The rotational spectrum of chloryl chloride, ClClO₂, in its ground vibrational state

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Rotational spectra of the four main isotopomers of ClClO₂ which together span the quantum numbers \(10 \leq J \leq 77\) and \(0 \leq K \leq 34\) have been studied in selected regions between 10 and 417 GHz. The \textit{in situ} syntheses using reactions between FClO₂ and either HCl or BC1₃ are described. Rotational and centrifugal distortion constants have been derived and used for structure and harmonic force field calculations. The quadrupole coupling constants for both Cl nuclei have been determined and the molecular dipole moment has been derived from low field Stark effect measurements in the submillimeter region. The results are discussed in relationship to published results from a matrix-isolation study, from theoretical calculations, and from studies of related molecules.

I. INTRODUCTION

Chlorine oxides are important intermediates in the atmospheric degradation of chlorofluorocarbons and other chlorine-containing compounds leading to catalytic ozone destruction. Molina and Molina\(^1\) proposed a catalytic cycle involving the C10 dimerization as playing a key role in the formation of the Antarctic ozone hole. They considered two possible products, dichlorine peroxide, ClOOC1, and chlorine chlorite, ClOCIO; they suggested that only the former would contribute to net ozone loss. \textit{Ab initio} calculations yielded three minima on the Cl₂O₂ potential energy surface,\(^2\) and high level calculations indicate chloryl chloride, ClClO₂, and ClOOCl to be of similar stability, whereas ClOCIO is approximately 40 kJ mol\(^{-1}\) less stable.\(^3\)

Birk \textit{et al.}\(^4\) observed the rotational spectra of the products of the C10 self reaction carried out in He at 220 K and total pressures of about 4 Torr. They found ClOOCl as only identifiable dimer product under those conditions and they derived its structure. Soon thereafter, Müller and Willner succeeded in the synthesis of ClClO₂. They used IR and UV/vis spectroscopy to characterize this molecule in rare gas matrices\(^5\) and in the gas phase,\(^5,6\) determined its structure using isotopic shifts of \(\nu_5\) and \(\nu_6\), and calculated its harmonic force field. Vibrational spectra and the photochemistry of all three Cl₂O₂ isomers isolated in Ar matrices were reported by Jacobs \textit{et al.}\(^7\)

More recently, the formation of ClClO₂ was reported in the ClO self reaction on ice\(^8\) and in the photochemistry of OCIO in ice\(^9\) and on ice.\(^10\) These findings were taken as indications that ClClO₂ may be formed in the heterogeneous processes taking place in and on polar stratospheric cloud particles.

The initial experiments to record its microwave spectrum were carried out at the University of Tübingen in conjunction with the work reported in Refs. 5 and 6, but an assignment was not achieved. The rotational spectrum of ClClO₂ was later studied at the Jet Propulsion Laboratory (JPL) as part of a program to provide a microwave to submillimeter spectroscopic data base of molecules potentially important in the upper atmosphere\(^11,13\) and to determine molecular properties that may influence chemical behavior.

Preliminary results obtained at JPL on the submillimeter spectra of the three most abundant isotopomers of ClClO₂ and a derived structure have been published previously.\(^14\) This study utilizes additional millimeter and submillimeter data as well as assignments of the initial Tübingen data. Spectra of the four main isotopomers of ClClO₂ in their ground vibrational states have been fit. An extensive set of rotational and centrifugal distortion constants are reported as well as the nuclear quadrupole coupling constants for both Cl nuclei and the molecular electric dipole moment. Ground-state effective, average, and equilibrium structural parameters as well as the harmonic force constants were derived from these data and those of earlier studies.\(^5,6\)
II. EXPERIMENTAL DETAILS

Caution! Although no explosion occurred in the course of our studies, ClF₃, OClO, and FCIO₂ should be handled only with proper safety precautions and in millimolar quantities. The contact of these substances with organic or other oxidizable material may lead to explosive reactions.

ClClO₂ is prepared best by reacting FCIO₂ with a volatile chloride in situ and passing the products through the absorption cell.⁵ At the university of Tübingen, FCIO₂ was prepared from OClO and F₂,⁵ and a commercial sample of BCl₃ was used as the chloride. Roughly equivalent amounts of FCIO₂ and BCl₃ were flowed through a UV-spectrometer into the microwave absorption cell at total pressures around 2 Pa and at a cell temperature of 243 K. The strong 296 nm absorption of ClClO₂ was used to optimize the flow conditions of the precursors.

The microwave spectrometer in Tübingen is a standard Stark modulated (50 kHz) spectrometer using phase-locked BWOs as sources. Spectra were recorded in the ranges 10–20 and 27–39 GHz. Initially, low J a- and c-type lines were specifically searched for, guided by various ab initio calculations.²,³,¹⁵ Because of strong OClO lines and lines of unreacted FCIO₂, no unambiguous assignment was made. Later, larger regions of the spectrum were recorded at a higher speed than normally used in order to achieve a large coverage of the microwave region. The accurately known frequencies of the ever present OClO lines were used to correct for any offset caused by rapid scans in one direction.

Although it appears that the yield of ClClO₂ was low, a significant number of transitions were eventually assigned.

At JPL, FCIO₂ was prepared from ClF₃ and KClO₃. The reaction was carried out in a glass container at 273 K overnight. In contrast to the syntheses described in Ref. 16, which were carried out in metal containers, O₂ was not a significant product in our experiments. A commercial sample of HCl was used as the chloride. The halogen exchange reaction was carried out using a flow system in which a relatively high pressure reaction region at several tens of Pascal was separated by a pinhole from the observation region which was in the 1 Pa range. This is similar to the flow systems described in Refs. 4, 17. Initial submillimeter observations showed that with this apparatus it was difficult at room temperature to achieve high yields of ClClO₂ with low consumptions of precursors. Large amounts of unreacted FCIO₂ remained even if significant amounts of OClO were already observable because of the decomposition of ClClO₂. Subsequently, conditions for ClClO₂ production were optimized by monitoring its strong absorption at 296 nm in the absorption cell used for rotational spectroscopy. It was found that at temperatures slightly below room temperature and at constant, slow flows of FCIO₂ and HCl the amount of FCIO₂ decreased while that of ClClO₂ increased much more than that of OClO. Below ~250 K the amount of ClClO₂ decreased, and below ~240 K OClO was the only observable product. Absorptions of HC₃ and HF were not monitored. Best results were obtained when approximately stoichiometric amounts of FCIO₂ and HCl were mixed in a ~1 m long, 2.5 cm i.d. reactor at pressures of 10–30 Pa, and the products were expanded through a ~1.5 mm pinhole into the 1 m long, 7.3 cm i.d. double path absorption cell. Both reactor and absorption cell were kept at ~255 K. The pumping speed was adjusted to keep the pressure in the absorption cell in the 1 Pa range; the residence time was of the order of 5 s. Under these conditions up to 30 % of the total pressure was due to ClClO₂.

The spectrometer has been described by Friedl et al. Phase-locked klystrons operating near 100 GHz were used as sources. Diode detectors were used for fundamental frequencies, and a liquid He-cooled InSb hot electron bolometer was used to detect harmonics. The entire region between 378.5 and 395.0 GHz was scanned. Additional measurements were made between 94.5 and 131.3 GHz, near 290 GHz, and between 365 and 417 GHz. Two Stark plates, consisting of 0.953 m long, 54.8 mm wide, and 6.35 mm thick aluminum bars 25.4 mm apart, were mounted inside the absorption cell. Both reactor and absorption cell were kept at ~255 K. The pumping speed was adjusted to keep the pressure in the absorption cell in the 1 Pa range; the residence time was of the order of 5 s. Under these conditions up to 30 % of the total pressure was due to ClClO₂.

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In order to eliminate OClO lines from consideration, published line positions as well as unpublished data from JPL for the (000), (010), (020), (100), and (001) vibrational state were analyzed¹⁸ and used for predictions. Lines of FCIO₂ in the reaction mixture were identified by recording each section of the spectrum both with pure FCIO₂ and with the reaction mixture. The FCIO₂ data were used with previous¹⁹ and additional measurements to obtain new and improved spectroscopic constants for its ground vibrational state.²⁰

III. RESULTS

A. Observed Spectra and Analysis

The pyramidal ClClO₂ is an asymmetric, prolate top with Κ = -0.7598 for ⁵⁵Cl⁵⁵ClO₂. It has C₄ᵥ symmetry with a large dipole component along the c axis and a smaller one along the a axis.

Initial simulations of the rotational spectrum of ClClO₂ were made using the structural parameters and the harmonic force field from the matrix-isolation study to derive rotational constants and quartic centrifugal distortion constants.
Initial Cl nuclear quadrupole coupling constants \( [I^{(35}Cl) = I^{(37}Cl) = \frac{3}{2}] \) were taken from an \textit{ab initio} calculation.\textsuperscript{15} Predictions and fittings of the spectra were done with Pickett’s programs \textsc{spcat} and \textsc{spfit}.\textsuperscript{21}

Recording the Cl\textsubscript{2}\textsuperscript{O} submillimeter spectrum provides opportunities for pattern recognition that are not readily available in the MW region. Large sections of the spectrum can be recorded in comparatively short time, the strongest transitions are \(^R\)R-type transitions in contrast to \(^Q\)-, \(^P\)-, and \(^R\)-type transitions, and the quadrupole patterns are in general more compact than those of the low \(J\) transitions which where sought in the original MW studies. A section of the submillimeter spectrum of Cl\textsubscript{2}\textsuperscript{O} is shown in Fig. 1.

In the region near 400 GHz, the strongest features belong to high \(K_a\) c-type \(^R\)-branches. These are among the strongest transitions in the entire rotational spectrum. Because \(A - (B + C)/2 \approx B + C\), some clustering of strong \(^R\)-type transitions with the same value of \(J + 2K_a\) occurs at high \(K_a\). This facilitates the identification of different series once one has been identified. Since Cl\textsubscript{2}\textsuperscript{O} is a fairly asymmetric top, the spacing between two successive transitions of one branch decreases fairly rapidly with increasing \(J\) for \(J \approx K_a\). This was an important criterion for assigning \(K_a\) quantum numbers to the identified sequences of transitions. In addition, the quadrupole splitting patterns are simple, but are sufficiently distinctive to facilitate the assignment. For \(J = K_a\) the lines are very narrow and particularly intense. For increasing \(J\) or decreasing \(K_a\) the transitions are observable first as broad lines and later as partially resolved doublets which permitted an estimate of \(\chi_{aa}\) at the terminal Cl atom. Among the three sequences first identified, one was assigned to the ground vibrational state of the main isotopomer \(35\text{Cl}^{35}\text{Cl}\textsubscript{2}\textsuperscript{O}\) because of its intensity, and it was extended to six consecutive members. Comparison with predicted spectra and some trial fits led to the correct assignment of the \(J'' = 24 - 29\) members of the \(K_a'' = 16\) \(^R\)-branch. Because of the asymmetry of the molecule these transitions contained sufficient information for the determination of all three rotational constants which allowed the assignment of additional transitions and more precise determination of the molecular parameters. Transitions near the oblate limit \((K_a \approx J)\) and \(Q\)-branch transitions \((K_a \approx 32)\) often appeared as widely spaced \((\geq 2\) MHz) doublets. The splitting depends primarily on \(\chi_{cc}\) at the central Cl and \(\chi_{aa}\) at the terminal Cl, respectively. Information on the remaining diagonal quadrupole coupling constants was contained in the few transitions near 400 GHz observed as quartets.

Rotational constants of \(^{37}\text{Cl}^{35}\text{Cl}\textsubscript{2}\textsuperscript{O}\) and \(^{35}\text{Cl}^{37}\text{Cl}\textsubscript{2}\textsuperscript{O}\) were predicted from a preliminary structure which was derived from the rotational constants of the main isotopomer and an estimate of \(\tau(\text{ClO})\). A harmonic force field calculation was performed with emphasis put on the reproduction of the quartic distortion constants of the main isotopomer in order to derive values for the monosubstituted isotopomers. Initial sextic distortion constants were taken from the main isotopomer. The calculated quartic constants were actually quite close to their final values and some lines were found within a few megahertz of the predictions for both isotopomers. The assignments proceeded in a straightforward manner with the fits first freeing the rotational constants and finally freeing the higher order terms after a substantial number of lines had been included in the fits. Fewer transitions were observed for the isotopomers with one \(^{37}\text{Cl}\) than for \(^{35}\text{Cl}^{35}\text{Cl}\textsubscript{2}\textsuperscript{O}\) due to their factor of \(~3\) lower abundance.

Spectroscopic constants \(C_{37,37}\) of \(^{37}\text{Cl}^{37}\text{Cl}\textsubscript{2}\textsuperscript{O}\) were estimated by applying the changes between \(^{35}\text{Cl}^{35}\text{Cl}\textsubscript{2}\textsuperscript{O}\) and both \(^{37}\text{Cl}^{35}\text{Cl}\textsubscript{2}\textsuperscript{O}\) and \(^{35}\text{Cl}^{37}\text{Cl}\textsubscript{2}\textsuperscript{O}\) to the main isotopomer:

\[
C_{37,37} = C_{37,35} + C_{35,37} - C_{35,35} \tag{1}
\]

Some transitions were found very close to the predictions. Because of the even lower abundance of \(^{37}\text{Cl}^{37}\text{Cl}\textsubscript{2}\textsuperscript{O}\) still fewer transitions were observed for this isotopomer. In the final fits only the rotational constants of \(^{37}\text{Cl}^{37}\text{Cl}\textsubscript{2}\textsuperscript{O}\) were released, whereas all other mechanical constants were constrained as described in Eq. (1). The final values of the rotational constants \(A, B,\) and \(C\) of \(^{37}\text{Cl}^{37}\text{Cl}\textsubscript{2}\textsuperscript{O}\) are only about 52, 258, and 524 kHz smaller than those calculated according to Eq. (1), thus justifying its use in calculating the less well determined distortion constants.

After essentially all of the observed c-type transitions had been assigned, some \(a\)-type \(R\)-branch lines could be identified tentatively. They were found very close to the predicted frequencies and had approximately the expected intensities. Because of their high quantum numbers \((J \approx 65)\) their predicted uncertainties were still several megahertz. Their assignments were confirmed by additional measurements of \(a\)-type transitions in the millimeter region which had smaller uncertainties. Inclusion of a large number of these transitions with \(J\)'s in the 50–70 range and \(K_a\)'s from 0 to 33 resulted in a significant improvement in the precision of the parameters. Finally, additional measurements were made of transitions with relatively large quadrupole splitting in order to improve the quadrupole coupling constants; an example transition is shown in Fig. 2.

All lines assigned in the Tübingen MW data had \(J \geq 10\). In general, the quadrupole splitting in the MW region was better determined than the absolute line positions. This was taken into account in the combined fit of the Tübingen and JPL data.

In the course of our investigations absorptions of the Coriolis coupled \(v_6 = 1\) and \(v_4 = 1\) vibrational states have been identified and analyzed. These results will be presented separately.

Since the effects due to the terminal and central Cl dominate the quadrupole splitting for very high and very low \(K_a\), respectively, it matters little which of the nuclear spin angular momenta is coupled to the rotational momentum.
first to yield the intermediate quantum number $F_1$. Since the largest quadrupole constant for the terminal Cl is larger than the largest one for the central Cl, the following coupling scheme was employed:

$$J + I(C\text{Cl}_t) = F_1$$  \hspace{1cm} (2)$$

$$F_1 + I(C\text{Cl}_c) = F$$  \hspace{1cm} (3)$$

In order to reduce the number of independent quadrupole coupling constants in the fit the isotopic ratios of the $x$'s were fixed to the ratio 1.268773\textsuperscript{22} with small, fixed corrections applied to account for inertial axes rotation with isotopic substitution. This ratio holds if vibrational effects are neglected. The inertial axis systems of $^{37}\text{Cl}^{35}\text{ClO}_2$, $^{35}\text{Cl}^{37}\text{ClO}_2$, and $^{37}\text{Cl}^{37}\text{ClO}_2$ are rotated by about 0.08, 0.17, and 0.25°, respectively, compared to the axis system of $^{35}\text{Cl}^{35}\text{ClO}_2$, as calculated from the structure. Differences from the quadrupolar axis systems to the respective inertial axis system were taken from a theoretical calculation.\textsuperscript{15} Thus, the total number of fitted quadrupole constants was reduced from 16 to 4 with no significant degradation of the quality of the fit. The isotopic corrections to the quadrupole constants were not significantly determined in trial fits where they were released.

Selected transitions of $^{35}\text{Cl}^{35}\text{ClO}_2$ are given in Table I. Statistical information describing the transitions used in the final fit of $\text{ClC}_1\text{O}_2$ is given in Table II. The complete list of lines used in the final fit, their uncertainties, as well as their positions calculated from the final set of parameters is available from the Electronic Physics Auxiliary Publication Service (E-PAPS) of the American Institute of Physics.\textsuperscript{23} A machine-readable list of $^{35}\text{Cl}^{35}\text{ClO}_2$, $^{37}\text{Cl}^{35}\text{ClO}_2$, and $^{35}\text{Cl}^{37}\text{ClO}_2$ frequencies (without hyperfine splitting), intensities, and assignments is available online in the JPL Submillimeter, Millimeter, and Microwave Line Catalog (http://spec.jpl.nasa.gov).\textsuperscript{11-13} The spectroscopic constants are given in Table III.

B. Dipole Moment

The Stark effect measurements were made at JPL in the submillimeter region under weak field conditions using the intensity weighted average of the unresolved Stark components. As long as the shifts of the individual Stark components were within a linewidth of the intensity weighted average, the measured shifts were proportional to the square of the applied fields.

In these experiments the polarization of the millimeter waves with respect to the applied electric field was not determined. However, the rooftop reflector used to obtain two passes through the sample also rotates the plane of polarization of the reflected radiation by 90°. Therefore, it is reasonable to assume that the the Stark shifted transition contains equal contributions from the $\Delta M = 0$ and $\Delta M = \pm 1$ components. For second order Stark shifts of the energy levels of the form

$$\Delta E/e^2 = A + BM^2$$  \hspace{1cm} (4)$$

the shift in frequency can be expressed in closed form as the intensity weighted average of all the Stark components. Here $A$ and $B$ are the Stark coefficients and $\varepsilon$ is the strength of the Stark field. For the present case of equal parallel and perpendicular polarization, one obtains

$$\Delta \nu/e^2 = \Delta A + \Delta B[8J(J+1) - 1]/20$$  \hspace{1cm} (5)$$

for $\Delta J = 0$ with $\Delta A$ and $\Delta B$ refering to the differences between upper and lower states and

$$\Delta \nu/e^2 = \pm[\Delta A + \Delta BJ(6J+7)/20 + BJ+1(J+1)/2]$$  \hspace{1cm} (6)$$

for a $J + 1 \leftrightarrow J$ or $J \leftrightarrow J + 1$ transition where $\Delta A = A_{J+1} - A_J$ and $\Delta B = B_{J+1} - B_J$. The upper sign is for $J + 1 \leftrightarrow J$ and the lower for $J \leftrightarrow J + 1$. For individual hyperfine transitions, $F$ is to be used instead of $J$.

Because the distribution of microwave power in the sample cell is a function of frequency and not well controlled and because the applied field is not very homogeneous, the transitions which are used for calibration should be preferably in the same frequency region as those used for the dipole determination. While this method is not as accurate or precise as measurements of individual components, it is quite useful when more conventional techniques are unavailable.

The $27_3,25 - 27_2,26$ transition of the ground and $v_2 = 1$ states of $\text{SO}_2$\textsuperscript{24,25} near 385.0 and 391.8 GHz were used for calibration. Five transitions of $^{35}\text{Cl}^{35}\text{ClO}_2$\textsuperscript{19,20} were used to determine its dipole moment for comparison with the previously reported values and as a demonstration of the validity of the method. The transitions are given in Table IV.
Seven transitions were used for the determination of the dipole components of $^{35}$Cl$^{35}$ClO$_2$. Taking into account that $\mu_a$ was expected to be much smaller than $\mu_c$, two transitions depended essentially only on $\mu_a$, three mostly on $\mu_c$, and two on both. The transitions are described in Table V. Some of the transitions investigated appeared as doublets or quartets due to $^{35}$Cl hyperfine splitting. In these cases the Stark shifts of the observed lines were averaged to yield the shifts of the whole transition. The dipole moments were calculated from a set of equations

$$\Delta \nu = (C_a \mu_a^2 + C_c \mu_c^2) / \epsilon^2$$

where $C_a$ and $C_c$ are calculated from Eqs. (5) or (6) for unit dipole moment components. All shifts for all the transitions were equally weighted and fitted to Eq. (6) using the method of least squares. The Stark coefficients, field strengths, observed Stark shifts as well as the residuals from the fits are presented in Tables IV and V, too.

Although the calibration factors determined for SO$_2$ agree with each other to within 1%, and the scatter within each data set is small, the constraints of the experimental setup mentioned above do not justify reporting the dipole moments derived here to better than about 2%. The dipole moment components of FCIO$_2$ and its total value are $\mu_a$, $\mu_c$, $\mu_{tot}$ = 0.534 (11), 1.647 (33), 1.731 (35) D. They are in very good agreement with the literature values of 0.551 (20), 1.632 (20), 1.723 (28) D. The result for ClCIO$_2$ is $\mu_a$, $\mu_c$, $\mu_{tot}$ = 0.457 (10), 1.502 (30), 1.570 (32) D. For both ClCIO$_2$ and FCIO$_2$ the 2% uncertainties reported are approximately double the 1σ uncertainties derived from the scatter within each data set. Possible centrifugal distortion effects on the SO$_2$, FCIO$_2$, and ClCIO$_2$ dipoles have not been taken into account as they are expected to be small compared with the experimental uncertainties.

C. Structural Parameters and Harmonic Force Field

The ground-state effective structure ($r_0$) of ClCIO$_2$ was calculated using Rudolph’s programs RU111J and RU115. The structural parameters were fit to the principal planar moments which were derived from the ground-state rotational constants of all four isotopomers weighted inversely proportional to the squares of their magnitudes. Following the suggestion by Rudolph, $P_0$ was omitted from the fit for all but the main isotopomer. The uncertainties in Table VI reflect only those from the fit.

The $r_0$ structure was used for a calculation of the harmonic force field as described below. The harmonic contributions to the $\alpha$ constants were then derived to obtain the ground-state average structure ($r_s$) of $^{35}$Cl$^{35}$ClO$_2$ using Tykpe’s program MWSTR. Isotopic variations in $r_s$ were accounted for using Eq. (9).9-31

$$r_s = r_0 - 3/2a(u^2) + K$$

$$\delta r_s = 3/2a\delta(u^2) - \delta K$$

Here ($u^2$) and $K$ are the zero-point mean-square amplitude of a given bond and its perpendicular amplitude correction, respectively, obtained from the harmonic force field. The constants $a$ are Morse anharmonicity parameters, which were approximated by values for the respective diatomics. Values of 1.709 and 2.021 Å$^{-1}$ were used for ClCIO$_2$ and ClO$_3$, respectively. It is assumed that isotopic variations in the ground-state average bond angles are negligible.9-31

The ground-state average structure ($r_0$) was calculated using Eq. (8). In this model, ground-state average and equilibrium bond angles are assumed to be equal. While this model yields good equilibrium values in some instances, $r_s$ and $L_s$ of the OCIO radical are smaller by ~0.2 pm (~33% of $r_0 - r_s$) and ~0.08°, respectively, than the values from Eq. (8). Errors of similar magnitude may be present in these $r_0$ parameters and should be considered when comparing them with theoretical results. Their effect on the results of the force field calculation is unimportant. All structural parameters, both experimental and from theoretical calculations, are given in Table VI.

The harmonic force field was calculated using Christen’s program NCA. The calculated $r_s$ structure given above was used to describe the geometry of the molecule. The force constants were defined in terms of internal coordinates. Data for $v_4$ were corrected because of Fermi resonance with 2$v_2$. Effects of anharmonicity were reduced as described in Ref. 36 by using for $\omega_4/v_4$ a value of 1.02 for the ClO$_2$ stretching mode and $v_1$ and $v_5$ and a value of 1.01 for all other vibrations. The input data were weighted inversely to the squares of their attributed uncertainties: The fundamentals of the main isotopomers were given uncertainties of 0.1 cm$^{-1}$, resolved isotopic shifts were given uncertainties of 0.03 cm$^{-1}$, except for the shifts of $v_1$ and $v_6$ where they were twice as large because of Fermi resonance and weakness of the band, respectively. Twenty five times the experimental uncertainties were used for the quartic centrifugal distortion constants. Since the differences between ground state and equilibrium distortion constants due to vibrational effects are difficult to evaluate, the ground state constants were used as determined. The relative weight of the distortion constants with respect to the vibrational data was chosen to ensure convergence of the fit and a satisfactory reproduction of both types of input data. The initial force field of Müller and Willner reproduced the distortion...
constants quite well, with the exception of $\Delta_K$ whose absolute values were predicted almost 0.7 kHz larger than the experimental values.

The resulting force constants, previous experimental values from Müller and Willner, as well as $ab\ initio$ and density functional theory (DFT) values are presented in Table VII. Most of the force constants were precisely determined. The largest scatters occur for $f_{\alpha\alpha}$ and the sum of $f_{\alpha\beta}$ and $f_{\alpha\alpha}$. The diagonal force constants and structural parameters of ClClO$_2$ and related molecules are given in Table VIII. A comparison of the input data with values calculated from the force field can be found in Table IX.

The potential energy distribution for the vibrations of ClClO$_2$ is very similar to that of the previous force field. A moderate change occurs for $\nu_2$: 0.88 $f_\beta + 0.07 f_{\alpha\beta}$, a somewhat larger for $\nu_3$: 0.31 $f_R + 0.53 f_\alpha + 0.19 f_\beta - 0.04 f_{R\beta} + 0.22 f_{\alpha\alpha} - 0.25 f_{\alpha\beta}$; only contributions larger than 0.03 are given.

### IV. DISCUSSION

#### A. Spectroscopic constants, structure, and harmonic force field

Precise rotational and centrifugal distortion constants have been obtained for ClClO$_2$. These constants have allowed the accurate prediction of ClClO$_2$ spectra throughout the microwave to submillimeter regions. As a result, it has been possible to review spectra taken during earlier studies of ClOCIC and ClOCIC$_2$ for the presence of ClClO$_2$. Under the conditions described in these references ClClO$_2$ was not an observable product in either of those experiments previously carried out in this laboratory.

The structure of matrix-isolated ClClO$_2$ had been determined using the product rule in the symmetry class $\alpha''$ ($\nu_5$ and $\nu_6$), assuming the ClO bond length from the comparison of ClO vibrations of ClClO$_2$, OCI$^+$, and FCIO$_2$. As can be seen in Table VI, these parameters agree well with the present, more precise gas phase values. This demonstrates that matrix IR spectroscopy can provide reasonable structural parameters if the number of elements in the symmetry class is two or less, if matrix effects are small (e.g., in neon), and if the isotopic shifts have been determined precisely.

It is shown in Table VI that the MP2/6-31G* calculation predicted a ClCl distance that is much too long. The ClO bond length and the OClO angle are also larger than those derived from the experimental data. When larger basis sets are employed the calculated structural parameters are in better agreement with experiment, particularly for the ClCl bond length. The highest level coupled cluster calculation published provided very good values for the bond angles, but the bond lengths are somewhat too long. Thus, even for the highest level $ab\ initio$ calculations published, the agreement with experiment is only moderate. DFT calculations with hybridized functionals yielded similar agreement with experiment, as demonstrated for one example in Table VI.

The MP2/6-31G* method is frequently used to estimate thermochemical properties of molecules. ClClO$_2$ was predicted to be higher in energy than ClOCIC by about 100 kJ mol$^{-1}$. Extrapolations based on different methods and large basis sets predicted this difference to be $\sim 4 \pm 8$ kJ mol$^{-1}$. Thus, the computations do not distinguish within their uncertainties which is the lowest energy form of Cl$_2$O$_2$.

It is shown in Table VIII that the difference in the XCl bond length is much larger between ClCl and ClClO$_2$ than between FCl and FCIO$_2$. The change is even more pronounced for the respective force constants. The larger XClO bond angle in ClClO$_2$ compared to FCIO$_2$ is probably caused by steric effects of the larger Cl atom. If electrostatic repulsion between X and O atoms was dominating this angle the situation would be opposite because F is more electronegative than Cl.

In ClClO$_2$ the electronegative halogen lowers the electron density in antibonding orbitals of the ClO$_2$ group, thus shortening the ClO bond and increasing the ClO force constant. As expected, both values for ClClO$_2$ are between those of OCI$^+$ and FCIO$_2$; and they are somewhat closer to the latter. The smaller OCI$^+$ bond angle in the chloryl halides compared to OCI$^+$ can be explained by the smaller steric requirements of 3/2 electron pairs compared to one electron pair and one halogen atom. The OCI$^+$ angle in ClClO$_2$ seems to be slightly smaller than in FCIO$_2$. The trends in the bending force constants are as expected.

It is demonstrated in Table IX that the present force constants reproduce the input data very well. In particular, it can be seen that $\Delta_K$, which was poorly reproduced initially, is reproduced well.

The differences between the present and the previous experimental force constants in Table VII are mainly in $f_R$, $f_\beta$, and $f_{\alpha\beta}$. The $ab\ initio$ and DFT force constants agree quite well with the experimental ones. It is interesting to note that present values for $f_{\alpha\beta}$ and $f_{R\beta}$ agree better with the theoretical values than the previous values. However, rather large differences compared to the experimental values and among the theoretical calculations, for example in some of the diagonal force constants, as well as $f_{R\beta}$ and $f_{\alpha\alpha}$, show that higher level calculations are needed to accurately describe ClClO$_2$. 

\[ f_{R\beta} = 0.22 f_{\alpha\alpha} - 0.25 f_{\alpha\beta}; \]
B. Dipole Moment

The dipole moment of ClCIO₂, its components along the inertial axes as well as along the ClCl bond and in the ClO₂ plane are shown in Fig. 3 and Table X. The latter also contains values from \textit{ab initio} calculations and experimental data for related molecules. The direction of the dipole moment is the one suggested by theoretical calculations\textsuperscript{3,15,44} in the present study, as is usually the case, only the magnitudes of the components along the principal axes were determined experimentally.

As can be seen in Table VI, the MP2/6-31G* dipole moment is twice the experimental value; even with much larger basis sets MP2 calculations overestimate the dipole moment\textsuperscript{3}. The coupled cluster and density functional theory results presented in Table X show good agreement for the dipole moment and the various components.

In the chloryl halides, the withdrawal of electron density from the ClO₂ moiety by the halogens reduce the dipole components in the ClO₂ plane compared to the OCIO radical, see Table X. Since Cl is less electronegative than F it seems reasonable that the ClCIO₂ value is slightly larger than the FClO₂ value. These small differences should be viewed cautiously because of the comparatively large uncertainties in the dipole components. It is interesting to note that µXCl in ClCIO₂ is almost as large as in FClO₂, an indication of a fairly ionic ClCl bond in the former molecule.

C. Nuclear Quadrupole Coupling Constants

Because of the $C₂$ symmetry of the molecule there is only one off-diagonal quadrupole coupling constant, $\chi_{ac}$, for each nucleus. Since it was not determined, certain assumptions have to be made in order to diagonalize the quadrupole tensors. For the terminal Cl, assumption I is that the $z$-axis lies along the ClCl bond; assumption II is that there is no $\pi$ bonding in the ClCl bond and therefore cylindrical symmetry about the $z$-axis. As can be seen in Table XI, the results are fairly similar: the ClCl bond is moderately ionic, comparable to the XCl bonds in HCl and ICl; even according to assumption I, the $\pi$ character of the ClCl bond is small. DFT calculations yield diagonal coupling constants which are in good agreement with the experiment, and they indicate a situation between assumption I and II, but very close to assumption I.

It is interesting to compare the quadrupole coupling constants of OCIO and FClO₂ with those at the central Cl in ClCIO₂. For this comparison, the OCIO molecule was rotated so that its molecular plane is in the ClO₂ plane of the ClCIO₂ molecule, and the axis through the O atoms is parallel to the $b$ axis; the quadrupole coupling constants have been transformed accordingly and are collected in Table XII. The constants of ClCIO₂ are between those of FClO₂ and those of OCIO, much closer to the former. Assuming that the changes in the quadrupole coupling constants from OCIO to the chloryl halides are a measure of the ionic character of the XCl bond and thus also a measure of the electron withdrawal at the central Cl, the ionic character of $\sim$1/3 for X=Cl yields an ionic character of $\sim$0.45 for X=F if one compares the $\chi_{bb}$ values. The slightly smaller values are obtained for the other $\chi_{ii}$ probably reflect an additional small reorientation of the field gradient in the ac symmetry plane. Parent and Gerry\textsuperscript{19} obtained an ionic character of 0.64 for the FCl bond in FClO₂ assuming the population of the $3p_b$ orbitals to be the same in FClO₂ and in OCIO in an orientation analogous to the present one. Considering the assumptions made in both studies, the agreement between both values is reasonable.

As can be seen in Table XII, DFT is capable of predicting diagonal quadrupole coupling constants of the central Cl well, too; one of the principal quadrupole axes is close to the ClCl bond, see Table XII and Fig. 4.

V. CONCLUSION

The present investigation of the rotational spectrum of ClCIO₂ allows the precise prediction of its spectrum in the ground vibrational state well into the submillimeter region.

The gas phase molecular structure, dipole moment, and quadrupole coupling constants have been determined experimentally for the first time. These properties provide important reference points for \textit{ab initio} or DFT calculations which are often used to evaluate thermochemical properties of molecules. The deficiencies of the highest level \textit{ab initio} and DFT calculations to describe the C₂O₂ isomers make them ideal candidates for further tests. The experimental data of ClCIO₂ fit well into the series of related compounds. The good agreement between the gas phase structural parameters and those from a matrix IR study shows that matrix-isolation can be used to determine reasonable structural parameters under favorable conditions.
ACKNOWLEDGMENTS

D.C. and H.S.P.M. thank Prof. H. Willner for support of the experiments in Tübingen through BMFT Project No. VOZ08, for providing a UV spectrometer system, and for some help during the experiments. D.C. also thanks the Deutsche Forschungsgemeinschaft (DFG) for travel grants to visit JPL. H.S.P.M. and E.A.C. thank Drs. C. M. Miller and S. P. Sander for making a UV spectrometer system available and for some help in the operation. H.S.P.M. thanks the National Research Council for a NASA-NRC Resident Research Associateship during this study. Part of the research was performed at the Jet Propulsion Laboratory, California Institute of Technology, under a contract with the National Aeronautics and Space Administration.

18. See AIP document No. E-PAPS: JCPAS ????-???? for observed frequencies of ClClO₂ used in the final fit, uncertainties, assignments, and residuals. E-PAPS document files may be retrieved free of charge from our FTP server (http://www.aip.org/epaps.html) or from ftp.aip.org in the directory /epaps/. For further information: e-mail: paps@aip.org or fax: 516-576-2223.
FIG. 1. Section of the submillimeter spectrum of ClClO₂. Lines of ³⁵Cl³⁵ClO₂ in the ground, \( v₃ = 1 \), and \( v₅ = 1 \) vibrational states are marked by 0, 4, and 6, respectively. The quantum numbers \( J₀, K₀, \) are given in Table I for the ground vibrational state. §, †, and ‡ indicate more than one transition of ClClO₂, a transition of OCIO and FCIO₂, respectively. Some lines show quadrupole splitting due to the Cl nuclei.

FIG. 2. The 13₁₁,₂ - 13₁₁,₃, 13₁₁,₂ - 13₁₁,₄ prolate paired transitions of ³⁵Cl³⁵ClO₂ showing quadrupole splitting due to both terminal (upper) and central Cl (lower) as indicated. The smallest splitting (< 210 kHz) was not resolved. The quantum numbers \( F', F'' = F' = F'' \) are given in Table I. The strong line in the middle, marked with †, is due to OCIO.

FIG. 3. Dipole vector for the ClClO₂ molecule and the dipole contributions along the ClCl bond and in the O₂Cl plane. A projection into the \( C₂ \) symmetry plane of the molecule is used. The inertial axes are also shown.

FIG. 4. The principal quadrupole axes of ClClO₂ in the \( C₂ \) symmetry plane according to DFT calculations; the \( y \) axes are perpendicular to the plane. The axes \( x' \) and \( z' \) were obtained under the assumption that the principal quadrupole tensor at the terminal Cl is cylindrically symmetric, i.e., there is no \( \pi \) bonding in the ClCl bond; further details are given in Sec. IV C.
TABLE I. Observed frequencies (MHz), assignments, uncertainties* (kHz), and residuals (kHz) (o-c) of selected rotational transitions of $^{35}\text{Cl}^{35}\text{Cl}_2$.

<table>
<thead>
<tr>
<th>assignment$^b$</th>
<th>frequency</th>
<th>unc</th>
<th>o-c</th>
</tr>
</thead>
<tbody>
<tr>
<td>$13_{1/2} - 13_{1/2}$</td>
<td>131 109.326</td>
<td>30</td>
<td>-16</td>
</tr>
<tr>
<td>11.5,10&amp;13</td>
<td>131 110.524</td>
<td>35</td>
<td>35</td>
</tr>
<tr>
<td>11.5,11&amp;12</td>
<td>131 111.320</td>
<td>30</td>
<td>29</td>
</tr>
<tr>
<td>14.5,14&amp;15</td>
<td>131 111.995</td>
<td>30</td>
<td>43</td>
</tr>
<tr>
<td>12.5,11&amp;14</td>
<td>131 115.673</td>
<td>30</td>
<td>8</td>
</tr>
<tr>
<td>13.5,12&amp;15</td>
<td>131 116.332</td>
<td>35</td>
<td>31</td>
</tr>
<tr>
<td>12.5,12&amp;13</td>
<td>131 117.118</td>
<td>30</td>
<td>-9</td>
</tr>
<tr>
<td>13.5,13&amp;14</td>
<td>131 117.746</td>
<td>30</td>
<td>-20</td>
</tr>
<tr>
<td>$42_{11,31} - 41_{10,31}$</td>
<td>378 052.556</td>
<td>30</td>
<td>-12</td>
</tr>
<tr>
<td>39.5,40&amp;39</td>
<td>378 053.508</td>
<td>30</td>
<td>-32</td>
</tr>
<tr>
<td>39.5,41&amp;38</td>
<td>378 054.492</td>
<td>30</td>
<td>-29</td>
</tr>
<tr>
<td>40.5,42&amp;39</td>
<td>378 055.449</td>
<td>30</td>
<td>-43</td>
</tr>
<tr>
<td>$38_{35-37,36}^c$</td>
<td>380 440.235</td>
<td>25</td>
<td>-20</td>
</tr>
<tr>
<td>33,34&amp;32,33</td>
<td>380 442.968</td>
<td>25</td>
<td>-15</td>
</tr>
<tr>
<td>53,31&amp;53,30</td>
<td>378 534.929</td>
<td>50</td>
<td>24</td>
</tr>
<tr>
<td>59,27&amp;58,26</td>
<td>378 570.352</td>
<td>60</td>
<td>64</td>
</tr>
<tr>
<td>$25_{17-24,16}$</td>
<td>365 934.286</td>
<td>25</td>
<td>-14</td>
</tr>
<tr>
<td>$26_{17-25,16}^e$</td>
<td>372 289.805</td>
<td>30</td>
<td>-13</td>
</tr>
<tr>
<td>$27_{17-26,16}$</td>
<td>378 640.374</td>
<td>60</td>
<td>14</td>
</tr>
<tr>
<td>$28_{17-27,16}^e$</td>
<td>384 983.395</td>
<td>35</td>
<td>-43</td>
</tr>
<tr>
<td>$21_{21-20,20}$</td>
<td>390 432.268</td>
<td>35</td>
<td>11</td>
</tr>
<tr>
<td>$23_{21-22,19}$</td>
<td>390 688.250</td>
<td>50</td>
<td>-6</td>
</tr>
<tr>
<td>$25_{19-24,18}$</td>
<td>390 930.352</td>
<td>60</td>
<td>16</td>
</tr>
<tr>
<td>$27_{18-26,17}$</td>
<td>391 320.084</td>
<td>60</td>
<td>15</td>
</tr>
<tr>
<td>$29_{17-28,16}$</td>
<td>391 393.720</td>
<td>60</td>
<td>2</td>
</tr>
<tr>
<td>$30_{17-29,16}^e$</td>
<td>397 647.734</td>
<td>35</td>
<td>-3</td>
</tr>
<tr>
<td>$50_{34-50,33}$</td>
<td>416 906.320</td>
<td>50</td>
<td>-3</td>
</tr>
<tr>
<td>$20_{16-19,15}$</td>
<td>129 760.136</td>
<td>30</td>
<td>-11</td>
</tr>
<tr>
<td>$20_{15-19,14}$</td>
<td>130 305.469</td>
<td>30</td>
<td>-1</td>
</tr>
<tr>
<td>$23_{23-22,22}$</td>
<td>130 506.179</td>
<td>15</td>
<td>-5</td>
</tr>
<tr>
<td>$64_{27-63,27}$</td>
<td>411 099.802</td>
<td>40</td>
<td>26</td>
</tr>
<tr>
<td>$65_{33-64,33}$</td>
<td>415 640.462</td>
<td>80</td>
<td>-7</td>
</tr>
<tr>
<td>$73_{71-72,70}$</td>
<td>416 925.227</td>
<td>60</td>
<td>21</td>
</tr>
</tbody>
</table>

*1σ confidence level.

$^b$ $J'_K, J'_K - J''_K, J'_K, J'_K, K_c$ has been omitted for prolate and oblate paired transitions, respectively; for the oblate paired transitions $K_c$ is preceded by a comma. $F_1', F_1''$ quantum numbers are given in some instances; $F_1''$ quantum numbers belonging to the same $F_1'$ are separated by &; $F_1', F_1''$ is given by $F_1' - F_1'' = F_1' - F_1'' = J' - J''$.

$^c$ Quadrupole splitting; the quantum numbers $F_1, F$ have been omitted for clarity.
TABLE II. Number of rotational levels\(^a\) and range of \( J \) and \( K_a \) quantum numbers for \( a-\) and \( c-\) type transitions, respectively, used in the final fit of ClC\(_{102}\).

<table>
<thead>
<tr>
<th>(^{35})Cl(^{35})Cl(_{102})</th>
<th>(^{37})Cl(^{35})Cl(_{102})</th>
<th>(^{35})Cl(^{37})Cl(_{102})</th>
<th>(^{37})Cl(^{37})Cl(_{102})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(N_{\text{rot}})^(b)</td>
<td>39</td>
<td>13</td>
<td>19</td>
</tr>
<tr>
<td>(J_{\text{min}} - J_{\text{max}})</td>
<td>16-73</td>
<td>16-70</td>
<td>16-70</td>
</tr>
<tr>
<td>(K_a \text{min} - K_a \text{max})</td>
<td>0-33</td>
<td>0-23</td>
<td>0-28</td>
</tr>
<tr>
<td>(N_{\text{rot}} &lt; 40 \text{ GHz}^e)</td>
<td>25</td>
<td>18</td>
<td>20</td>
</tr>
<tr>
<td>(J_{\text{min}} - J_{\text{max}})</td>
<td>11-75</td>
<td>11-54</td>
<td>10-56</td>
</tr>
<tr>
<td>(K_a \text{min} - K_a \text{max})</td>
<td>2-27</td>
<td>2-18</td>
<td>2-16</td>
</tr>
<tr>
<td>(N_{\text{rot}} &gt; 129 \text{ GHz}^b)</td>
<td>74</td>
<td>35</td>
<td>40</td>
</tr>
<tr>
<td>(J_{\text{min}} - J_{\text{max}})</td>
<td>12-77</td>
<td>20-47</td>
<td>20-59</td>
</tr>
<tr>
<td>(K_a \text{min} - K_a \text{max})</td>
<td>0-34</td>
<td>1-31</td>
<td>2-32</td>
</tr>
</tbody>
</table>

\(^a\)Prolate paired or oblate paired transitions are only counted once.
\(^b\)Measured at the Jet Propulsion Laboratory.
\(^e\)Measured at the Universitat Tubingen.

TABLE III. Spectroscopic constants\(^a\) (MHz) of ClC\(_{102}\).

<table>
<thead>
<tr>
<th>(^{35})Cl(^{35})Cl(_{102})</th>
<th>(^{37})Cl(^{35})Cl(_{102})</th>
<th>(^{35})Cl(^{37})Cl(_{102})</th>
<th>(^{37})Cl(^{37})Cl(_{102})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A)</td>
<td>9450.92947 (61)</td>
<td>9449.8121 (61)</td>
<td>9414.6797 (50)</td>
</tr>
<tr>
<td>(B)</td>
<td>3588.057744 (272)</td>
<td>3469.59275 (106)</td>
<td>3565.08510 (98)</td>
</tr>
<tr>
<td>(C)</td>
<td>2787.937669 (289)</td>
<td>2715.95964 (74)</td>
<td>2777.26518 (42)</td>
</tr>
<tr>
<td>(\Delta J \cdot 10^3)</td>
<td>1.753777 (146)</td>
<td>1.66186 (44)</td>
<td>1.73369 (33)</td>
</tr>
<tr>
<td>(\Delta J_K \cdot 10^3)</td>
<td>6.50256 (50)</td>
<td>6.2261 (36)</td>
<td>6.4526 (27)</td>
</tr>
<tr>
<td>(\Delta K \cdot 10^3)</td>
<td>-1.20755 (139)</td>
<td>-0.8544 (81)</td>
<td>-1.2259 (66)</td>
</tr>
<tr>
<td>(\delta J \cdot 10^3)</td>
<td>0.384970 (81)</td>
<td>0.35494 (32)</td>
<td>0.375609 (195)</td>
</tr>
<tr>
<td>(\delta K \cdot 10^3)</td>
<td>6.13462 (80)</td>
<td>5.88751 (227)</td>
<td>6.0359 (210)</td>
</tr>
<tr>
<td>(\Phi_J \cdot 10^9)</td>
<td>0.121 (20)</td>
<td>-0.170 (69)</td>
<td>-0.134 (49)</td>
</tr>
<tr>
<td>(\Phi_{JK} \cdot 10^9)</td>
<td>9.18 (49)</td>
<td>9.79 (132)</td>
<td>11.12 (103)</td>
</tr>
<tr>
<td>(\Phi_{KJ} \cdot 10^9)</td>
<td>27.5 (17)</td>
<td>22.0 (47)</td>
<td>23.4 (38)</td>
</tr>
<tr>
<td>(\phi_{J9} \cdot 10^9)</td>
<td>25.9 (13)</td>
<td>-26.8 (55)</td>
<td>-18.3 (48)</td>
</tr>
<tr>
<td>(\phi_{JK} \cdot 10^9)</td>
<td>0.108 (11)</td>
<td>0.075 (49)</td>
<td>0.112 (29)</td>
</tr>
<tr>
<td>(\phi_{KJ} \cdot 10^9)</td>
<td>3.66 (24)</td>
<td>3.66 (56)</td>
<td>3.49 (45)</td>
</tr>
</tbody>
</table>

\(^a\)Numbers in parentheses are one standard deviation in units of the least significant figures. Watson's \(A\) reduction in the representation \(I'\) was used. \(\chi_{ii}\) and \(\chi_{ij}\) refer to the nuclear quadrupole coupling constants at the terminal and central Cl, respectively. Isotopic changes for the \(\chi_{ii}\) were calculated from a theoretical calculation, see Sec. IIIA.

\(^b\)Fixed according to Eq. (1); isotopic ratios have been taken into account for the quadrupole coupling constants, see Sec. IIIA.

\(^c\)Derived constant; isotopic ratio fixed, see Sec. IIIA.
TABLE IV. Transitions, frequencies (MHz), Stark field strengths $\mathcal{E}$ (V cm$^{-1}$), Stark shifts $\Delta \nu$ (kHz), and difference between observed and calculated Stark shifts (kHz) used for the redetermination of the dipole moment of FCIO$_2$.

<table>
<thead>
<tr>
<th>Transition</th>
<th>Frequency</th>
<th>Stark Coefficients</th>
<th>$\mathcal{E}^2$</th>
<th>$\Delta \nu$</th>
<th>obs-calc</th>
</tr>
</thead>
<tbody>
<tr>
<td>$22_{12,11} - 21_{11,11}$</td>
<td>386824.373</td>
<td>$C_a = -1.3204081 \cdot 10^{-10}$</td>
<td>0.1785 \cdot 10^4</td>
<td>-0.009</td>
<td>0.001</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$C_c = -1.9808196 \cdot 10^{-4}$</td>
<td>0.6151 \cdot 10^2</td>
<td>-0.029</td>
<td>0.004</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$C_L = -0.2510 \cdot 10^3$</td>
<td>-0.125</td>
<td>0.010</td>
<td></td>
</tr>
<tr>
<td>$22_{13,10} - 21_{12,10}$</td>
<td>385702.423</td>
<td>$C_a = -1.1979055 \cdot 10^{-8}$</td>
<td>0.3063 \cdot 10^4</td>
<td>-0.120</td>
<td>-0.015</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$C_c = -1.2675217 \cdot 10^{-5}$</td>
<td>0.3374 \cdot 10^4</td>
<td>-0.134</td>
<td>-0.018</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$C_L = 0.5938 \cdot 10^4$</td>
<td>-0.203</td>
<td>0.001</td>
<td></td>
</tr>
<tr>
<td>$21_{16,5} - 20_{15,5}$</td>
<td>375848.162</td>
<td>$C_a = 4.6349352 \cdot 10^{-5}$</td>
<td>0.2967 \cdot 10^4</td>
<td>0.046</td>
<td>0.007</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$C_c = 2.2963686 \cdot 10^{-9}$</td>
<td>0.5367 \cdot 10^4</td>
<td>0.076</td>
<td>0.005</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$C_L = 0.9315 \cdot 10^4$</td>
<td>0.123</td>
<td>0.000</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$C_L = 0.1359 \cdot 10^5$</td>
<td>0.172</td>
<td>-0.008</td>
<td></td>
</tr>
<tr>
<td>$21_{16,5} - 20_{15,5}$</td>
<td>*</td>
<td>$C_a = 0.3413 \cdot 10^4$</td>
<td>0.043</td>
<td>-0.002</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$C_c = 0.5908 \cdot 10^4$</td>
<td>0.082</td>
<td>0.004</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$C_L = 0.9315 \cdot 10^4$</td>
<td>0.134</td>
<td>0.011</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$C_L = 0.1356 \cdot 10^5$</td>
<td>0.183</td>
<td>0.004</td>
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</tr>
<tr>
<td>$21_{16,6} - 20_{15,6}$</td>
<td>376294.671</td>
<td>$C_a = -4.6355038 \cdot 10^{-5}$</td>
<td>0.2977 \cdot 10^4</td>
<td>-0.042</td>
<td>-0.003</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$C_c = -4.9685606 \cdot 10^{-9}$</td>
<td>0.5908 \cdot 10^4</td>
<td>-0.080</td>
<td>-0.002</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$C_L = 0.9813 \cdot 10^4$</td>
<td>-0.130</td>
<td>0.000</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$C_L = 0.1356 \cdot 10^5$</td>
<td>-0.170</td>
<td>0.009</td>
<td></td>
</tr>
<tr>
<td>$26_{16,11} - 25_{16,10}$</td>
<td>382448.751</td>
<td>$C_a = 1.5927958 \cdot 10^{-7}$</td>
<td>0.3420 \cdot 10^4</td>
<td>0.012</td>
<td>0.000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$C_c = 1.3155269 \cdot 10^{-5}$</td>
<td>0.5908 \cdot 10^4</td>
<td>0.023</td>
<td>0.002</td>
</tr>
<tr>
<td></td>
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<td>$C_L = 0.1361 \cdot 10^3$</td>
<td>0.062</td>
<td>0.003</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>$C_L = 0.2430 \cdot 10^5$</td>
<td>0.085</td>
<td>-0.003</td>
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<td></td>
<td></td>
<td>$C_L = 0.3817 \cdot 10^5$</td>
<td>0.124</td>
<td>-0.014</td>
<td></td>
</tr>
</tbody>
</table>

*Two independent experiments were done for this transition.*
TABLE V. Transitions, frequencies (MHz), Stark field strengths $\mathcal{E}$ (V cm$^{-1}$), Stark shifts $\Delta \nu$ (kHz), and difference between observed and calculated Stark shifts (kHz) used for the determination of the dipole moment of ClC102.

<table>
<thead>
<tr>
<th>Transition</th>
<th>Frequency</th>
<th>Stark Coefficients</th>
<th>$\mathcal{E}^2$</th>
<th>$\Delta \nu$</th>
<th>obs-calc</th>
</tr>
</thead>
<tbody>
<tr>
<td>$42_{11,31} - 41_{10,31}$</td>
<td>378053.085</td>
<td>$C_a = 0.431557 \cdot 10^{-6}$</td>
<td>0.2448 $\cdot 10^3$</td>
<td>0.005</td>
<td>-0.001</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$C_c = 0.607332 \cdot 10^{-7}$</td>
<td>0.9866 $\cdot 10^5$</td>
<td>0.023</td>
<td>0.001</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.1541 $\cdot 10^9$</td>
<td>0.031</td>
<td>-0.004</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.2214 $\cdot 10^9$</td>
<td>0.047</td>
<td>-0.003</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.3005 $\cdot 10^9$</td>
<td>0.067</td>
<td>-0.001</td>
</tr>
<tr>
<td>$41_{10,32} - 40_{9,32}$</td>
<td>379035.047</td>
<td>$C_a = -0.843449 \cdot 10^{-7}$</td>
<td>0.6120 $\cdot 10^4$</td>
<td>-0.009</td>
<td>-0.001</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$C_c = -0.599347 \cdot 10^{-6}$</td>
<td>0.2448 $\cdot 10^5$</td>
<td>-0.037</td>
<td>-0.003</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.5517 $\cdot 10^5$</td>
<td>0.074</td>
<td>0.002</td>
</tr>
<tr>
<td>$40_{11,30} - 39_{10,30}$</td>
<td>380100.604</td>
<td>$C_a = -0.130682 \cdot 10^{-5}$</td>
<td>0.2448 $\cdot 10^5$</td>
<td>-0.017</td>
<td>-0.007</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$C_c = -0.570495 \cdot 10^{-7}$</td>
<td>0.5517 $\cdot 10^5$</td>
<td>-0.025</td>
<td>-0.003</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.9841 $\cdot 10^5$</td>
<td>-0.046</td>
<td>-0.006</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.1539 $\cdot 10^9$</td>
<td>-0.067</td>
<td>-0.005</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.2214 $\cdot 10^9$</td>
<td>-0.097</td>
<td>-0.008</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.3007 $\cdot 10^9$</td>
<td>-0.127</td>
<td>-0.006</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.3912 $\cdot 10^9$</td>
<td>-0.156</td>
<td>0.001</td>
</tr>
<tr>
<td>$45_{10,35} - 44_{9,35}$</td>
<td>381180.576</td>
<td>$C_a = 0.154511 \cdot 10^{-7}$</td>
<td>0.9601 $\cdot 10^4$</td>
<td>0.008</td>
<td>0.000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$C_c = 0.379831 \cdot 10^{-6}$</td>
<td>0.3810 $\cdot 10^5$</td>
<td>0.031</td>
<td>-0.002</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.7540 $\cdot 10^5$</td>
<td>0.066</td>
<td>0.001</td>
</tr>
<tr>
<td>$38_{12,27} - 37_{11,27}$</td>
<td>381874.147</td>
<td>$C_a = -0.531763 \cdot 10^{-4}$</td>
<td>0.2391 $\cdot 10^4$</td>
<td>-0.029</td>
<td>-0.002</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$C_c = -0.410952 \cdot 10^{-6}$</td>
<td>0.6181 $\cdot 10^4$</td>
<td>-0.070</td>
<td>-0.001</td>
</tr>
<tr>
<td></td>
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<td></td>
<td>0.9601 $\cdot 10^4$</td>
<td>-0.102</td>
<td>0.005</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.1382 $\cdot 10^5$</td>
<td>-0.149</td>
<td>0.005</td>
</tr>
<tr>
<td>$40_{12,26} - 39_{11,26}$</td>
<td>391987.017</td>
<td>$C_a = 0.144187 \cdot 10^{-4}$</td>
<td>0.1589 $\cdot 10^4$</td>
<td>0.005</td>
<td>0.000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$C_c = 0.407061 \cdot 10^{-7}$</td>
<td>0.6181 $\cdot 10^4$</td>
<td>0.016</td>
<td>-0.003</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.9639 $\cdot 10^4$</td>
<td>0.033</td>
<td>0.003</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.1382 $\cdot 10^4$</td>
<td>0.044</td>
<td>0.001</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.2448 $\cdot 10^5$</td>
<td>0.072</td>
<td>-0.004</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.3817 $\cdot 10^5$</td>
<td>0.117</td>
<td>-0.002</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.4758 $\cdot 10^5$</td>
<td>0.150</td>
<td>0.003</td>
</tr>
<tr>
<td>$42_{10,33} - 41_{9,33}$</td>
<td>387263.823</td>
<td>$C_a = -0.515435 \cdot 10^{-7}$</td>
<td>0.4185 $\cdot 10^3$</td>
<td>-0.003</td>
<td>-0.002</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$C_c = -0.915059 \cdot 10^{-6}$</td>
<td>0.1598 $\cdot 10^4$</td>
<td>-0.007</td>
<td>-0.004</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.6212 $\cdot 10^4$</td>
<td>-0.016</td>
<td>-0.003</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.9678 $\cdot 10^4$</td>
<td>-0.020</td>
<td>0.000</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.1391 $\cdot 10^5$</td>
<td>-0.030</td>
<td>-0.001</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.3112 $\cdot 10^5$</td>
<td>-0.061</td>
<td>0.004</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.4755 $\cdot 10^5$</td>
<td>-0.096</td>
<td>0.003</td>
</tr>
<tr>
<td>parameter</td>
<td>$r_0$</td>
<td>$r_e$</td>
<td>matrix$^c$</td>
<td>$</td>
<td>\mu</td>
</tr>
<tr>
<td>--------------</td>
<td>-------</td>
<td>-------</td>
<td>------------</td>
<td>-------</td>
<td></td>
</tr>
<tr>
<td>$r$(ClCl)</td>
<td>219.66 (15)</td>
<td>219.87 (14)</td>
<td>219.21   222. (6)</td>
<td>1.570 (32)</td>
<td></td>
</tr>
<tr>
<td>$r$(ClO)</td>
<td>143.67 (8)</td>
<td>143.90 (7)</td>
<td>143.68   144.0 (5)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\ell$(ClClO)</td>
<td>104.14 (9)</td>
<td>104.02 (8)</td>
<td>104.02   103.5 (10)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\ell$(OCIO)</td>
<td>114.96 (10)</td>
<td>114.63 (9)</td>
<td>114.63   116.0 (5)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| $|\mu|$ | $ab	ext{ initio}^d$ | DFT$^d$ |
|-------|----------------------|--------|
|       | MP2$^*$               | MP2$^f$ | CCSD(T)$^g$ | B3LYP$^h$ |
| $r$(ClCl) | 245.9               | 226.9   | 227.9   | 224.5   |
| $r$(ClO)  | 146.9               | 144.2   | 146.8   | 145.1   |
| $\ell$(ClClO)| 104.2             | 103.8   | 104.1   | 104.4   |
| $\ell$(OCIO)| 116.7              | 115.0   | 114.9   | 114.4   |
| $|\mu|$ | 3.38                 | 2.20    | 1.79    | 1.73    |

$^a$This work. Numbers in parentheses are one standard deviation of the fits in units of the least significant figures.

$^b$Approximate equilibrium parameters derived from $r_2$; see Sec. III C for details.

$^c$Reference 5.

$^d$Equilibrium values.

$^e$Reference 2. Möller-Plesset calculation second order with 6-31G* basis set (double zeta type with one set of d polarization functions).

$^f$Reference 3. TZ2Pf basis set (triple zeta with two sets of d and one set of f polarization functions; see also previous footnote.)

$^g$Reference 3. Coupled cluster calculation with single, double, and perturbative treatment of triple excitations. TZ2P basis set; see also previous footnote.

$^h$References 37, 15. Becke's three-parameter hybrid functional with gradient-corrected correlation functional of Lee, Yang, and Parr. A 6-311+G(2df) basis set was used (triple zeta with one set each of diffuse s and p functions as well as two sets of d and one set of f polarization functions).
### TABLE VII. Harmonic force constants (N m⁻¹) of chloryl chloride, ClClO₂.

<table>
<thead>
<tr>
<th></th>
<th>exptl.</th>
<th>theoretical</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>this work</td>
<td>matrix²</td>
</tr>
<tr>
<td>( f_R )</td>
<td>119.4</td>
<td>124.6</td>
</tr>
<tr>
<td>( f_r )</td>
<td>852.1</td>
<td>816.7</td>
</tr>
<tr>
<td>( f_α )</td>
<td>120.6</td>
<td>117.5</td>
</tr>
<tr>
<td>( f_β )</td>
<td>190.3</td>
<td>170.2</td>
</tr>
<tr>
<td>( f_{Rr} )</td>
<td>-5.8</td>
<td>-13.5</td>
</tr>
<tr>
<td>( f_{Rα} )</td>
<td>1.2</td>
<td>-1.1</td>
</tr>
<tr>
<td>( f_{Rβ} )</td>
<td>-12.3</td>
<td>-4.2</td>
</tr>
<tr>
<td>( f_{rα} )</td>
<td>-26.3</td>
<td>-26.3</td>
</tr>
<tr>
<td>( f_{rβ} )</td>
<td>3.2</td>
<td>3.4</td>
</tr>
<tr>
<td>( f_{αα} )</td>
<td>-2.3</td>
<td>-10.1</td>
</tr>
<tr>
<td>( f_{αβ} )</td>
<td>12.3</td>
<td>5.7</td>
</tr>
<tr>
<td>( f_{αβ} )</td>
<td>45.1</td>
<td>41.2</td>
</tr>
<tr>
<td>( f_{αα} )</td>
<td>40.3</td>
<td>10.2</td>
</tr>
</tbody>
</table>

*aCalculated in internal coordinates \( R = r(\text{ClCl}) \), \( r = r(\text{ClO}) \), \( α = \zeta(\text{ClClO}) \), and \( β = \zeta(\text{OCIO}) \); for further details on the calculation of the force field can be found in Sec. III C.

*bSee footnotes in Table VI.

cReference 5.

dReference 3.

*eReference 3. A TZ2Pf basis set was used.

fReference 15.

### TABLE VIII. Structural parameters (pm, deg.) and diagonal force constants (N m⁻¹) of ClClO₂ and related molecules.

<table>
<thead>
<tr>
<th></th>
<th>FCIO₂*</th>
<th>ClClO₂b</th>
<th>OCIOc</th>
<th>FCId</th>
<th>ClCif</th>
</tr>
</thead>
<tbody>
<tr>
<td>( r_XC1 )</td>
<td>169.07</td>
<td>219.21</td>
<td>162.83</td>
<td>198.8</td>
<td></td>
</tr>
<tr>
<td>( r_C1 )</td>
<td>141.99</td>
<td>143.68</td>
<td>146.98</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( ζ(\text{XClO}) )</td>
<td>101.69</td>
<td>104.02</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( ζ(\text{OCIO}) )</td>
<td>115.03</td>
<td>114.63</td>
<td>117.40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( f_XC1 )</td>
<td>236.2</td>
<td>119.4</td>
<td>445.2</td>
<td>322.5</td>
<td></td>
</tr>
<tr>
<td>( f_C1 )</td>
<td>936.0</td>
<td>852.1</td>
<td>703.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( f_{XC1} )</td>
<td>156.4</td>
<td>120.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( f_{C1} )</td>
<td>205.2</td>
<td>190.3</td>
<td>140.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*aReferences 39, 20 for approximate \( r_e \) structure and force constants, respectively.

*bThis work; approximate \( r_e \) structure.

*cReference 18; \( r_e \) structure.

dReferences 40, 41; \( r_e \) structure.

*eReference 42; \( r_e \) structure.
### TABLE IX. Comparison of experimental spectroscopic constants (cm⁻¹, kHz) with those calculated from the force field.

<table>
<thead>
<tr>
<th></th>
<th>³⁵Cl³⁵ClO₂</th>
<th></th>
<th>³⁷Cl³⁵ClO₂</th>
<th></th>
<th>³⁵Cl³⁷ClO₂</th>
<th></th>
<th>³⁵Cl³⁵Cl¹⁸O₂</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>obs</td>
<td>calc</td>
<td>obs</td>
<td>calc</td>
<td>obs</td>
<td>calc</td>
<td>obs</td>
<td>calc</td>
</tr>
<tr>
<td>(Δ) ω₁</td>
<td>1062.84</td>
<td>1062.96</td>
<td>-</td>
<td>-0.07</td>
<td>-7.46</td>
<td>-7.15</td>
<td>-45.15</td>
<td>-45.23</td>
</tr>
<tr>
<td>(Δ) ω₂</td>
<td>527.73</td>
<td>526.01</td>
<td>-</td>
<td>-0.12</td>
<td>-4.08</td>
<td>-4.32</td>
<td>-20.54</td>
<td>-20.61</td>
</tr>
<tr>
<td>(Δ) ω₂</td>
<td>443.51</td>
<td>442.40</td>
<td>-1.15</td>
<td>-1.19</td>
<td>-7.10</td>
<td>-7.16</td>
<td>-7.84</td>
<td>-7.86</td>
</tr>
<tr>
<td>(Δ) ω₄</td>
<td>274.08</td>
<td>271.89</td>
<td>-4.28</td>
<td>-4.43</td>
<td>-</td>
<td>-0.44</td>
<td>-5.55</td>
<td>-5.60</td>
</tr>
<tr>
<td>(Δ) ω₅</td>
<td>1240.70</td>
<td>1240.98</td>
<td>-</td>
<td>-0.00</td>
<td>-13.39</td>
<td>-13.42</td>
<td>-42.31</td>
<td>-42.28</td>
</tr>
<tr>
<td>(Δ) ω₅</td>
<td>253.16</td>
<td>251.49</td>
<td>-1.25</td>
<td>-1.23</td>
<td>-0.78</td>
<td>-0.84</td>
<td>-10.14</td>
<td>-10.07</td>
</tr>
<tr>
<td>ΔJ</td>
<td>1.759</td>
<td>1.759</td>
<td>1.662</td>
<td>1.663</td>
<td>1.734</td>
<td>1.735</td>
<td>-</td>
<td>1.614</td>
</tr>
<tr>
<td>ΔK</td>
<td>-1.208</td>
<td>-1.219</td>
<td>-0.855</td>
<td>-0.560</td>
<td>-1.226</td>
<td>-1.246</td>
<td>-</td>
<td>-1.558</td>
</tr>
<tr>
<td>δJ</td>
<td>0.3850</td>
<td>0.3849</td>
<td>0.3549</td>
<td>0.3550</td>
<td>0.3756</td>
<td>0.3757</td>
<td>-</td>
<td>0.3800</td>
</tr>
<tr>
<td>δK</td>
<td>6.135</td>
<td>6.015</td>
<td>5.888</td>
<td>5.772</td>
<td>6.036</td>
<td>5.923</td>
<td>-</td>
<td>5.344</td>
</tr>
</tbody>
</table>

aω for ³⁵Cl³⁵ClO₂; Δωᵢ := ωᵢ(ClClO₂)−ωᵢ(³⁵Cl³⁵ClO₂) else; see also text. Vibrational data of ³⁷Cl³⁷ClO₂, ³⁷Cl³⁵Cl¹⁸O₂, and ³⁵Cl³⁷Cl¹⁸O₂ were also used in the calculation; the respective data have been omitted from the table because of little additional information.

### TABLE X. Dipole moment and dipole components (D) of ClClO₂ and related molecules.

<table>
<thead>
<tr>
<th></th>
<th>ClClO₂</th>
<th></th>
<th>FCIO₂</th>
<th>OCIO²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>exptl.¹</td>
<td>CCSD(T)²</td>
<td>B3LYP²</td>
<td>exptl.</td>
</tr>
<tr>
<td>μ</td>
<td>1.570</td>
<td>1.793</td>
<td>1.732</td>
<td>1.722</td>
</tr>
<tr>
<td>μ₆</td>
<td>0.457</td>
<td>0.691</td>
<td>0.598</td>
<td>0.551</td>
</tr>
<tr>
<td>μ₇</td>
<td>1.502</td>
<td>1.655</td>
<td>1.626</td>
<td>1.632</td>
</tr>
<tr>
<td>μₓCl</td>
<td>1.416</td>
<td>1.731</td>
<td>1.645</td>
<td>1.552</td>
</tr>
<tr>
<td>μ₀₂Cl²</td>
<td>1.564</td>
<td>1.695</td>
<td>1.687</td>
<td>1.539</td>
</tr>
</tbody>
</table>

¹Reference 19.
²Reference 43.
³This work.
⁴Reference 44. See also footnotes in Table VI.
⁵Reference 15. See also footnotes in Table VI.
TABLE XI. Quadrupole coupling constants\(^a\) (MHz) at the terminal Cl nucleus of ClClO\(_2\), angle \(\Theta_{za}\) between \(z\) - and \(\alpha\) -axes (deg.), and ionic and \(\pi\) characters of the ClCl bond.

<table>
<thead>
<tr>
<th></th>
<th>ClClO(_2)</th>
<th>HCl(^b)</th>
<th>B3LYP(^a)</th>
<th>ICl(^c)</th>
<th>exptl</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\chi_{aa})</td>
<td>-66.738 (162)</td>
<td>-62.416</td>
<td>-67.609</td>
<td>-85.84</td>
<td></td>
</tr>
<tr>
<td>(\chi_{bb})</td>
<td>37.671 (89)</td>
<td>34.247</td>
<td>28.169</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\chi_{cc})</td>
<td>29.067 (126)</td>
<td>28.169</td>
<td>18.124</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\chi_{ac})(^g)</td>
<td>17.340</td>
<td>29.972</td>
<td>18.124</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\chi_{zc})</td>
<td>-69.780</td>
<td>-75.342</td>
<td>-65.908</td>
<td>-85.84</td>
<td></td>
</tr>
<tr>
<td>(\chi_{xc})</td>
<td>32.109</td>
<td>37.671</td>
<td>31.661</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\chi_{xy})</td>
<td>37.671</td>
<td>34.247</td>
<td>34.247</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\eta_x)</td>
<td>0.0772</td>
<td>0.0</td>
<td>0.0392</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>(\Theta_{za})(^i)</td>
<td>9.95</td>
<td>16.02</td>
<td>10.90</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(i_e)</td>
<td>0.36</td>
<td>0.33</td>
<td>0.40</td>
<td>0.39</td>
<td>0.23</td>
</tr>
<tr>
<td>(\pi_e)</td>
<td>0.03</td>
<td>0.0</td>
<td>0.015</td>
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</tr>
</tbody>
</table>

\(^a\)\(v = 0, J = 0\).
\(^b\)Reference 45.
\(^c\)Reference 46.
\(^d\)This work; differences in column I and II are due to the different assumptions made when diagonalizing the quadrupole tensor.
\(^e\)Reference 15; see also footnotes in Table VI.
\(^f\)Assumed, see Sec. IV.C.
\(^g\)According to Reference 15, \(\text{sig}(\chi_{ac}^\alpha) = -\text{sig}(\chi_{ac}^\beta)\); see Table XII.

TABLE XII. Quadrupole coupling constants\(^a\) (MHz) at the central Cl nucleus of ClClO\(_2\) and angle \(\Theta_{zc}\) between \(z\)- and \(c\)-axes (deg.).

<table>
<thead>
<tr>
<th></th>
<th>ClClO(_2)</th>
<th>FCIO(_2)(^b)</th>
<th>B3LYP(^a)</th>
<th>OCIO(^c)</th>
<th>exptl</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\chi_{aa})</td>
<td>-19.322 (174)</td>
<td>-16.343</td>
<td>-34.901</td>
<td>32.516</td>
<td></td>
</tr>
<tr>
<td>(\chi_{bb})</td>
<td>-26.319 (93)</td>
<td>-24.519</td>
<td>-17.109</td>
<td>-51.842</td>
<td></td>
</tr>
<tr>
<td>(\chi_{cc})</td>
<td>45.641 (126)</td>
<td>40.862</td>
<td>52.009</td>
<td>19.326</td>
<td></td>
</tr>
<tr>
<td>(\chi_{ac})(^g)</td>
<td>5.87</td>
<td>5.168</td>
<td>18.10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\chi_{zc})(^g)</td>
<td>46.167</td>
<td>41.325</td>
<td>55.77</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\chi_{xc})(^g)</td>
<td>-19.848</td>
<td>-16.806</td>
<td>-38.66</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\chi_{xy})</td>
<td>-26.319</td>
<td>-24.519</td>
<td>-17.109</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\eta_x)(^g)</td>
<td>0.1402</td>
<td>0.1866</td>
<td>-0.3864</td>
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<td></td>
</tr>
<tr>
<td>(\Theta_{zc})(^h)</td>
<td>5.12</td>
<td>5.12</td>
<td>11.31</td>
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<td></td>
</tr>
</tbody>
</table>

\(^a\)\(v = 0, J = 0\).
\(^b\)Reference 20.
\(^c\)Reference 18; values adjusted so that OCIO lies in the ClO\(_2\) plane of ClClO\(_2\).
\(^d\)This work.
\(^e\)Reference 15; see also footnotes in Table VI.
\(^f\)According to Reference 15, \(\text{sig}(\chi_{ac}^\alpha) = -\text{sig}(\chi_{ac}^\beta)\); see Table XI.
\(^g\)Derived from \(\Theta_{zc}, \chi_{cc}, \) and \(\chi_{aa}\).
\(^h\)Taken from B3LYP calculation.