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HIGH RESOLUTION RO-VIBRATIONAL ANALYSIS OF THE ν_3 FUNDAMENTAL OF CHLORINE DIOXIDE $^{16}O^{35}Cl^{16}O$

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КОЛЕБАТЕЛЬНО-ВРАЩАТЕЛЬНЫЙ АНАЛИЗ СПЕКТРОВ ВЫСОКОГО РАЗРЕШЕНИЯ ФУНДАМЕНТАЛЬНОЙ ПОЛОСЫ ν_3 ДИОКСИДА ХЛОРА $^{16}O^{35}Cl^{16}O$

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Аннотация. *С использованием Фурье-спектрометра Bruker IFS 125 HR была зарегистрирована колебательно-вращательная структура полосы ν_3 молекулы ClO_2 с разрешением 0,0015 см$^{-1}$. Данная полоса была проанализирована с использованием улучшенной модели эффективного Гамильтониана и разработанной новой компьютерной программой для анализа колебательно-вращательных спектров молекул свободных радикалов с открытой оболочкой, учитывающей спин-вращательные взаимодействия. Более 4200 переходов, принадлежащих данной полосе, были проинтерпретированы с максимальными значениями $N^{max} = 68$ и $K_a^{max} = 21$, что впоследствии было использовано для определения набора из 13 спектроскопических параметров исследуемого колебательного состояния. Среднеквадратичное отклонение составило $d_{rms} = 2{,}4 \cdot 10^{-4}$ см$^{-1}$.*

Introduction. The chlorine dioxide molecule is interesting both from a theoretical point of view, since it is one of the few stable molecules with the odd number of electrons, and from a more practical point of view, since it has been discovered in the stratospheric ozone hole of Antarctica. The observation of *OClO* was the first evidence of the role of chlorine in the ozone depletion cycle [1–3].

Chlorine dioxide is also of relevance in other contexts. Chlorine dioxide is used for bleaching wood pulp in combination with pure chlorine. It is the most used whitening method in the world. Chlorine dioxide is one of the most effective, fast-acting disinfectants, capable of eliminating bacteria, viruses, biofilms, molds, and spores. Its function as a biocide, algaecide, fungicide, makes it a very powerful general disinfectant while at the same time being gentle with the items to be disinfected [4, 5].

Materials and methods. The recorded spectrum is presented in Fig. 1, the band center is positioned near the value of 1110.104 cm^{-1}. The band under study is an *a*-type band; therefore, it is characterized by strong *R*-, *P*- and *Q*- branches. Transitions of the *a*-type satisfy the following selection rules: $\Delta N = 0, \pm 1$; $\Delta K_a = 0$ [6]. The

spectrum was interpreted using the combination difference method. The necessary data about vibrational-rotational energy levels of the ground state were taken from the work of our colleagues, which has not been published yet. As an illustration, Table 1 presents a small fragment of the determined vibrational-rotational *b*-type transitions for the ν_3 band, where N, K_a, K_c are quantum numbers of the ground vibrational state levels; N', K_a', K_c' are quantum numbers of the excited vibrational state levels; and δ is the difference between the experimental value of the line positions and the theoretically calculated one.

Transitions identified for the band under study were then used for the determination of the vibrational state ($\nu_3 = 1$) energy structure.

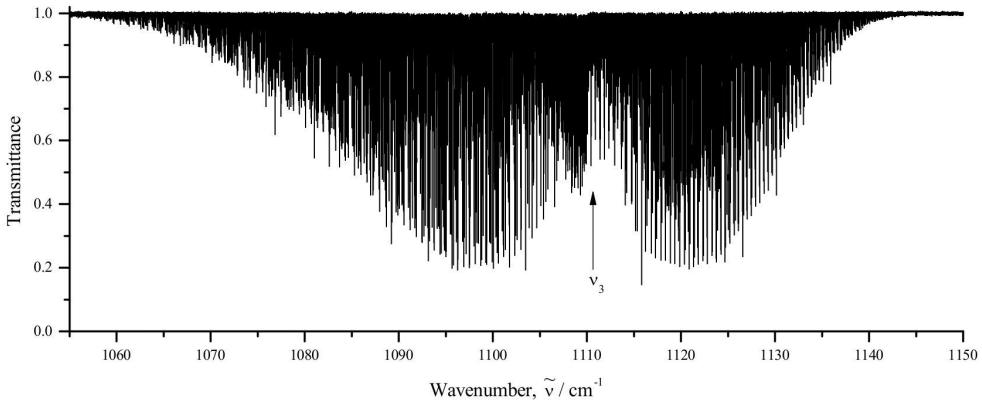

Fig. 1. Spectrum of the ClO_2 molecule, where the ν_3 band is located

Results. Most of the lines in this band look like doublets due to the spin-rotation interaction present in this molecule. In addition, throughout the entire spectrum, there is a gradual splitting of the pairs of spin-rotation transitions, which complicated their interpretation. The data on these lines were included in the final fitting procedure with a relative weight of 0.5, or not included at all. As a result, a set of 13 spectroscopic parameters was determined, which is due to 1646 (1527 without taking into account lines with a relative weight of 0) energy levels. The root-mean-square deviation amounts to $d_{rms} = 2.4 \cdot 10^{-4}$ cm^{-1}.

Table 1

Fragment of determined transitions corresponding to the ν_3 band

$N\ K_a\ K_c$	$N'\ K_a'\ K_c'$	J*	Line Position, cm^{-1}	$\delta \cdot 10^{-4}$, cm^{-1}
17 15 3	18 15 4	-	1095.3918	3
17 15 3	18 15 4	+	1095.3559	7
19 15 5	20 15 6	-	1094.0494	-1
19 15 5	20 15 6	+	1094.0198	-4
21 15 7	22 15 8	-	1092.6967	-12
21 15 7	22 15 8	+	1092.6714	-11

*J – total angular momentum $J = N \pm 1/2$ including electron spin, where $J = N + 1/2$ states labeled as "+", and states with $J = N - 1/2$ as "-".

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