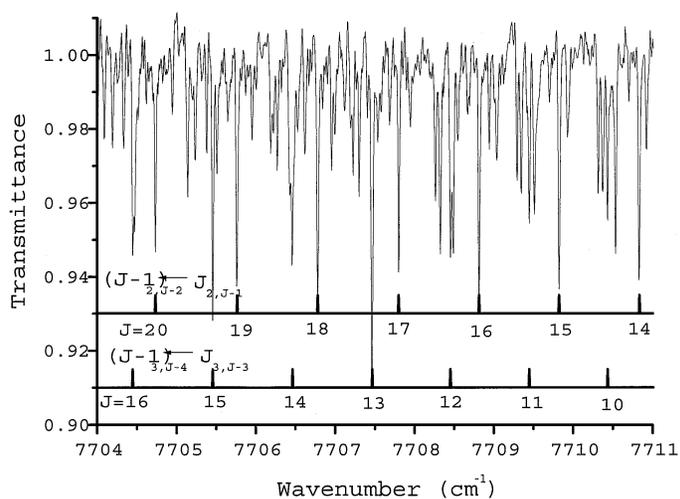
$$H^{eff.} = \sum_{v,v'} |v\rangle\langle v'| H^{vv'}. \quad [1]$$

Here the diagonal operators  $H^{vv}$  are the usual Watson's rotational operators in the  $A$ -reduction (6),

$$\begin{aligned} H^{vv} = & E^v + \left[ A^v - \frac{1}{2}(B^v + C^v) \right] J_z^2 + \frac{1}{2}(B^v + C^v) J^2 \\ & + \frac{1}{2}(B^v - C^v) J_{xy}^2 - \Delta_K^v J_z^4 - \Delta_{JK}^v J_z^2 J^2 \\ & - \Delta_J^v J^4 - \delta_K^v [J_z^2, J_{xy}^2] - 2\delta_J^v J^2 J_{xy}^2 + H_K^v J_z^6 \end{aligned}$$



**FIG. 2.** The overview spectrum of the  $3\nu_1$  second overtone band of the DOCl.



**FIG. 3.** Small portion of the  $P$ -branch transitions in the  $3\nu_1$  second overtone band of the DOCl.

$$\begin{aligned} & + H_{KJ}^v J_z^4 J^2 + H_{JK}^v J_z^2 J^4 + H_J^v J^6 \\ & + [J_{xy}^2, h_K^v J_z^4 + h_{JK}^v J^2 J_z^2 + h_J^v J^4]_+ + \dots, \quad [2] \end{aligned}$$

and the off-diagonal operators  $H^{vv'}$  ( $v \neq v'$ ) account for the resonance interactions. As we have mentioned, three vibrational coordinates of DOCl molecule are transformed according to the totally symmetric irreducible representation of the  $C_s$  group. As a consequence, all resonance interaction blocks have the similar form and should be written as the sum of two terms:

$$H^{vv'} = H^{v'v'+} = H_{F.}^{vv'} + H_{C.}^{vv'}. \quad [3]$$

Here  $H_{F.}^{vv'}$  and  $H_{C.}^{vv'}$  describe the resonance interactions of the Fermi type and Coriolis type, respectively:

$$\begin{aligned} H_{F.}^{vv'} = & F_0^{v'v} + F_K^{vv'} J_z^2 + F_J^{vv'} J^2 + F_{KK}^{vv'} J_z^4 + \dots \\ & + F_{xy}^{vv'} J_{xy}^2 + F_{xyK}^{vv'} [J_{xy}^2, J_z^2]_+ \\ & + F_{xyKK}^{vv'} [J_{xy}^2, J_z^4]_+ + \dots, \quad [4] \\ H_{C.}^{vv'} = & C_y^{vv'} i J_y + C_{yK}^{vv'} [i J_y, J_z^2]_+ + C_{yJ}^{vv'} i J_y J^2 + \dots \\ & + C_{xz}^{vv'} [J_x, J_z]_+ + C_{xzK}^{vv'} [[J_x, J_z]_+, J_z^2]_+ \\ & + C_{xzJ}^{vv'} [J_x, J_z]_+ J^2 + \dots. \quad [5] \end{aligned}$$

In Eqs. [2]–[5] the following notations are used:  $J_{xy}^2 = J_x^2 - J_y^2$  and  $J^2 = \sum_{\alpha} J_{\alpha}^2$ .

It is necessary to explain here that why we may use the  $A$ -reduction of the Hamiltonian [2] in spite of the fact that the difference  $(B - C)$  is very small [ $(B - C) \sim 0.02 \text{ cm}^{-1}$ ]. The answer is: As it follows the procedure of the construction of the effective Hamiltonian of an asymmetric top molecule, Ref. (6)

(see also Ref. (7), where the problem of reduction of an effective Hamiltonian was discussed for an arbitrary polyatomic molecule), the possibility of using the  $A$ -reduction depends not only on the difference of the rotational constants  $B$  and  $C$ , but also on the values of the so-called parameters of ambiguity  $S_{pqr}$  (see Ref. (6) for details). When an absolute value of the ratio  $S_{pqr}/(B - C)$  is small, there is no reason to reject the very efficient Hamiltonian's  $A$ -reduction even for a molecule with a small value of the difference  $(B - C)$ . The DOCl molecule just satisfies this condition. It can be understood, e.g., with the analysis of the quartic centrifugal distortion coefficients. As it follows with Eq. [51] of Ref. (6), only one (namely,  $\delta_K$ ) of the five quartic centrifugal distortion coefficients depends on the  $S_{pqr}/(B - C)$ . It means that  $\delta_K$  (and/or related coefficients  $h_K$ , etc.) can show the anomalous behavior when the  $A$ -reduction is used. However, as one can see, e.g., from Table 2, the value of  $\delta_K$  is very small in comparison with the values of the parameters  $A$ ,  $B$ ,  $C$  and even the difference  $(B - C)$ . In turn, the  $h$ -type coefficients are small in comparison with the related  $\delta$ -type ones. All the above said allow one to make the conclusion that the  $A$ -reduction of the effective Hamiltonian is correct for the theoretical study of the DOCl molecule.

#### 4. ANALYSIS OF THE $2\nu_1$ BAND

The recorded transitions were assigned using the ground state combination differences method, and the ground state rotational energies were calculated on the basis of the parameters taken from Ref. (1). As a result of the analysis, we assigned 907 transitions with  $J^{max.} = 35$  and  $K_a^{max.} = 6$  to the  $2\nu_1$  band. The upper rovibrational energies of the (200) state were found. They are presented in column 2 of Table 1. These upper energies were determined as the mean values of some energies obtained from different transitions which reach the same upper state. Column 3 of Table 1 presents the value  $\Delta$  which is the experimental uncertainty of the energy value, equal to one standard deviation in units of  $10^{-4} \text{ cm}^{-1}$ . The  $\Delta$  is not quoted when the energy was obtained from only one transition.

At the next step of analysis, energies from Table 1 were fitted with the Hamiltonian model of an isolated vibrational state, Eq. [2]. It is interesting to mark that, if one omits all the energies with the value of  $K_a = 6$ , the parameters presented in column 3 of Table 2 can be obtained from the fit and the initial values of energies can be reproduced with the accuracies closed to experimental uncertainties. For comparison, calculated values of the rotational parameters and centrifugal distortion coefficients, obtained from interpolation of the values of corresponding parameters of the (000) and (100) states from Ref. (1), are presented in column 2 of Table 2. One can maintain good correlations between the sets of parameters in columns 3 and those in column 2. This fact shows that the Hamiltonian of an isolated vibrational state is physically suitable for the description of the rovibrational energy levels with the value of quantum number  $K_a \leq 5$ . At the same time, if one uses the

set of parameters from column 3 to predict the energies with the value  $K_a = 6$ , then it will be found that all predicted energies  $E_{[J, K_a=6, K_c]}$  shift from corresponding experimental energies with  $0.0060\text{--}0.0080 \text{ cm}^{-1}$ . If one includes the energies  $E_{[J, K_a=6, K_c]}$  in the fit procedure and uses the same number of fitted parameters as in the previous case, it can be seen that the results of the fit will be considerably worse. The *rms* deviation will be over 2 times larger. Even when six extra parameters are added into the fit procedure (see column 4 of Table 2), the results will not be improved. This fact shows the presence of strong resonance perturbation of the rovibrational states  $E_{[J, K_a=6, K_c]}$ .

To make a conclusion of such accidental perturbations, we made rough estimations of the rovibrational structures of different vibrational states which can be presented in the spectral region near  $5250 \pm 300 \text{ cm}^{-1}$ . The band centers were taken from (8), and the values of rotational parameters and centrifugal distortion coefficients were estimated on the basis of the values of corresponding parameters of the (000), (100), (020), Ref. (1), and (010), (001), Ref. (9) states. As a result, we found that the mostly possible origin of the perturbations of the  $[J, K_a = 6, K_c]$  (200) states is their resonance interactions with the states  $[J, K_a = 5, K_c]$  of the (130) vibrational state. The values of parameters of the (130) state predicted from calculations are shown in column 6 of Table 2. Finally, the fit of all the energies from Table 1 with the Hamiltonian [1]–[5] leads to the set of parameters which are presented in column 5 of Table 2. Two interacting states were taken into account in the fit. The center of the  $\nu_1 + 3\nu_2$  band and one of the Coriolis-type interaction parameters were also fitted. The value of the interaction parameter  $C_{\gamma K}$  was found to be  $-0.4759(507) \times 10^{-3} \text{ cm}^{-1}$ . The band center of  $\nu_1 + 3\nu_2$  is presented in column 6 of Table 2. It should be mentioned that this value,  $5327.45(143) \text{ cm}^{-1}$ , correlates very well with the result of the *ab initio* prediction,  $5324.6 \text{ cm}^{-1}$ , in Ref. (8).

#### 5. THE $3\nu_1$ BAND

The  $3\nu_1$  band is located in the shorter wavelength region  $7670\text{--}7770 \text{ cm}^{-1}$ , and, in accordance with the *ab initio* prediction, Ref. (8), it is about 30 times weaker than the  $2\nu_1$  band. Fortunately, contrary to the  $2\nu_1$  band, which is covered by the stronger bands  $\nu_1 + \nu_3$  (band center  $5373.9026 \text{ cm}^{-1}$ ) and  $2\nu_1(5291.7226 \text{ cm}^{-1})$  of the  $\text{D}_2\text{O}$ , Ref. (10), and  $2\nu_1(5364.3 \text{ cm}^{-1})$  of the  $\text{HDO}$ , Ref. (11), the  $3\nu_1$  band of the DOCl is located far enough from the absorption bands of the contaminants, either  $\text{D}_2\text{O}$ , or  $\text{HDO}$  (see Fig. 2). So, although the  $3\nu_1$  band is extremely weak, we were able to assign its 453 transitions with  $J^{max.} = 35$  and  $K_a^{max.} = 5$ . The obtained upper rovibrational energies of the (300) state are presented in column 2 of Table 3.

Theoretical analysis of the rotational structure of the (300) vibrational state was started with the  $E_{[J, K_a=0, K_c=J]}$  set of levels. The Hamiltonian of an isolated vibrational state, Eq. [2], was

**TABLE 1**  
**Experimental Rovibrational Energy Values for the (200) Vibrational States of the DOCI Molecule (in cm<sup>-1</sup>)<sup>a</sup>**

| <i>J</i> | <i>K<sub>a</sub></i> | <i>K<sub>c</sub></i> | <i>E</i>  | $\Delta$ | $\delta$ | <i>J</i> | <i>K<sub>a</sub></i> | <i>K<sub>c</sub></i> | <i>E</i>  | $\Delta$ | $\delta$ | <i>J</i> | <i>K<sub>a</sub></i> | <i>K<sub>c</sub></i> | <i>E</i>  | $\Delta$ | $\delta$ |
|----------|----------------------|----------------------|-----------|----------|----------|----------|----------------------|----------------------|-----------|----------|----------|----------|----------------------|----------------------|-----------|----------|----------|
| 1        |                      | 2                    | 3         | 4        |          | 1        |                      | 2                    | 3         | 4        |          | 1        |                      | 2                    | 3         | 4        |          |
| 1        | 0                    | 1                    | 5242.1077 | 4        | 8        | 12       | 1                    | 12                   | 5322.7972 | 10       | -1       | 6        | 2                    | 4                    | 5300.5883 | 9        | -5       |
| 3        | 0                    | 3                    | 5246.7552 | 30       | 0        | 12       | 1                    | 11                   | 5324.4850 | 7        | 6        | 7        | 2                    | 6                    | 5307.0929 | 10       | 12       |
| 4        | 0                    | 4                    | 5250.4737 | 12       | 2        | 13       | 1                    | 13                   | 5334.7328 | 4        | 0        | 7        | 2                    | 5                    | 5307.0947 | 10       | -14      |
| 5        | 0                    | 5                    | 5255.1201 |          | -9       | 13       | 1                    | 12                   | 5336.7004 | 15       | -3       | 8        | 2                    | 7                    | 5314.5261 | 13       | 2        |
| 6        | 0                    | 6                    | 5260.6976 | 3        | 2        | 14       | 1                    | 14                   | 5347.5851 |          | 2        | 8        | 2                    | 6                    | 5314.5332 | 3        | 0        |
| 7        | 0                    | 7                    | 5267.2026 |          | 2        | 14       | 1                    | 13                   | 5349.8539 |          | -12      | 9        | 2                    | 8                    | 5322.8886 | 10       | -1       |
| 8        | 0                    | 8                    | 5274.6356 | 16       | 0        | 15       | 1                    | 15                   | 5361.3532 | 7        | 1        | 9        | 2                    | 7                    | 5322.8993 | 3        | -9       |
| 9        | 0                    | 9                    | 5282.9969 | 10       | 2        | 15       | 1                    | 14                   | 5363.9486 | 3        | 15       | 10       | 2                    | 9                    | 5332.1792 |          | -8       |
| 10       | 0                    | 10                   | 5292.2854 | 8        | 4        | 16       | 1                    | 16                   | 5376.0372 | 7        | 0        | 10       | 2                    | 8                    | 5332.1980 |          | 6        |
| 11       | 0                    | 11                   | 5302.4998 | 10       | -3       | 16       | 1                    | 15                   | 5378.9760 | 2        | -2       | 11       | 2                    | 10                   | 5342.3994 |          | -1       |
| 12       | 0                    | 12                   | 5313.6420 | 17       | 5        | 17       | 1                    | 17                   | 5391.6368 | 10       | 2        | 11       | 2                    | 9                    | 5342.4253 | 4        | 7        |
| 13       | 0                    | 13                   | 5325.7081 | 3        | -3       | 17       | 1                    | 16                   | 5394.9417 | 16       | -3       | 12       | 2                    | 11                   | 5353.5477 | 2        | 6        |
| 14       | 0                    | 14                   | 5338.6996 | 5        | -8       | 18       | 1                    | 18                   | 5408.1508 | 12       | -2       | 12       | 2                    | 10                   | 5353.5830 | 15       | 9        |
| 15       | 0                    | 15                   | 5352.6164 | 15       | 0        | 18       | 1                    | 17                   | 5411.8444 | 4        | 3        | 13       | 2                    | 12                   | 5365.6220 | 3        | -2       |
| 16       | 0                    | 16                   | 5367.4558 | 8        | -2       | 19       | 1                    | 19                   | 5425.5799 | 5        | -1       | 13       | 2                    | 11                   | 5365.6693 | 9        | -6       |
| 17       | 0                    | 17                   | 5383.2177 | 11       | -3       | 19       | 1                    | 18                   | 5429.6818 | 11       | -1       | 14       | 2                    | 13                   | 5378.6255 | 11       | 7        |
| 18       | 0                    | 18                   | 5399.9016 | 1        | -2       | 20       | 1                    | 20                   | 5443.9227 | 6        | -2       | 14       | 2                    | 12                   | 5378.6884 | 7        | 0        |
| 19       | 0                    | 19                   | 5417.5064 |          | 0        | 20       | 1                    | 19                   | 5448.4553 | 11       | 3        | 15       | 2                    | 14                   | 5392.5563 | 4        | 18       |
| 20       | 0                    | 20                   | 5436.0306 | 11       | -3       | 21       | 1                    | 21                   | 5463.1805 | 4        | 9        | 15       | 2                    | 13                   | 5392.6366 | 10       | -9       |
| 21       | 0                    | 21                   | 5455.4740 | 6        | -2       | 21       | 1                    | 20                   | 5468.1625 | 3        | -2       | 16       | 2                    | 15                   | 5407.4103 | 13       | -5       |
| 22       | 0                    | 22                   | 5475.8349 |          | -3       | 22       | 1                    | 22                   | 5483.3491 | 2        | -1       | 16       | 2                    | 14                   | 5407.5180 | 5        | 5        |
| 23       | 0                    | 23                   | 5497.1123 | 9        | -7       | 22       | 1                    | 21                   | 5488.8051 | 8        | 6        | 17       | 2                    | 16                   | 5423.1940 | 10       | 6        |
| 24       | 0                    | 24                   | 5519.3068 | 5        | 3        | 23       | 1                    | 23                   | 5504.4316 | 6        | 3        | 17       | 2                    | 15                   | 5423.3278 | 4        | -7       |
| 25       | 0                    | 25                   | 5542.4139 | 5        | -5       | 23       | 1                    | 22                   | 5510.3793 | 12       | -3       | 18       | 2                    | 17                   | 5439.9019 | 9        | -1       |
| 26       | 0                    | 26                   | 5566.4372 | 2        | 15       | 24       | 1                    | 24                   | 5526.4254 |          | 0        | 18       | 2                    | 16                   | 5440.0707 | 8        | 0        |
| 27       | 0                    | 27                   | 5591.3707 | 14       | 15       | 24       | 1                    | 23                   | 5532.8875 | 5        | 0        | 19       | 2                    | 18                   | 5457.5356 |          | -5       |
| 28       | 0                    | 28                   | 5617.2136 | 4        | 1        | 25       | 1                    | 25                   | 5549.3307 | 9        | -2       | 19       | 2                    | 17                   | 5457.7446 | 2        | 4        |
| 29       | 0                    | 29                   | 5643.9678 | 4        | 2        | 25       | 1                    | 24                   | 5556.3279 | 6        | 4        | 20       | 2                    | 19                   | 5476.0954 | 6        | 1        |
| 30       | 0                    | 30                   | 5671.6302 | 3        | 1        | 26       | 1                    | 25                   | 5580.6986 | 11       | -2       | 20       | 2                    | 18                   | 5476.3485 | 4        | -6       |
| 31       | 0                    | 31                   | 5700.2006 |          | 6        | 27       | 1                    | 27                   | 5597.8722 |          | -14      | 21       | 2                    | 20                   | 5495.5786 | 5        | -4       |
| 32       | 0                    | 32                   | 5729.6759 | 12       | 1        | 27       | 1                    | 26                   | 5606.0012 | 2        | 5        | 21       | 2                    | 19                   | 5495.8855 | 5        | -4       |
| 33       | 0                    | 33                   | 5760.0572 | 17       | 8        | 28       | 1                    | 28                   | 5623.5100 |          | 3        | 22       | 2                    | 21                   | 5515.9867 | 1        | -2       |
| 34       | 0                    | 34                   | 5791.3431 |          | 26       | 28       | 1                    | 27                   | 5632.2333 |          | 9        | 22       | 2                    | 20                   | 5516.3540 | 5        | -5       |
| 35       | 0                    | 35                   | 5823.5276 |          | 7        | 29       | 1                    | 29                   | 5650.0549 |          | 3        | 23       | 2                    | 22                   | 5537.3180 | 4        | -3       |
| 1        | 1                    | 1                    | 5252.0715 | 3        | -9       | 29       | 1                    | 28                   | 5659.3937 | 13       | 6        | 23       | 2                    | 21                   | 5537.7547 | 3        | -4       |
| 1        | 1                    | 0                    | 5252.0946 | 3        | 4        | 30       | 1                    | 30                   | 5677.5077 | 8        | -1       | 24       | 2                    | 23                   | 5559.5732 |          | 4        |
| 2        | 1                    | 2                    | 5253.9094 | 12       | -7       | 30       | 1                    | 29                   | 5687.4820 | 3        | 0        | 24       | 2                    | 22                   | 5560.0875 | 5        | -4       |
| 2        | 1                    | 1                    | 5253.9748 | 9        | -2       | 31       | 1                    | 31                   | 5705.8677 |          | -7       | 25       | 2                    | 24                   | 5582.7500 | 16       | 2        |
| 3        | 1                    | 3                    | 5256.6649 | 18       | -16      | 31       | 1                    | 30                   | 5716.4977 | 9        | -3       | 25       | 2                    | 23                   | 5583.3530 | 1        | 0        |
| 3        | 1                    | 2                    | 5256.8003 | 13       | 38       | 32       | 1                    | 32                   | 5735.1371 |          | 12       | 26       | 2                    | 25                   | 5606.8482 | 4        | -5       |
| 4        | 1                    | 4                    | 5260.3416 | 5        | 0        | 32       | 1                    | 31                   | 5746.4396 | 14       | -8       | 26       | 2                    | 24                   | 5607.5526 |          | 20       |
| 4        | 1                    | 3                    | 5260.5578 | 1        | -3       | 33       | 1                    | 33                   | 5765.3104 | 15       | 9        | 27       | 2                    | 26                   | 5631.8685 | 5        | -5       |
| 5        | 1                    | 5                    | 5264.9357 | 8        | 4        | 33       | 1                    | 32                   | 5777.3090 | 4        | 8        | 27       | 2                    | 25                   | 5632.6809 | 7        | 3        |
| 5        | 1                    | 4                    | 5265.2595 | 7        | -5       | 34       | 1                    | 34                   | 5796.3888 | 2        | 4        | 28       | 2                    | 27                   | 5657.8099 | 10       | 0        |
| 6        | 1                    | 6                    | 5270.4481 | 2        | 7        | 34       | 1                    | 33                   | 5809.1002 | 4        | -2       | 28       | 2                    | 26                   | 5658.7435 | 1        | 1        |
| 6        | 1                    | 5                    | 5270.9009 | 10       | -10      | 35       | 1                    | 35                   | 5828.3724 | 5        | 5        | 29       | 2                    | 28                   | 5684.6693 | 10       | -15      |
| 7        | 1                    | 7                    | 5276.8781 | 6        | 2        | 35       | 1                    | 34                   | 5841.8155 | 11       | -4       | 29       | 2                    | 27                   | 5685.7385 | 10       | -4       |
| 7        | 1                    | 6                    | 5277.4839 | 8        | 0        | 2        | 2                    | 1                    | 5283.8577 | 6        | 10       | 30       | 2                    | 28                   | 5713.6677 |          | 6        |
| 8        | 1                    | 8                    | 5284.2264 | 3        | 0        | 2        | 2                    | 0                    | 5283.8577 | 6        | 9        | 31       | 2                    | 29                   | 5742.5286 | 11       | 5        |
| 8        | 1                    | 7                    | 5285.0053 | 13       | -2       | 3        | 2                    | 2                    | 5286.6452 | 8        | 1        | 32       | 2                    | 31                   | 5770.7693 |          | 24       |
| 9        | 1                    | 9                    | 5292.4921 | 4        | -7       | 3        | 2                    | 1                    | 5286.6452 | 8        | -1       | 32       | 2                    | 30                   | 5772.3237 |          | 19       |
| 9        | 1                    | 8                    | 5293.4669 | 15       | 2        | 4        | 2                    | 3                    | 5290.3632 | 5        | 2        | 33       | 2                    | 32                   | 5801.3013 | 10       | 3        |
| 10       | 1                    | 10                   | 5301.6778 | 3        | 8        | 4        | 2                    | 2                    | 5290.3632 | 5        | -3       | 34       | 2                    | 33                   | 5832.7518 |          | 2        |
| 10       | 1                    | 9                    | 5302.8671 | 4        | 1        | 5        | 2                    | 4                    | 5295.0099 | 11       | -2       | 34       | 2                    | 32                   | 5834.7069 |          | 0        |
| 11       | 1                    | 11                   | 5311.7787 | 7        | 1        | 5        | 2                    | 3                    | 5295.0099 | 11       | -4       | 35       | 2                    | 34                   | 5865.1190 | 6        | 13       |
| 11       | 1                    | 10                   | 5313.2065 | 10       | 2        | 6        | 2                    | 5                    | 5300.5868 | 8        | 4        | 35       | 2                    | 33                   | 5867.2974 |          | -7       |

<sup>a</sup> In this table,  $\Delta$  is the experimental uncertainty of the energy value, equal to one standard deviation in units of  $10^{-4}$  cm<sup>-1</sup>;  $\delta$  is the difference  $E^{exp.} - E^{calc.}$ , also in units of  $10^{-4}$  cm<sup>-1</sup>;  $\Delta$  is not quoted when the energy value was obtained from only one transition.

TABLE 1—Continued

| <i>J</i> | <i>K<sub>a</sub></i> | <i>K<sub>c</sub></i> | <i>E</i>  | $\Delta$ | $\delta$ | <i>J</i> | <i>K<sub>a</sub></i> | <i>K<sub>c</sub></i> | <i>E</i>  | $\Delta$ | $\delta$ | <i>J</i> | <i>K<sub>a</sub></i> | <i>K<sub>c</sub></i> | <i>E</i>  | $\Delta$ | $\delta$ |
|----------|----------------------|----------------------|-----------|----------|----------|----------|----------------------|----------------------|-----------|----------|----------|----------|----------------------|----------------------|-----------|----------|----------|
| 1        | 2                    | 3                    | 4         | 1        | 2        | 3        | 4                    | 1                    | 2         | 3        | 4        | 1        | 2                    | 3                    | 4         | 3        | 4        |
| 4        | 3                    | 2                    | 5340.1695 | 3        | 0        | 26       | 3                    | 24                   | 5656.7697 | 25       | 3        | 7        | 5                    | 3                    | 5515.8604 | 19       | -1       |
| 4        | 3                    | 1                    | 5340.1695 | 3        | 0        | 26       | 3                    | 23                   | 5656.7850 |          | -8       | 8        | 5                    | 4                    | 5523.2868 | 15       | -1       |
| 5        | 3                    | 3                    | 5344.8158 | 6        | 4        | 27       | 3                    | 25                   | 5681.8132 |          | -7       | 9        | 5                    | 5                    | 5531.6411 | 9        | 0        |
| 5        | 3                    | 2                    | 5344.8158 | 6        | 4        | 27       | 3                    | 24                   | 5681.8345 |          | 1        | 10       | 5                    | 6                    | 5540.9235 | 5        | 4        |
| 6        | 3                    | 4                    | 5350.3909 | 8        | 1        | 28       | 3                    | 25                   | 5707.2717 |          | -2       | 11       | 5                    | 7                    | 5551.1332 | 4        | 5        |
| 6        | 3                    | 3                    | 5350.3909 | 8        | 1        | 29       | 3                    | 27                   | 5734.6730 | 6        | -9       | 12       | 5                    | 8                    | 5562.2702 |          | 6        |
| 7        | 3                    | 5                    | 5356.8946 | 10       | -3       | 30       | 3                    | 28                   | 5762.4892 | 10       | 6        | 13       | 5                    | 9                    | 5574.3335 | 5        | -3       |
| 7        | 3                    | 4                    | 5356.8946 | 10       | -3       | 31       | 3                    | 29                   | 5791.2255 | 12       | -2       | 14       | 5                    | 10                   | 5587.3255 | 15       | 8        |
| 8        | 3                    | 6                    | 5364.3273 | 4        | -6       | 31       | 3                    | 28                   | 5791.2717 | 8        | -2       | 15       | 5                    | 11                   | 5601.2430 | 9        | 2        |
| 8        | 3                    | 5                    | 5364.3273 | 4        | -6       | 32       | 3                    | 30                   | 5820.8855 | 9        | 8        | 17       | 5                    | 13                   | 5631.8579 | 10       | 0        |
| 9        | 3                    | 7                    | 5372.6894 | 3        | -3       | 32       | 3                    | 29                   | 5820.9405 | 16       | 1        | 18       | 5                    | 14                   | 5648.5540 | 4        | -5       |
| 9        | 3                    | 6                    | 5372.6894 | 3        | -3       | 33       | 3                    | 31                   | 5851.4657 | 8        | 5        | 19       | 5                    | 15                   | 5666.1760 | 5        | -9       |
| 10       | 3                    | 8                    | 5381.9805 | 6        | 3        | 33       | 3                    | 30                   | 5851.5320 | 14       | 0        | 20       | 5                    | 16                   | 5684.7231 | 4        | -15      |
| 10       | 3                    | 7                    | 5381.9805 | 6        | 2        | 34       | 3                    | 32                   | 5882.9651 |          | -15      | 21       | 5                    | 17                   | 5704.1970 | 5        | -4       |
| 11       | 3                    | 9                    | 5392.1992 | 7        | 0        | 34       | 3                    | 31                   | 5883.0453 | 2        | -8       | 22       | 5                    | 18                   | 5724.5947 | 2        | -2       |
| 11       | 3                    | 8                    | 5392.1992 | 7        | -1       | 35       | 3                    | 32                   | 5915.4819 |          | -6       | 23       | 5                    | 19                   | 5745.9167 | 10       | 0        |
| 12       | 3                    | 10                   | 5403.3469 | 12       | 3        | 5        | 4                    | 2                    | 5414.4417 | 8        | -2       | 24       | 5                    | 20                   | 5768.1627 | 18       | 2        |
| 12       | 3                    | 9                    | 5403.3469 | 12       | 1        | 6        | 4                    | 3                    | 5420.0151 | 10       | 2        | 25       | 5                    | 21                   | 5791.3325 | 14       | 5        |
| 13       | 3                    | 11                   | 5415.4223 | 11       | 1        | 7        | 4                    | 4                    | 5426.5166 | 7        | 1        | 26       | 5                    | 22                   | 5815.4241 | 2        | -5       |
| 13       | 3                    | 10                   | 5415.4223 | 11       | -1       | 8        | 4                    | 5                    | 5433.9467 | 3        | 1        | 27       | 5                    | 23                   | 5840.4390 | 9        | -9       |
| 14       | 3                    | 12                   | 5428.4260 | 9        | 2        | 9        | 4                    | 6                    | 5442.3054 | 4        | 4        | 28       | 5                    | 24                   | 5866.3776 | 9        | 0        |
| 14       | 3                    | 11                   | 5428.4260 | 9        | -3       | 10       | 4                    | 7                    | 5451.5920 | 2        | 3        | 29       | 5                    | 25                   | 5893.2376 | 6        | 4        |
| 15       | 3                    | 13                   | 5442.3575 | 10       | 2        | 11       | 4                    | 8                    | 5461.8066 | 4        | 2        | 6        | 6                    | 1                    | 5618.3114 |          | 0        |
| 15       | 3                    | 12                   | 5442.3575 | 10       | -5       | 12       | 4                    | 9                    | 5472.9495 | 10       | 4        | 7        | 6                    | 2                    | 5624.8065 |          | 9        |
| 16       | 3                    | 14                   | 5457.2172 | 22       | 8        | 13       | 4                    | 10                   | 5485.0190 | 6        | -5       | 8        | 6                    | 3                    | 5632.2268 | 3        | -5       |
| 16       | 3                    | 13                   | 5457.2172 | 22       | -2       | 14       | 4                    | 11                   | 5498.0167 | 8        | -7       | 9        | 6                    | 4                    | 5640.5773 | 10       | 10       |
| 17       | 3                    | 15                   | 5473.0020 | 16       | -9       | 15       | 4                    | 12                   | 5511.9430 | 9        | 4        | 10       | 6                    | 5                    | 5649.8525 | 6        | 3        |
| 17       | 3                    | 14                   | 5473.0038 | 12       | -5       | 16       | 4                    | 13                   | 5526.7946 | 5        | -3       | 11       | 6                    | 6                    | 5660.0564 | 5        | 12       |
| 18       | 3                    | 16                   | 5489.7166 | 4        | 0        | 17       | 4                    | 14                   | 5542.5746 | 10       | 6        | 12       | 6                    | 7                    | 5671.1850 | 12       | 0        |
| 18       | 3                    | 15                   | 5489.7180 | 12       | -5       | 18       | 4                    | 15                   | 5559.2800 | 3        | 3        | 13       | 6                    | 8                    | 5683.2426 | 3        | 9        |
| 19       | 3                    | 17                   | 5507.3572 | 5        | 0        | 19       | 4                    | 16                   | 5576.9118 | 13       | 2        | 14       | 6                    | 9                    | 5696.2244 | 6        | 3        |
| 19       | 3                    | 16                   | 5507.3592 | 6        | -6       | 20       | 4                    | 17                   | 5595.4700 | 19       | 4        | 15       | 6                    | 10                   | 5710.1332 | 4        | 3        |
| 20       | 3                    | 18                   | 5525.9263 | 7        | 19       | 21       | 4                    | 18                   | 5614.9532 | 15       | 0        | 16       | 6                    | 11                   | 5724.9681 | 7        | 5        |
| 20       | 3                    | 17                   | 5525.9275 | 3        | -4       | 22       | 4                    | 19                   | 5635.3634 | 15       | 11       | 17       | 6                    | 12                   | 5740.7276 | 10       | -3       |
| 21       | 3                    | 19                   | 5545.4165 | 4        | -14      | 23       | 4                    | 20                   | 5656.6970 | 16       | 7        | 18       | 6                    | 13                   | 5757.4151 |          | 16       |
| 21       | 3                    | 18                   | 5545.4232 | 8        | -11      | 24       | 4                    | 21                   | 5678.9539 | 4        | -11      | 19       | 6                    | 14                   | 5775.0249 |          | 8        |
| 22       | 3                    | 20                   | 5565.8376 | 10       | 1        | 25       | 4                    | 22                   | 5702.1381 | 5        | 0        | 20       | 6                    | 15                   | 5793.5585 | 3        | -9       |
| 22       | 3                    | 19                   | 5565.8439 | 10       | 3        | 26       | 4                    | 23                   | 5726.2487 |          | 37       | 21       | 6                    | 16                   | 5813.0183 | 5        | -7       |
| 23       | 3                    | 21                   | 5587.1827 | 10       | -1       | 27       | 4                    | 24                   | 5751.2763 | 8        | 8        | 22       | 6                    | 17                   | 5833.4036 | 5        | 8        |
| 23       | 3                    | 20                   | 5587.1901 | 2        | -7       | 28       | 4                    | 25                   | 5777.2286 | 2        | -4       | 23       | 6                    | 18                   | 5854.7112 | 5        | 11       |
| 24       | 3                    | 22                   | 5609.4538 | 10       | 4        | 29       | 4                    | 26                   | 5804.1052 | 5        | 0        | 24       | 6                    | 19                   | 5876.9406 | 7        | -1       |
| 24       | 3                    | 21                   | 5609.4631 |          | -6       | 5        | 5                    | 1                    | 5503.7915 |          | -5       | 25       | 6                    | 20                   | 5900.0934 | 1        | -6       |
| 25       | 3                    | 23                   | 5632.6496 | 1        | 5        | 6        | 5                    | 2                    | 5509.3622 | 7        | 0        | 27       | 6                    | 22                   | 5949.1678 |          | 0        |
| 25       | 3                    | 22                   | 5632.6608 | 7        | -11      |          |                      |                      |           |          |          |          |                      |                      |           |          |          |

used in the fit. The initial values of the rotational and centrifugal distortion parameters were predicted on the basis of a linear interpolation of corresponding parameters of the (000) and (100) states from Ref. (1) and of the (200) state from column 5 of Table 2 of the present contribution. They are presented in column 2 of Table 4. As the result of the fit, 31 energies  $E_{[J,K_a=0,K_c=J]}$  with  $J^{max.} = 34$  were reproduced by the three fitted parameters,  $E$ ,  $C$ , and  $\Delta_J$ , with the accuracies close to experimental uncertainties. The further analysis showed that for the sets of energies  $E_{[J,K_a=1,K_c=J]}$ ,  $E_{[J,K_a=1,K_c=J-1]}$ , and  $E_{[J,K_a=2,K_c=J-1]}$  (in all, 122 levels with  $J^{max.} = 35$ ),

(1) they are predicted satisfactorily by the parameters obtained from the fit of the  $E_{[J,K_a=0,K_c=J]}$  energies;

(2) they can be fitted and reproduced with the accuracies only a little bit worse than the experimental uncertainties by the seven parameters  $E$ ,  $A$ ,  $B$ ,  $C$ ,  $\Delta_{JK}$ ,  $\Delta_J$ , and  $\delta_J$  of the Hamiltonian model of an isolated vibrational state. The parameters obtained from fit are presented in column 3 of Table 4. From that column, one can see that these parameters are close to the predicted values from column 2 of Table 4.

Contrary to the situation mentioned above, a prediction of the energy values  $E_{[J,K_a=3,K_c]}$  and  $E_{[J,K_a=4,K_c]}$  leads to unexpectedly large values of differences  $\Delta = E^{predict.} - E^{exp.}$ , where  $E^{predict.}$  are the energy values calculated with the parameters of column 3 of Table 4, and  $E^{exp.}$  are the "experimental" energies

**TABLE 2**  
**Spectroscopic Parameters of the (200) and (130) Vibrational States of the DOCl Molecule (in  $\text{cm}^{-1}$ )<sup>a</sup>**

| Parameter                 | (200)                | (200)                 | (200)              | (200)                 | (130)                      |
|---------------------------|----------------------|-----------------------|--------------------|-----------------------|----------------------------|
|                           | calc.                | fit. <sup>b)</sup>    | fit. <sup>c)</sup> | fit. <sup>d)</sup>    | calc.                      |
| 1                         | 2                    | 3                     | 4                  | 5                     | 6                          |
| $E$                       | 5248.6 <sup>e)</sup> | 5241.177136(234)      | 5241.177703(215)   | 5241.177220(110)      | 5327.45(143) <sup>f)</sup> |
| $A$                       | 10.4358              | 10.442476(137)        | 10.442280(325)     | 10.4424937(321)       | 11.7022                    |
| $B$                       | 0.4756               | 0.475713(752)         | 0.475715(714)      | 0.47571248(137)       | 0.4762                     |
| $C$                       | 0.4539               | 0.453999(807)         | 0.453990(856)      | 0.45399905(138)       | 0.4508                     |
| $\Delta_K \times 10^4$    | 12.3255              | 12.19538(358)         | 12.13656(408)      | 12.3047(231)          | 23.9066                    |
| $\Delta_{JK} \times 10^4$ | 0.246                | 0.24871(692)          | 0.24141(498)       | 0.246641(346)         | 0.241                      |
| $\Delta_J \times 10^4$    | 0.00749              | 0.0074707(221)        | 0.0074078(325)     | 0.00747365(411)       | 0.00758                    |
| $\delta_K \times 10^4$    | 0.1457               | 0.15269(882)          | 0.19869(934)       | 0.15282(518)          | 0.3812                     |
| $\delta_J \times 10^4$    | 0.000319             | 0.00032163(542)       | 0.00027854(554)    | 0.00032236(415)       | 0.000357                   |
| $H_K \times 10^7$         | 6.84                 | 6.0554(576)           | 7.1510(694)        | 10.480(443)           | 20.47                      |
| $H_{KJ} \times 10^7$      | -                    | -                     | -0.3262(829)       | -                     | -                          |
| $H_{JK} \times 10^7$      | -                    | -                     | 0.01557(553)       | -                     | -                          |
| $H_J \times 10^{11}$      | -                    | -                     | -0.4131(904)       | -                     | -                          |
| $h_K \times 10^7$         | -                    | -0.9356 <sup>g)</sup> | 10.2210(766)       | -0.9356 <sup>g)</sup> | -                          |
| $h_{JK} \times 10^7$      | -                    | -                     | -0.03239(244)      | -                     | -                          |
| $h_J \times 10^{11}$      | -                    | -                     | -0.05296(431)      | -                     | -                          |

<sup>a</sup> Values in parentheses are the  $1\sigma$  statistical confidence intervals.

<sup>b</sup> Parameters obtained from the fit with the omitted states  $[J, K_a = 6, K_c]$ . The Hamiltonian model of an isolated vibrational state was used.

<sup>c</sup> Parameters obtained from the fit of all energies from Table 1. The Hamiltonian model of an isolated vibrational state was used.

<sup>d</sup> Parameters obtained from the final fit of all energies from Table 1. The Hamiltonian, Eqs. [1]–[5], which takes into account resonance interactions, was used.

<sup>e</sup> From Ref. (8).

<sup>f</sup> Obtained from the final fit (see text, for details).

<sup>g</sup> Fixed to the value of corresponding parameter of the ground vibrational state.

from Table 3. In order to illustrate this, Fig. 4 shows the plots of dependency of the  $\Delta$ -differences on the quantum number  $J$  for sets of energies  $E_{[J, K_a=3, K_c]}$  (plot I) and  $E_{[J, K_a=4, K_c]}$  (plot II). The plots apparently show the presence of strong perturbation of sets of the states  $[J, K_a = 3, K_c]$  and, especially,  $[J, K_a = 4, K_c]$ . An attempt to fit the energies  $E_{[J, K_a=3, K_c]}$  and  $E_{[J, K_a=4, K_c]}$  together with the other energies in the framework of the model of an isolated vibrational state leads to large change of the  $A$  and  $\Delta_K$  parameters. So one can expect that the resonance interaction will be the Fermi-type one, and rovibrational states with equal values of the quantum number  $K_a$  will have the strongest interaction.

Concerning a band the rovibrational states of which would satisfy the conditions mentioned above, we made rough estimations of rovibrational structures of vibrational states those may be located closed to the  $3\nu_1$  band. The initial vibrational parameters  $\omega_\lambda, x_{\lambda\mu}, y_{\lambda\mu\nu}$  which are necessary for such rough estimates of the band centers were first calculated from the fit of band centers from the longer wavelength region. The rotational parameters and centrifugal quartic and sextic parameters of different vibrational states were estimated from the interpo-

lations of corresponding parameters of the states (000), (100), (010), (020), (200), and (001) from Refs. (1, 8) and Section 3 of the present paper. As the result, we found that the most suitable vibrational state is the (221) one. The predicted values of the parameters of this state are shown in column 5 of Table 4.

Then all the levels mentioned above were fitted in the framework of the Hamiltonian model, Eq. [1]–[5], which took into account the Fermi-type resonance interactions between the states (300) and (221). As the result, we determined the set of seven fitted parameters which reproduced the initial energy values with the accuracies close to experimental uncertainties. The parameters obtained from this fit are shown in columns 4 and 5 of Table 4 and column 2 of Table 5 together with their  $1\sigma$  statistical confidence intervals. It is interesting that the value  $7701.120 \text{ cm}^{-1}$  (see column 5 of Table 4) of the band center of  $2\nu_1 + 2\nu_2 + \nu_3$  is very closed to the corresponding value  $7704.9 \text{ cm}^{-1}$  predicted from rough calculations discussed above.

The next step of the study was the analysis of the situation with the  $E_{[J, K_a=2, K_c=J-2]}$  energy levels. It is interesting that both the model which takes into account the interactions

between the states (300) and (221) and, moreover, the model of an isolated vibrational state do not give possibility to predict the values of the  $E_{[J,K_a=2,K_c=J-2]}$  energies with a satisfactory accuracy. As an illustration, the curve III in Fig. 4 shows the difference  $\Delta = E^{predict.} - E^{exp.}$  against the value of quantum number  $J$ . Here  $E^{predict.}$  are the energy values of the  $E_{[J,K_a=2,K_c=J-2]}$  calculated with the parameters from columns 4

and 5 of Table 4 and of column 2 of Table 5. It should be noticed that even adding eight or nine extra parameters into the fit procedure will not improve the results in comparison with the model discussed above (see columns 4, 5 of Table 4 and column 2 of Table 5). This shows the presence of at least one additional vibrational state which strongly perturbs the (300) one.

**TABLE 3**  
**Experimental Rovibrational Term Values for the (300) Vibrational States of the DOCl Molecule (in  $\text{cm}^{-1}$ )<sup>a</sup>**

| $J$ | $K_a$ | $K_c$ | $E$      | $\Delta$ | $\delta$ | $J$ | $K_a$ | $K_c$ | $E$      | $\Delta$ | $\delta$ | $J$ | $K_a$ | $K_c$ | $E$      | $\Delta$ | $\delta$ |   |     |
|-----|-------|-------|----------|----------|----------|-----|-------|-------|----------|----------|----------|-----|-------|-------|----------|----------|----------|---|-----|
| 1   | 2     | 3     | 4        | 1        | 2        | 3   | 4     | 1     | 2        | 3        | 4        | 1   | 2     | 3     | 4        | 1        | 2        | 3 | 4   |
| 3   | 0     | 3     | 7733.454 | 1        | -1       | 10  | 1     | 10    | 7787.998 | 2        | 0        | 34  | 1     | 33    | 8294.591 |          |          |   | -2  |
| 4   | 0     | 4     | 7737.166 | 2        | 0        | 10  | 1     | 9     | 7789.221 | 6        | 7        | 35  | 1     | 34    | 8327.256 |          |          |   | 4   |
| 5   | 0     | 5     | 7741.805 |          | 0        | 11  | 1     | 11    | 7798.078 | 1        | 0        | 2   | 2     | 1     | 7769.463 | 2        |          |   | -2  |
| 7   | 0     | 7     | 7753.863 | 3        | 0        | 11  | 1     | 10    | 7799.537 | 2        | 1        | 2   | 2     | 0     | 7769.462 | 2        |          |   | -3  |
| 8   | 0     | 8     | 7761.282 | 3        | 1        | 12  | 1     | 12    | 7809.071 | 1        | -1       | 3   | 2     | 2     | 7772.246 | 4        |          |   | -1  |
| 9   | 0     | 9     | 7769.625 | 3        | -1       | 12  | 1     | 11    | 7810.798 | 4        | 2        | 3   | 2     | 1     | 7772.246 | 4        |          |   | -2  |
| 10  | 0     | 10    | 7778.895 | 0        | -1       | 13  | 1     | 13    | 7820.980 | 1        | 0        | 4   | 2     | 3     | 7775.959 | 1        |          |   | 1   |
| 11  | 0     | 11    | 7789.092 | 1        | 1        | 13  | 1     | 12    | 7822.994 | 2        | 2        | 4   | 2     | 2     | 7775.959 | 1        |          |   | -1  |
| 12  | 0     | 12    | 7800.212 | 1        | 2        | 14  | 1     | 14    | 7833.804 | 1        | 0        | 5   | 2     | 4     | 7780.596 | 2        |          |   | 0   |
| 13  | 0     | 13    | 7812.253 | 2        | 0        | 14  | 1     | 13    | 7836.126 | 2        | 2        | 5   | 2     | 3     | 7780.596 | 2        |          |   | -4  |
| 14  | 0     | 14    | 7825.219 | 0        | 0        | 15  | 1     | 15    | 7847.542 | 1        | 1        | 6   | 2     | 5     | 7786.165 | 5        |          |   | 4   |
| 15  | 0     | 15    | 7839.107 | 0        | 0        | 15  | 1     | 14    | 7850.194 | 2        | 2        | 6   | 2     | 4     | 7786.165 | 5        |          |   | -5  |
| 16  | 0     | 16    | 7853.918 | 0        | 1        | 16  | 1     | 16    | 7862.192 | 1        | -1       | 7   | 2     | 6     | 7792.657 | 9        |          |   | 4   |
| 17  | 0     | 17    | 7869.646 | 1        | -1       | 16  | 1     | 15    | 7865.200 | 3        | 4        | 7   | 2     | 5     | 7792.657 | 9        |          |   | -13 |
| 18  | 0     | 18    | 7886.296 | 1        | 0        | 17  | 1     | 17    | 7877.757 | 1        | 0        | 8   | 2     | 7     | 7800.072 | 3        |          |   | 0   |
| 19  | 0     | 19    | 7903.865 | 1        | 0        | 17  | 1     | 16    | 7881.137 | 2        | 1        | 9   | 2     | 8     | 7808.420 | 1        |          |   | 2   |
| 20  | 0     | 20    | 7922.350 | 3        | 0        | 18  | 1     | 18    | 7894.234 | 0        | 0        | 10  | 2     | 9     | 7817.691 | 3        |          |   | 0   |
| 21  | 0     | 21    | 7941.754 | 1        | 1        | 18  | 1     | 17    | 7898.008 | 1        | -2       | 10  | 2     | 8     | 7817.744 | 3        |          |   | -7  |
| 22  | 0     | 22    | 7962.070 | 1        | -1       | 19  | 1     | 19    | 7911.624 |          | 0        | 11  | 2     | 10    | 7827.892 | 3        |          |   | 2   |
| 23  | 0     | 23    | 7983.304 | 1        | 1        | 19  | 1     | 18    | 7915.819 | 1        | 11       | 11  | 2     | 9     | 7827.965 |          |          |   | -7  |
| 24  | 0     | 24    | 8005.449 | 1        | 0        | 20  | 1     | 20    | 7929.927 |          | 1        | 12  | 2     | 11    | 7839.015 |          |          |   | -1  |
| 25  | 0     | 25    | 8028.507 | 1        | 0        | 20  | 1     | 19    | 7934.560 | 0        | 0        | 12  | 2     | 10    | 7839.125 |          |          |   | 1   |
| 26  | 0     | 26    | 8052.474 | 3        | -1       | 21  | 1     | 21    | 7949.139 | 2        | -1       | 13  | 2     | 12    | 7851.067 | 2        |          |   | 0   |
| 27  | 0     | 27    | 8077.353 | 4        | -1       | 21  | 1     | 20    | 7954.232 | 1        | -2       | 13  | 2     | 11    | 7851.212 |          |          |   | 5   |
| 28  | 0     | 28    | 8103.141 | 2        | 0        | 22  | 1     | 22    | 7969.264 | 1        | 0        | 14  | 2     | 13    | 7864.044 | 3        |          |   | 0   |
| 29  | 0     | 29    | 8129.834 | 1        | -1       | 22  | 1     | 21    | 7974.836 |          | -6       | 15  | 2     | 14    | 7877.944 | 1        |          |   | -2  |
| 30  | 0     | 30    | 8157.436 | 0        | 1        | 23  | 1     | 23    | 7990.300 | 1        | 1        | 15  | 2     | 13    | 7878.165 |          |          |   | 2   |
| 31  | 0     | 31    | 8185.937 | 3        | -4       | 23  | 1     | 22    | 7996.394 |          | 13       | 16  | 2     | 15    | 7892.771 | 2        |          |   | -2  |
| 32  | 0     | 32    | 8215.350 | 7        | 0        | 24  | 1     | 24    | 8012.242 | 1        | -1       | 16  | 2     | 14    | 7893.036 |          |          |   | 0   |
| 33  | 0     | 33    | 8245.660 | 0        | 2        | 24  | 1     | 23    | 8018.854 | 3        | 2        | 17  | 2     | 16    | 7908.523 | 2        |          |   | -2  |
| 34  | 0     | 34    | 8276.867 |          | -2       | 25  | 1     | 25    | 8035.097 | 1        | 0        | 17  | 2     | 15    | 7908.840 |          |          |   | 2   |
| 1   | 1     | 1     | 7738.507 |          | 3        | 25  | 1     | 24    | 8042.254 | 1        | 1        | 18  | 2     | 17    | 7925.195 | 2        |          |   | -5  |
| 2   | 1     | 2     | 7740.339 | 2        | 1        | 26  | 1     | 26    | 8058.859 | 1        | -1       | 18  | 2     | 16    | 7925.572 |          |          |   | 2   |
| 3   | 1     | 3     | 7743.088 |          | 0        | 26  | 1     | 25    | 8066.584 | 0        | 1        | 19  | 2     | 18    | 7942.798 | 2        |          |   | -2  |
| 4   | 1     | 4     | 7746.754 | 2        | -1       | 27  | 1     | 27    | 8083.529 | 2        | -2       | 19  | 2     | 17    | 7943.232 |          |          |   | 0   |
| 4   | 1     | 3     | 7746.976 |          | 0        | 27  | 1     | 26    | 8091.844 | 2        | 1        | 20  | 2     | 19    | 7961.322 | 1        |          |   | -1  |
| 5   | 1     | 5     | 7751.339 | 1        | 0        | 28  | 1     | 28    | 8109.108 | 3        | -1       | 20  | 2     | 18    | 7961.819 |          |          |   | -3  |
| 5   | 1     | 4     | 7751.664 |          | 6        | 28  | 1     | 27    | 8118.030 | 0        | -1       | 21  | 2     | 20    | 7980.764 | 4        |          |   | -4  |
| 6   | 1     | 6     | 7756.838 | 4        | 0        | 29  | 1     | 29    | 8135.594 | 3        | 0        | 22  | 2     | 21    | 8001.132 | 2        |          |   | -4  |
| 6   | 1     | 5     | 7757.303 | 1        | 0        | 29  | 1     | 28    | 8145.144 | 2        | -2       | 22  | 2     | 20    | 8001.784 |          |          |   | -5  |
| 7   | 1     | 7     | 7763.252 | 2        | -2       | 30  | 1     | 30    | 8162.986 |          | 0        | 23  | 2     | 22    | 8022.410 |          |          |   | -15 |
| 7   | 1     | 6     | 7763.873 | 2        | -1       | 30  | 1     | 29    | 8173.184 | 1        | -4       | 23  | 2     | 21    | 8023.167 |          |          |   | 1   |
| 8   | 1     | 8     | 7770.592 |          | 5        | 31  | 1     | 31    | 8191.283 | 2        | 0        | 25  | 2     | 24    | 8067.775 |          |          |   | 7   |
| 8   | 1     | 7     | 7771.387 | 5        | 4        | 31  | 1     | 30    | 8202.151 | 2        | -4       | 26  | 2     | 25    | 8091.821 | 2        |          |   | 1   |
| 9   | 1     | 9     | 7778.833 | 4        | -2       | 32  | 1     | 32    | 8220.484 | 1        | -1       | 27  | 2     | 26    | 8116.790 |          |          |   | -1  |
| 9   | 1     | 8     | 7779.829 | 2        | 0        | 33  | 1     | 32    | 8262.855 | 1        | 0        | 28  | 2     | 27    | 8142.681 | 2        |          |   | 0   |

<sup>a</sup> In this table,  $\Delta$  is the experimental uncertainty of the energy value, equal to one standard deviation in units of  $10^{-3} \text{ cm}^{-1}$ ;  $\delta$  is the difference  $E^{exp.} - E^{calc.}$ , also in units of  $10^{-3} \text{ cm}^{-1}$ ;  $\Delta$  is not quoted when the energy value was obtained from only one transition.

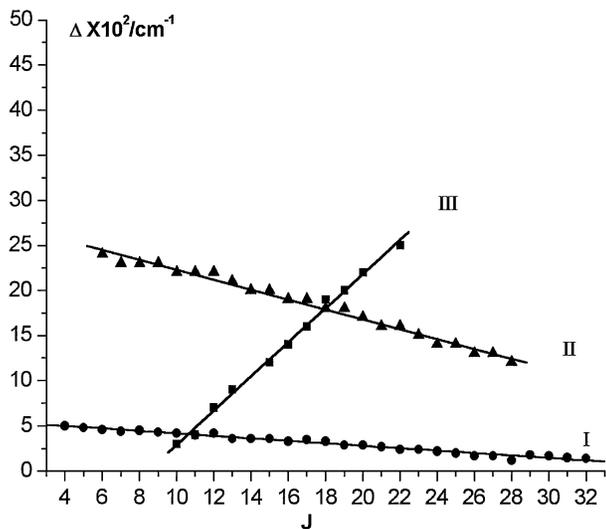
TABLE 3—Continued

| <i>J</i> | <i>K<sub>a</sub></i> | <i>K<sub>c</sub></i> | <i>E</i> | $\Delta$ | $\delta$ | <i>J</i> | <i>K<sub>a</sub></i> | <i>K<sub>c</sub></i> | <i>E</i> | $\Delta$ | $\delta$ | <i>J</i> | <i>K<sub>a</sub></i> | <i>K<sub>c</sub></i> | <i>E</i> | $\Delta$ | $\delta$ |
|----------|----------------------|----------------------|----------|----------|----------|----------|----------------------|----------------------|----------|----------|----------|----------|----------------------|----------------------|----------|----------|----------|
| 1        |                      |                      | 2        | 3        | 4        | 1        |                      |                      | 2        | 3        | 4        | 1        |                      |                      | 2        | 3        | 4        |
| 29       | 2                    | 28                   | 8169.487 | 2        | -2       | 28       | 3                    | 25                   | 8191.324 | 4        | -4       | 26       | 4                    | 23                   | 8208.040 | 3        | -3       |
| 30       | 2                    | 29                   | 8197.212 | 2        | -2       | 29       | 3                    | 26                   | 8218.176 |          | 2        | 27       | 4                    | 24                   | 8233.014 |          | -5       |
| 31       | 2                    | 30                   | 8225.855 | 2        | -1       | 30       | 3                    | 27                   | 8245.934 |          | -7       | 28       | 4                    | 25                   | 8258.911 |          | -5       |
| 32       | 2                    | 31                   | 8255.417 |          | -2       | 31       | 3                    | 28                   | 8274.629 | 7        | -2       | 29       | 4                    | 26                   | 8285.731 | 2        | -4       |
| 3        | 3                    | 0                    | 7820.725 |          | -3       | 32       | 3                    | 29                   | 8304.247 | 2        | -4       | 30       | 4                    | 27                   | 8313.466 |          | -10      |
| 4        | 3                    | 1                    | 7824.439 | 1        | 2        | 33       | 3                    | 30                   | 8334.773 |          | 5        | 8        | 5                    | 3                    | 8004.215 |          | 7        |
| 5        | 3                    | 2                    | 7829.071 | 3        | -2       | 34       | 3                    | 31                   | 8366.216 |          | 3        | 9        | 5                    | 4                    | 8012.532 |          | 5        |
| 6        | 3                    | 3                    | 7834.635 | 1        | -1       | 4        | 4                    | 1                    | 7892.358 | 8        | 2        | 10       | 5                    | 5                    | 8021.772 | 1        | 2        |
| 7        | 3                    | 4                    | 7841.125 | 1        | -1       | 5        | 4                    | 2                    | 7896.984 | 2        | -4       | 11       | 5                    | 6                    | 8031.936 | 1        | 0        |
| 8        | 3                    | 5                    | 7848.543 | 2        | 0        | 6        | 4                    | 3                    | 7902.542 | 2        | -4       | 12       | 5                    | 7                    | 8043.026 |          | -1       |
| 9        | 3                    | 6                    | 7856.887 | 1        | 0        | 7        | 4                    | 4                    | 7909.029 |          | -1       | 13       | 5                    | 8                    | 8055.040 |          | -1       |
| 10       | 3                    | 7                    | 7866.156 | 2        | -2       | 8        | 4                    | 5                    | 7916.438 | 2        | -3       | 14       | 5                    | 9                    | 8067.978 |          | -2       |
| 11       | 3                    | 8                    | 7876.354 | 1        | -1       | 9        | 4                    | 6                    | 7924.774 | 2        | -3       | 15       | 5                    | 10                   | 8081.842 | 1        | 0        |
| 12       | 3                    | 9                    | 7887.480 | 2        | 1        | 10       | 4                    | 7                    | 7934.038 | 1        | -2       | 16       | 5                    | 11                   | 8096.625 | 1        | -3       |
| 13       | 3                    | 10                   | 7899.529 | 2        | 0        | 11       | 4                    | 8                    | 7944.229 | 1        | 0        | 17       | 5                    | 12                   | 8112.337 | 3        | 0        |
| 14       | 3                    | 11                   | 7912.505 | 1        | -1       | 12       | 4                    | 9                    | 7955.345 | 3        | 2        | 18       | 5                    | 13                   | 8128.970 | 1        | 0        |
| 15       | 3                    | 12                   | 7926.409 | 1        | 1        | 13       | 4                    | 10                   | 7967.383 | 1        | 0        | 19       | 5                    | 14                   | 8146.524 | 1        | -2       |
| 16       | 3                    | 13                   | 7941.237 | 0        | 0        | 14       | 4                    | 11                   | 7980.348 | 1        | 0        | 20       | 5                    | 15                   | 8165.000 | 6        | -5       |
| 17       | 3                    | 14                   | 7956.994 | 2        | 3        | 15       | 4                    | 12                   | 7994.242 | 1        | 3        | 21       | 5                    | 16                   | 8184.406 | 1        | -1       |
| 18       | 3                    | 15                   | 7973.673 | 1        | 2        | 16       | 4                    | 13                   | 8009.062 | 7        | 7        | 22       | 5                    | 17                   | 8204.732 | 2        | 1        |
| 19       | 3                    | 16                   | 7991.276 | 1        | -1       | 17       | 4                    | 14                   | 8024.800 | 3        | 5        | 23       | 5                    | 18                   | 8225.982 | 2        | 3        |
| 20       | 3                    | 17                   | 8009.808 | 1        | 1        | 18       | 4                    | 15                   | 8041.462 | 0        | 1        | 24       | 5                    | 19                   | 8248.148 |          | 0        |
| 21       | 3                    | 18                   | 8029.263 | 2        | 0        | 19       | 4                    | 16                   | 8059.053 | 3        | 3        | 25       | 5                    | 20                   | 8271.241 |          | 1        |
| 22       | 3                    | 19                   | 8049.643 | 1        | 0        | 20       | 4                    | 17                   | 8077.567 | 2        | 3        | 26       | 5                    | 21                   | 8295.254 | 1        | 1        |
| 23       | 3                    | 20                   | 8070.947 | 2        | 0        | 21       | 4                    | 18                   | 8097.004 | 1        | 2        | 27       | 5                    | 22                   | 8320.185 | 2        | -3       |
| 24       | 3                    | 21                   | 8093.175 | 2        | -1       | 22       | 4                    | 19                   | 8117.365 | 1        | 1        | 28       | 5                    | 23                   | 8346.042 | 4        | -2       |
| 25       | 3                    | 22                   | 8116.328 | 1        | -1       | 23       | 4                    | 20                   | 8138.650 | 2        | 0        | 29       | 5                    | 24                   | 8372.822 |          | 0        |
| 26       | 3                    | 23                   | 8140.402 |          | -4       | 24       | 4                    | 21                   | 8160.857 | 1        | -1       | 30       | 5                    | 25                   | 8400.521 | 0        | 1        |
| 27       | 3                    | 24                   | 8165.405 | 3        | 0        | 25       | 4                    | 22                   | 8183.988 | 2        | -1       |          |                      |                      |          |          |          |

TABLE 4  
Spectroscopic Parameters of the (300), (221), and (230) Vibrational States of the DOCl Molecule (in  $\text{cm}^{-1}$ )<sup>a</sup>

| Parameter                               | (300)    | (300)            | (300)            | (221)         | (300)           | (221)         | (230)          |
|---|----------|------------------|------------------|---------------|-----------------|---------------|----------------|
|   | calc.    | I                | II               | II            | III             | III           | III            |
| 1                                       | 2        | 3                | 4                | 5             | 6               | 7             | 8              |
| <i>E</i>                                | 7726.80  | 7727.887630(728) | 7727.887477(368) | 7701.120(554) | 7727.3640(400)  | 7698.806(237) | 7765.9829(626) |
| <i>A</i>                                | 10.1481  | 10.166330(271)   | 10.1650038(974)  | 11.0598       | 10.155180(674)  | 11.0598       | 11.3735        |
| <i>B</i>                                | 0.4751   | 0.47505354(497)  | 0.47506882(127)  | 0.4731        | 0.4754636(153)  | 0.4731        | 0.4755         |
| <i>C</i>                                | 0.4530   | 0.45286011(420)  | 0.45285099(108)  | 0.4469        | 0.45304263(888) | 0.4469        | 0.4497         |
| $\Delta_K \times 10^4$                  | 11.676   | 11.676           | 11.676           | 19.408        | 11.676          | 19.408        | 22.652         |
| $\Delta_{JK} \times 10^4$               | 0.242    | 0.29042(516)     | 0.242            | 0.239         | 0.242           | 0.239         | 0.219          |
| $\Delta_J \times 10^4$                  | 0.00747  | 0.0072345(263)   | 0.00747          | 0.00769       | 0.00747         | 0.00769       | 0.00760        |
| $\delta_K \times 10^4$                  | 0.150    | 0.150            | 0.150            | 0.331         | 0.150           | 0.331         | 0.280          |
| $\delta_J \times 10^4$                  | 0.000368 | 0.0002854(230)   | 0.000368         | 0.000350      | 0.000368        | 0.000350      | 0.000328       |
| <i>H<sub>K</sub></i> × 10 <sup>7</sup>  | 10.97    | 10.97            | 10.97            | 14.08         | 10.97           | 14.08         | 19.12          |
| <i>H<sub>KJ</sub></i> × 10 <sup>7</sup> | -        | -                | -                | -             | -               | -             | -              |
| <i>H<sub>JK</sub></i> × 10 <sup>7</sup> | -        | -                | -                | -             | -               | -             | -              |
| <i>H<sub>J</sub></i> × 10 <sup>11</sup> | -        | -                | -                | -             | -               | -             | -              |
| <i>h<sub>K</sub></i> × 10 <sup>7</sup>  | -        | -                | -                | -             | -               | -             | -              |
| <i>h<sub>JK</sub></i> × 10 <sup>7</sup> | -        | -                | -                | -             | -               | -             | -              |
| <i>h<sub>J</sub></i> × 10 <sup>11</sup> | -        | -                | -                | -             | -               | -             | -              |

<sup>a</sup> Values in parentheses are the 1 $\sigma$  statistical confidence intervals.



**FIG. 4.** Dependences of the  $\Delta$ -differences against the quantum number  $J$ . The real values of  $\Delta$ -differences are marked by dots, squares, and triangles for  $\Delta = E_{[J, K_a=3, K_c]}^{exp.} - E_{[J, K_a=3, K_c]}^{calc.}$ ,  $\Delta = E_{[J, K_a=4, K_c]}^{exp.} - E_{[J, K_a=4, K_c]}^{calc.}$ , and  $\Delta = E_{[J, K_a=2, K_c=J-2]}^{exp.} - E_{[J, K_a=2, K_c=J-2]}^{calc.}$ , respectively. See text for details.

To make the picture of this resonance interaction clearer, the following preliminary consideration is important. In principle, the set of the states  $[J, K_a = 2, K_c = J - 2]$  can be perturbed by any from corresponding sets  $[J, K'_a = k, K'_c]$  ( $k$  is fixed) belonging to some other vibrational state. However, since the  $[J, K_a = 2, K_c = J - 1]$  (300) states are not perturbed, they cannot be  $[J, K'_a \geq 1, K'_c]$  states. Because

$[J, K'_a \geq 1, K'_c]$  states would perturb with the analogous manner not only the  $[J, K_a = 2, K_c = J - 2]$  (300), but also the  $[J, K_a = 2, K_c = J - 1]$  (300) rovibrational states. In this case, an improvement of the situation with the  $[J, K_a = 2, K_c = J - 2]$  (300) states will be accompanied by getting worse with the  $[J, K_a = 2, K_c = J - 1]$  (300) states. As the result, only the  $[J, K'_a = 0, K'_c = J]$  ( $v_1 v_2 v_3$ ) rovibrational states of an additional vibrational state ( $v_1 v_2 v_3$ ) may be a possible origin of perturbations of the  $[J, K_a = 2, K_c = J - 2]$  (300) states.

As the rough calculations of the band centers discussed above showed, the (230) band may be considered as a vibrational state which strongly perturbs the  $[J, K_a = 2, K_c = J - 2]$  (300) states. Finally, the  $[J, K_a = 5, K_c = J - 5]$  (300) states were also added, and the fit of all “experimental” energies of the (300) state was made with the Hamiltonian [1]–[5], which took into account three interacting vibrational states. A total of 222 energies were fitted with the 16 parameters. They are presented in columns 6, 7, and 8 of Table 4 and column 3 of Table 5.

We believe that the sets of parameters determined in the present study from the fit of experimental data are physically meaningful because

- (1) they reproduce the initial experimental data with the accuracies closed to experimental uncertainties (see columns 4 of Tables 1 and 3);
- (2) the sets of spectroscopic parameters of the (200) and (300) vibrational states determined from the fit are well correlated with the sets of corresponding parameters of the relative states (000) and (100) from Ref. (1).

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**TABLE 5**  
Some Resonance Interaction Parameters  
for the DOCl Molecule (in  $\text{cm}^{-1}$ )<sup>a</sup>

| Parameter                        | II            | III           |
|----------------------------------|---------------|---------------|
| 1                                | 2             | 3             |
| $F_0^{300-221}$                  |               | 3.903(136)    |
| $F_K^{300-221} \times 10^2$      | 11.802(258)   | -2.554(573)   |
| $F_J^{300-221} \times 10^2$      | -0.08164(186) | -0.08303(459) |
| $F_{KK}^{300-221} \times 10^4$   |               | 13.190(946)   |
| $F_{xy}^{300-221} \times 10^2$   |               | 0.02885(263)  |
| $F_{xyK}^{300-221} \times 10^4$  |               | -4.4429(786)  |
| $F_{xyKK}^{300-221} \times 10^4$ |               | 0.10637(224)  |
| $C_{xz}^{300-230} \times 10^2$   |               | 0.26313(748)  |
| $C_{xzJ}^{300-230} \times 10^6$  |               | 0.8101(893)   |

<sup>a</sup> Values in parentheses are the  $1\sigma$  statistical confidence intervals.