

Vibrational and Electronic Spectra of Chlorine Dioxide, OClO, and Chlorine Superoxide, ClOO, Isolated in Cryogenic Matrices

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Neon and argon matrix FTIR spectra of chlorine dioxide, OClO, in natural isotopic abundance and enriched in ^{18}O have been recorded. All fundamentals, and two overtones, as well as two combination bands have been observed for six isotopomers. Anharmonic constants, bond angles, and force constants have been calculated. The neon matrix data are very close to values from gas-phase studies, whereas the argon matrix data show more prominent deviations. Irradiation of matrix-isolated, monomeric OClO with visible light ($\lambda \geq 395\text{ nm}$) quantitatively converted it to the chlorine superoxide radical, ClOO. The ratio of IR and UV band intensities of both ClO₂ isomers was determined. All fundamentals, four overtones, and five combination bands were observed for eight isotopomers of ClOO. The Cl–OO stretching vibration ν_3 near 200 cm^{-1} has been observed for the first time, and the band near 390 cm^{-1} , previously assigned to ν_3 , has been shown to be due to $2\nu_3$. Anharmonic constants, harmonic wavenumbers, and force constants agree well with data from recent ab initio calculations and fit well in the series of related XEO molecules ($\text{X} = \text{F}, \text{Cl}; \text{E} = \text{C}, \text{N}, \text{O}$). The description of ν_2 and ν_3 respectively in terms of internal coordinates is discussed. Photolysis of a small fraction of matrix-isolated OClO van der Waals dimers resulted in ClOClO₃, ClOClO₂, and ClOClO as byproducts. IR spectroscopic evidence for this dimer was obtained from neon matrix experiments.

Introduction

For the ClO₂ species, two different connectivities are possible: symmetric (C_{2v}) chlorine dioxide, OClO, and asymmetric (C_s) chlorine superoxide, ClOO. Both are radicals because of their odd numbers of electrons. OClO has been known for nearly 200 years. It was prepared from sulfuric acid and potassium chlorate by R. Chevenix in 1802 and identified by H. Davy and F. von Stadion in 1815/16. It is the most widely used bleaching agent in the pulp, paper, textile, and food industries.¹ Its properties have been studied extensively, including microwave spectra of the ground² and excited vibrational states;³ high-resolution FTIR spectra;^{4–6} UV–vis spectra;^{7,8} photoelectron, VUV, and photoion mass spectra;⁹ X-ray diffraction of single crystals;¹⁰ and its photochemistry in the high-¹¹ and low-pressure regimes.¹² For further studies, cf. ref 13.

The chlorine superoxide radical, ClOO, was first postulated by Porter and Wright as an intermediate in the flash photolysis of Cl₂/O₂ mixtures to yield the observed ClO radical.¹⁴ Rochkind and Pimentel assigned bands at 1438 and 1428 cm^{-1} tentatively to the OO stretching vibration of ClOO during their investigations of the photochemistry of Cl₂O isolated in a N₂ matrix.¹⁵ The photochemistry of matrix-isolated OClO was studied in detail by Arkell and Schwager. They observed bands in an argon matrix at 1441 , 407 , and 373 cm^{-1} with ^{18}O counterparts, which they assigned to the OO stretching, deformation and ClO stretching vibration, respectively, of ClOO. They derived a force field which reproduced their observed wavenumbers satisfactorily.¹⁶ Because of its low stability, ClOO has rarely been studied in the gas phase. Kinetic,^{17–20} UV,^{17,19–21} and IR spectroscopic investigations¹⁷ have been reported.

Several ab initio calculations were performed on the electronic states,^{22–24} the structure,^{24–26} and the vibrational spectrum^{25,26} of ClOO. Some of them were focused on the photoisomerization of OClO in matrix and thus contained calculations on this species as well.^{22,24,26}

Although the heats of formation of OClO and ClOO are quite similar (97° and 98 kJ mol^{-1} ,^{19,26} respectively, at 298 K), their stabilities at ambient temperature are very different: pure gaseous OClO is stable at room temperature in the absence of light for days and shows no tendency to dimerize, whereas ClOO rapidly decomposes to Cl and O₂.^{17–20}

Both ClO₂ isomers play an important role in stratospheric chemistry. OClO is suggested to be the predominant product of the reaction of ClO with BrO, and it is thus an indicator for BrO chemistry.^{27,28} Several reactions could lead to ClOO;²⁸ for example, a catalytic cycle involving the dimerization of ClO, where ClOO is postulated to be the primary photolysis product of the dimer ClOOC₂, is suggested to play a main role in the destruction of polar stratospheric ozone.²⁹ However, ClOO has not yet been observed in the stratosphere directly.

Our interest in ClOO was roused by the paper of Gole,²² who discussed an assignment of metastable bands at 1415 and 435 cm^{-1} , measured by Arkell and Schwager,¹⁶ to ClOO in a long-lived excited electronic state, instead of ground-state ClOO in different matrix surroundings. In a very recent high-level ab initio calculation on the ClO₂ isomers,²⁶ it was suggested that the vibration previously assigned to ν_3 should be assigned to $2\nu_3$.

We decided to reinvestigate the spectroscopic properties of ClOO under improved experimental conditions to clarify these problems. Some novel data on the spectroscopy and photochemistry of OClO, obtained in the course of this study, are also included in this work.

Experimental Section

Chemicals. *Caution!* Although no explosion occurred during our studies, chlorine oxides are potentially explosive, especially in the presence of organic material. They should be handled only with proper safety precautions and in millimolar quantities.

OClO was synthesized from KClO₃, oxalic acid, and dilute sulfuric acid.³⁰ The preparation of ^{18}O -enriched OClO from ClF₃ and H₂¹⁸O is described in ref 31.

Cl₂ (99%, Merck) was purified by fractional condensation prior to use. Neon (99.999%, Linde) and argon (99.9999%, Messer-Griesheim) were used as matrix material without further purification.

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TABLE I: Vibrational Wavenumbers^a (cm⁻¹) of the Chlorine Dioxide Radical, OClO, Isolated in a Neon Matrix, Relative Band Strengths *I*,^b and Assignment^c

isotopomers of OClO						<i>I</i>	assignment
16/35/16	16/37/16	16/35/18	16/37/18	18/35/18	18/37/18		
2954.79	2931.56					0.025 }	$2\nu_1 + \nu_3$ (b_2)
2953.40	2930.16						
2204.07	2180.76					0.092 }	$2\nu_3$ (a_1)
2203.26	2179.95						
2035.86	2018.27	1998.92	1980.98	1960.42	1942.01	8.0 }	$\nu_1 + \nu_3$ (b_2)
2034.96	2017.37	1998.03	1980.09	1959.56	1941.14		
1881.07	1869.22	1836.75	1824.20	1801.73	1789.12	1.0 }	$2\nu_1$ (a_1)
1880.06	1868.22	1835.75	1822.22	1800.77			
1107.63	1095.84	1091.43	1079.54	1070.78	1058.55	100 }	$\nu_3 = \nu_{as}(\text{ClO}_2)$ (b_2)
1107.26	1095.45	1091.06	1079.15	1070.46	1058.18		
944.83	938.85	922.64	916.32	904.81	898.44	12 }	$\nu_1 = \nu_s(\text{ClO}_2)$ (a_1)
944.34	938.36	922.16	915.85	904.34	897.97		
448.70	445.84	439.0	436.2	429.13	426.36	14 }	$\nu_2 = \delta(\text{ClO}_2)$ (a_1)

^a Most intense component of each matrix pattern at higher wavenumber. Precision: see Experimental Section. ^b Cl^{16}O_2 isotopomers, $I(\nu_3) = 100$. ^c According to point group C_{2v} .

TABLE II: Vibrational Wavenumbers (cm⁻¹) of the Chlorine Dioxide Radical, OClO, Isolated in an Argon Matrix and Assignment^a

isotopomers of OClO						assignment
16/35/16	16/37/16	16/35/18	16/37/18	18/35/18	18/37/18	
2040.63	2023.13	2003.40	1985.67	1964.63	1946.27	$\nu_1 + \nu_3$
2037.20	2019.77	2000.03	1982.27	1961.33	1943.07	
2025.40	2007.90	1988.63	1970.77	1950.33	1923.03	
1888.6		1844.0		1808.8		$2\nu_1$
1885.9		1841.2		1806.0		
1873.7				1794.7		
1108.23	1096.60	1092.00	1080.20	1071.20	1059.03	ν_3
1106.50	1094.80	1090.23	1078.47	1069.47	1057.33	
		1084.97	1073.13			
1100.80	1089.07	1084.50	1072.67	1064.20	1052.00	ν_1
948.53	942.53	926.10	919.80	908.20	901.90	
947.13	941.1	924.73		906.90	900.63	
941.10	935.13		912.87			ν_2
			912.57	901.27	894.90	
451.50	448.57	441.70	438.83	431.8		
450.70	447.80	440.93	438.10	430.93	428.1	
		437.37	435.53			
447.07	444.20	436.87		427.67	424.83	

^a Cf. Table I.

Preparation of the Matrices. The vibrational spectrum of OClO isolated in an argon matrix was obtained from OClO observed as a byproduct in a previous study of ClClO_2 (cf. ref 31).

For the study of ClO_2 isomers isolated in neon matrices, OClO and neon were mixed (1:600) in a Duran glass vacuum line and transferred via a quartz glass capillary onto the cold (5 K) matrix support, which consisted of a copper block with two diamond-cut surfaces coated with aluminum. The constant spray-on rate (~ 10 mmol h⁻¹) was controlled with a needle valve, and cooling was achieved with a liquid helium continuous flow cryostat (Cryovac). Then, 0.15, 0.3, and 5 mmol of matrix containing OClO in natural isotopic abundance, as well as 0.25 and 7.5 mmol of matrix containing OClO with 80% enriched in ¹⁸O, were deposited.

For some argon matrix experiments, a different matrix assembly was used; 4 mmol of OClO/Ar 1:400 were deposited on a CsI plate within 1 h. The CsI plate was maintained at ~ 15 K by a closed-cycle helium refrigerator (cti-cryogenetics) surrounded by a liquid nitrogen-cooled radiation shield.

Instrumentation. Neon matrix IR spectra were recorded on a Bruker IFS 66v FT spectrometer in reflectance mode using a transfer optic (Bruker). A DTGS detector together with a KBr beam splitter operated in the region 5000–400 cm⁻¹. In this region, 64 scans were coadded for each spectrum using an apodized resolution of 0.35 cm⁻¹. A liquid helium-cooled Si bolometer (Infrared Laboratories) together with a 6- μm Mylar beam splitter

was used in the region 550–80 cm⁻¹. In this region, 256 scans were coadded for each spectrum using an apodized resolution of 0.25 cm⁻¹.

The precision of measured band positions quoted to 0.01 and 0.1 cm⁻¹ is 0.03 and 0.1 cm⁻¹, respectively. The uncertainty of relative band strengths is suggested to be between 10% for strong and 30% for very weak bands.

All other IR spectra in the course of this study were recorded on a FTIR spectrometer MX-1 (Nicolet) operating between 4800 and 400 cm⁻¹ in transmission mode.

UV spectra were recorded in reflection mode using a 1024 Diode Array spectrometer system with quartz glass fiber optics (Spectroscopy International) with a CLD 30-W deuterium lamp (Zeiss) as light source. Wavelengths were calibrated using a Hg pen-ray lamp (LOT); the spectral resolution was 0.4 nm.

Photolysis experiments were undertaken with a Hg medium-pressure lamp TQ 150 (Heraeus) combined with a water-cooled quartz lens optic (*f*-number: 1) and various cut-off filters (Schott).

Results and Discussion

(a) Vibrational Spectrum of Matrix-Isolated OClO. The band positions and their assignments of OClO isolated in neon and argon matrices are listed in Tables I and II, respectively. In an argon matrix, three (and four) bands of similar intensity accompanied by several weaker features are observed for each

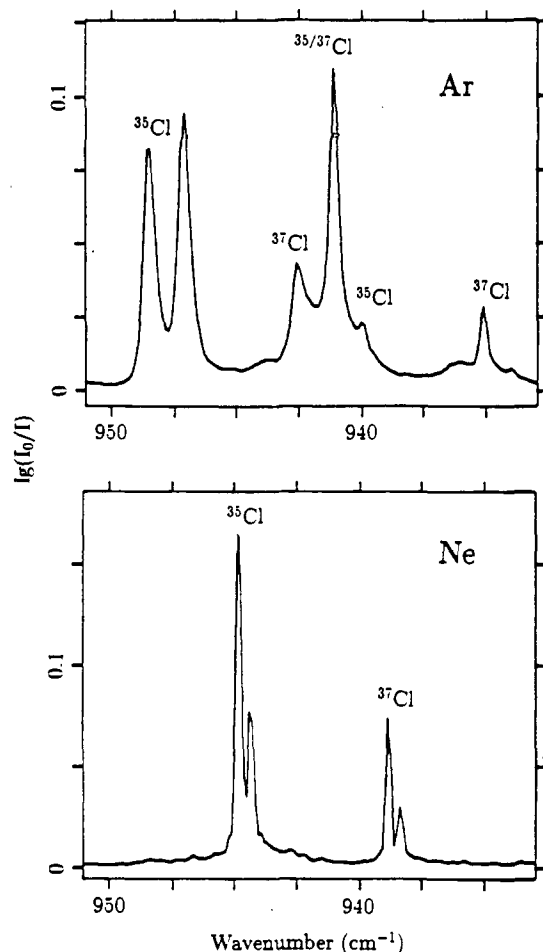


Figure 1. Infrared spectrum of the chlorine dioxide radical, OCIO (natural isotopic abundance), isolated in noble gas matrices in the region of ν_1 . Bands of the $^{35/37}\text{Cl}$ isotopomers are indicated.

TABLE III: Comparison of Observed Fundamental Vibrations, $^{35/37}\text{Cl}$ Isotopic Shifts, and Anharmonic Constants (cm^{-1}) of OCIO Isolated in a Neon Matrix and in the Gas Phase

constant	neon matrix ^a	gas phase ^b	gas phase ^c
ν_1	944.83	945.592	945.2
ν_2	448.70	447.702	447.3
ν_3	1107.63	1110.106	1110.8
$\Delta\nu_1$	5.98	5.990	5.8
$\Delta\nu_2$	2.86	2.878	3.3
$\Delta\nu_3$	11.79	11.859	12.7
x_{11}	-4.30	-4.335	-4.2
x_{12}		-3.993	-4.5
x_{13}	-16.60	-16.765	-15.0
x_{22}			-0.15
x_{23}			-2.4
x_{33}	-5.61		-6.75

^a This work. ^b References 4–6. ^c Reference 34.

vibration and each isotopomer. In contrast, only one strong band and a mostly weaker one at the low-wavenumber side were observed in a neon matrix (cf. Figure 1).

To our knowledge, ^{18}O shifts of OCIO have not been reported previously. IR spectra of OCIO in natural isotopic abundance isolated in argon matrices were reported in refs 32 and 33. Deviations of these wavenumbers from those in Table II are attributed to incomplete resolution of matrix and isotopic splittings as well as to the averaging of the observed matrix splittings.

The agreement between gas-phase and neon matrix data is excellent for band positions (deviation between 0.08% and 0.23%), isotopic shifts (0–0.6%), and anharmonic constants (<1%, cf. Table III).^{4–6} Nevertheless, nearly all of the small deviations are

significant. Results of a previous low-resolution gas-phase study show greater deviations due to the lower precision.³⁴ The combination band $2\nu_1 + \nu_3$ is observed 0.7 cm^{-1} lower than calculated from the fundamentals and anharmonic constants x_{ij} ; this might be indicative of contributions from higher order anharmonic constants.

The argon matrix data show more pronounced deviations from gas-phase values, and the OCIO species at distinct matrix sites are perturbed by the argon matrix in different ways: $\Delta\nu_3(^{35/37}\text{Cl}) = 11.63, 11.70, 11.73 \text{ cm}^{-1}$ and $x_{13} = -16.13, -16.43, -16.50 \text{ cm}^{-1}$ for the $^{16}\text{O}^{35}\text{Cl}^{16}\text{O}$ species which show absorptions of ν_3 at 1108.23, 1106.50, and 1100.80 cm^{-1} , respectively. Interestingly, the molecule which shows the absorption closest to gas-phase values exhibits the greatest deviation for the isotopic shift and the anharmonic constant x_{13} .

The absolute band strengths were measured for several vibrations of OCIO at 300 K,³⁵ and the derived relative values (9.0, 0.5, 100, 16.4, and 17.0 for $\nu_1 + \nu_3$, $2\nu_1$, ν_3 , ν_1 , and ν_2 , respectively) agree well with those from neon matrix (8.0, 1.0, 100, 12, and 14, respectively). Some deviations are attributed to uncertainties in both studies, whereas the contributions from the different temperatures and matrix perturbation cannot be quantified yet. No attempts were made to determine relative band strengths of OCIO isolated in an argon matrix, because uncertainties arising from matrix splittings would be more significant than any deviation due to different matrix surroundings.

(b) Bond Angles and General Valence Force Fields of Matrix-Isolated OCIO. The bond angle of OCIO was determined from microwave spectroscopy. Values of 117.6 and 117.4033 were obtained for β_0^{36} and β_e^{31} , respectively. In the following section, it is shown that the bond angle of matrix-isolated OCIO can be determined precisely and reliably from vibrational data.

The bond angle β_e of a bent XY_2 molecule with C_{2v} symmetry can be calculated using the product rule in the symmetry class b_2^{37}

$$\cos \beta_e = 1 + \frac{\mu'_y \omega_3^2 - \mu_y \omega'_3{}^2}{\mu'_x \omega_3^2 - \mu_x \omega'_3{}^2} \quad (1)$$

μ_x and μ_y denote the reduced mass of atom X and Y, respectively, for a given isotopic species, and ω_3 is the corresponding harmonic wavenumber of the asymmetric stretching vibration. A prime denotes the respective values for a different isotopic species. Neglecting anharmonic contributions, isotopic substitution of X and Y, respectively, usually (for $\omega_3 > \nu_3$) results in a lower and upper limit for β_e , respectively. With respect to the strongest component of OCIO isolated in a neon matrix, 114.29° and 122.43° respectively are obtained for the isotopic pairs $^{35/37}\text{Cl}^{16}\text{O}_2$ and $^{35}\text{Cl}^{16/18}\text{O}_2$.

Let δ_i be defined as $\omega_i = \nu_i (1 + \delta_i)$. Values of δ are mostly small and positive. According to ref 38, the isotopic shifts $\Delta\nu_i$ of the anharmonic fundamentals ν_i have to be scaled by $1 + \delta_i$ to account for anharmonic contributions in the calculation of structural parameters, unknown isotopic shifts, etc., using the product rule. Wavenumbers, corrected in this way, have to be scaled by $1 + \delta_i$ (according to the definition of δ_i) to obtain harmonic wavenumbers or at least a good approximation.

If values of δ_i are unknown, they might be estimated by comparison with related molecules. For OCIO, chlorine and oxygen isotopic shifts are known and thus might be used to calculate β_e and δ_3 simultaneously: going from $\delta_3 = 0$ to $\delta_3 = 0.1$ causes the calculated bond angle to be smaller and larger for the isotopic pairs $^{35/37}\text{Cl}^{16}\text{O}_2$ and $^{35}\text{Cl}^{16/18}\text{O}_2$, respectively. Taking $\delta_3 = 0.0212$, a value of $\beta_e = 117.30^\circ$ is obtained for both isotopic pairs as well as $\omega_3 = 1131.1 \text{ cm}^{-1}$ for $^{35}\text{Cl}^{16}\text{O}_2$. The error bars of 0.0019, 0.29°, and 2.1 cm^{-1} for δ_3 , β_e , and ω_3 , respectively, correspond to an uncertainty of 0.03 cm^{-1} of the isotopic shifts. Considering the uncertainties in our results and taking into account the lower precision of the data from ref 34 (cf. Table III), we find

TABLE IV: Internal Force Constants (10^2 N m^{-1}) of OCIO and Average Deviation Δ (cm^{-1}) between Observed and Calculated Wavenumbers from the Force Field^a

constant	I	II	III	IV	V
f_r	6.722	6.753	7.024	7.055	7.110
f_β	1.392	1.369	1.398	1.382	1.372
f_{rr}	-0.201	-0.178	-0.188	-0.193	-0.250
$f_{r\beta}$	-0.059	0.003	-0.005	0.018	-0.027
Δ	0.28	0.032	0.033		

^a Input data: Wavenumbers from neon matrix for models I–III; $\Delta\nu_1$ and $\Delta\nu_3$ scaled by 1.02, $\Delta\nu_2$ scaled by 1.01 for model II; ν_1 and $\Delta\nu_1$ scaled correspondingly for model III; ref 3, harmonic wavenumbers from gas phase for model IV; centrifugal distortion constants of the ground state from ref 5 for model V; r_0 , β_0 for models I and V, r_e , β_e elsewhere. See also text.

that deviations from neon matrix data are negligible: $\delta_3 = 0.020$ (derived from ref 34), $\beta_e = 117.4033^\circ$ (27)³, and $\omega_3 = 1133.0 \text{ cm}^{-1}$.³⁴

In an argon matrix, more prominent perturbations of the OCIO molecule are observed. Using the same isotopic pairs as above, $\delta_3 = 0.0243$, 0.0202 , and 0.0210 lead to $\beta_e = 115.61$, 116.15 , and 117.46° , and $\omega_3 = 1135.2$, 1128.9 , and 1123.9 cm^{-1} , respectively, for the $^{35}\text{Cl}^{16}\text{O}_2$ species which show absorptions of ν_3 at 1108.23 , 1106.50 , and 1100.80 cm^{-1} , respectively.

The influence of the matrix surroundings on the bond angle β was investigated previously for SO_2 and SeO_2 in neon,³⁹ SO_2 in krypton,⁴⁰ and O_3 in argon and krypton matrices.⁴¹ The respective values were calculated by averaging data from different isotopic pairs (neglecting anharmonic contributions). As in this study, it was observed that a matrix-isolated molecule is perturbed more strongly by the heavier noble gas matrix. It should be pointed out that uncertainties obtained by the method of refs 39–41 are larger than the observed perturbations.

General valence force constants were calculated with the program NORCOR⁴² using the fundamental wavenumbers of OCIO isolated in neon matrix (cf. Tables I and III), r_0 and β_0 ³⁶ (model I and V), and r_e and β_e ³ (models II–IV) as input data. Only isotopomers with C_{2v} symmetry were considered. Various harmonic corrections were employed (cf. Table IV). Included also are harmonic force constants; these were calculated from harmonic wavenumbers as well as structural parameters, centrifugal distortion constants, and Coriolis constants of $^{35/37}\text{Cl}^{16}\text{O}_2$ in the equilibrium state.³ Furthermore, a set of force constants was computed with the program NCA⁴² from r_0 , β_0 , and the centrifugal distortion constants of $^{35/37}\text{Cl}^{16}\text{O}_2$ in the ground vibrational state⁵ (model V).

Neglecting anharmonic contributions, a fair approximation of the harmonic force constants is obtained (model I). The diagonal force constants are too small, whereas the absolute values of the interaction force constants are too large. The measured wavenumbers are reproduced with deviations much larger than the experimental error of 0.03 cm^{-1} .

Scaling the isotopic shifts of $\Delta\nu_1$ and $\Delta\nu_3$ by 1.02 and of $\Delta\nu_2$ by 1.01 (derived from ref 34, model II) yields an improved set of force constants; however, the absolute value of each force constant is too small. A better result is obtained when the wavenumbers are also scaled correspondingly (model III). These values are very close to those of ref 3 (model IV). Both models reproduce the centrifugal distortion constants in the equilibrium state well (cf. Table V). Centrifugal distortion constants of the ground vibrational state differ significantly from those of the equilibrium state (cf. Table V); however, they also lead to a fair approximation of the harmonic force field (model V in Table IV). If both anharmonic wavenumbers and centrifugal distortion constants are used to calculate force constants, it should be taken into account that each set of constants leads to different deviations from the harmonic force field (cf. models I and V). The force constants of models III and IV might be improved further when

TABLE V: Comparison of Measured Centrifugal Distortion Constants of $^{16}\text{O}^{35}\text{Cl}^{16}\text{O}$ (kHz) with Those from Force Field Calculations^a

	measured		calculated for model		
	ground st. ^b	equil. ^c	I ^d	III ^d	IV ^e
Δ_N	8.7694	8.540	9.003	8.738	8.647
Δ_{NK}	-114.707	-114.09	-112.06	-110.96	-110.34
Δ_K	2053.31	1952.5	1956.9	1947.0	1964.5
δ_N	2.29897	2.2612	2.325	2.289	2.2695
δ_K	29.637	26.12	27.59	26.57	26.35

^a Cf. Table IV. ^b Reference 5. ^c Reference 3. ^d This work. ^e This work, calculated from force constants of ref 3.

more precise anharmonic constants and equilibrium centrifugal distortion constants are included in the fit.

(c) Vibrational Spectrum of ClOO Isolated in a Neon Matrix. Irradiation of OCIO isolated in a neon matrix with filtered light of a Hg medium-pressure lamp ($\lambda \geq 395 \text{ nm}$) caused its complete decomposition within 5 min. The bands near 1440 , 410 , and 390 cm^{-1} were observed in the mid-IR spectrum of ClOO (cf. Table VI), similar to the argon matrix study of Arkell and Schwager.¹⁶ Their isotopic shifts, as far as were measured, agree quite well with ours. In the far-IR region, absorptions near 200 cm^{-1} were present (cf. Figure 2), which showed the same pattern as the band at 390 cm^{-1} . Therefore, the latter must be assigned to $2\nu_3$ of ClOO, while the former one is due to the ν_3 fundamental. The bands near 1440 and 410 cm^{-1} are assigned to ν_1 and ν_2 , respectively, in accordance with ref 16. The fundamentals fit well in the series of related XEO molecules ($X = \text{F, Cl; E} = \text{C, N, O}$; cf. Table VII), and fair to excellent agreement exists for higher level ab initio calculations (cf. Table VIII). In addition, three more overtones, which exhibit similar patterns as the respective fundamentals, and five combination bands are observed for ClOO. Their assignments are straightforward, and the wavenumbers of the strongest component of each matrix pattern and isotopomer are listed in Table VI together with the relative band strengths. The complete set of band positions is given in the appendix. Figure 2 shows the IR spectrum of $\text{Cl}^{16}\text{O}^{16}\text{O}$ in the region of the fundamentals and the first overtones, while all other bands are presented in the appendix. (Unlabeled atoms always indicate both isotopes, $^{16/18}\text{O}$ or $^{35/37}\text{Cl}$.)

Despite the clear-cut assignment of nearly all bands, there are some details that must be pointed out. The strongest component of $\nu_2(^{37}\text{ClOO})$ nearly coincides with a weaker component of $^{35}\text{ClOO}$ (cf. Figure 2), resulting in an increased isotopic shift of 0.64 cm^{-1} . $^{35/37}\text{Cl}$ isotopic shifts of 0.60 cm^{-1} observed for all other matrix components are unadulterated, and this value is used for all calculations.

Strong anharmonic interaction (Fermi resonance) between ν_2 and $2\nu_3$ might be expected due to their small separation and their similar band strengths for $\text{Cl}^{16}\text{O}^{16}\text{O}$. However, the oxygen isotopic shifts suggest only a small perturbation of ν_2 by Fermi resonance, because the shifts $^{35}\text{Cl}^{16}\text{O}^{16}\text{O}/^{35}\text{Cl}^{16}\text{O}^{18}\text{O}$ (6.14 cm^{-1}) and $^{35}\text{Cl}^{18}\text{O}^{16}\text{O}/^{35}\text{Cl}^{18}\text{O}^{18}\text{O}$ (6.36 cm^{-1}) are very similar, despite great differences in the band separations from $2\nu_3$ (20 and 10 cm^{-1} , respectively). Thus, it seems very likely that, using the data available at present, any correction of the band positions of ν_2 and $2\nu_3$ due to Fermi resonance would be insignificant with respect to the error bars. It is noteworthy that the intensity ratio $2\nu_3:\nu_2$ decreases from $1:1.6$ to ca. $1:4.5$ for $\text{Cl}^{16}\text{O}^{16}\text{O}$ and $\text{Cl}^{18}\text{O}^{18}\text{O}$, respectively, although stronger perturbation is expected for the latter isotopomer. Furthermore, there is no indication that Fermi resonance is more prominent for any other pair of combination bands. Consequently, no correction of the measured data was undertaken for the subsequent calculations.

Bands of ^{18}O monosubstituted ClOO were assigned to $\text{Cl}^{18}\text{O}^{16}\text{O}$ and $\text{Cl}^{16}\text{O}^{18}\text{O}$ according to ab initio^{26,53,54} and force field calculations. The assignments are discussed in greater detail in section d.

TABLE VI: Vibrational Wavenumbers (cm⁻¹)^a of the Chlorine Superoxide Radical, ClOO, Isolated in a Neon Matrix, Relative Band Strengths I_i ^b and Assignment^c

isotopomers of ClOO								I	assignment
35/16/16	37/16/16	35/18/16	37/18/16	35/16/18	37/16/18	35/18/18	37/18/18		
4177.5								0.17	3ν ₁
3036.91	3034.17							0.33	2ν ₁ + ν ₃
2832.56		2758.75		2753.58		2677.49		3.1	2ν ₁
1834.3								0.05	ν ₁ + 2ν ₃
1641.32	1638.76					1555.33	1552.69	0.53	ν ₁ + ν ₃
1438.56		1400.02		1397.98		1358.19		100	ν ₁ = ν(OO)
809.93	808.7					768.7	767.5	0.22	2ν ₂
784.8	780.2							0.13	ν ₂ + 2ν ₃
604.03	601.23					577.81	574.7	2.1	ν ₂ + ν ₃
413.73	413.09 ^d	398.62	397.99 ^d	407.59	406.96 ^d	392.19	391.54 ^d	2.7	ν ₂ = δ
394.29	389.70					383.60	378.88	1.7	2ν ₃
201.38	198.92	199.1 ^e		197.78		195.83	193.25	4.0	ν ₃ = ν(Cl-OO)

^a Most intense component of matrix pattern. Precision: see Experimental Section. ^b Cl¹⁶O¹⁶O isotopomers, see text; $I(\nu_1) = 100$. ^c In the point group C₂; for the description of modes, see force field section. ^d Overlap with a matrix component of ³⁵ClOO, see text. ^e Overlap with a matrix component of ³⁵Cl¹⁸O¹⁸O.

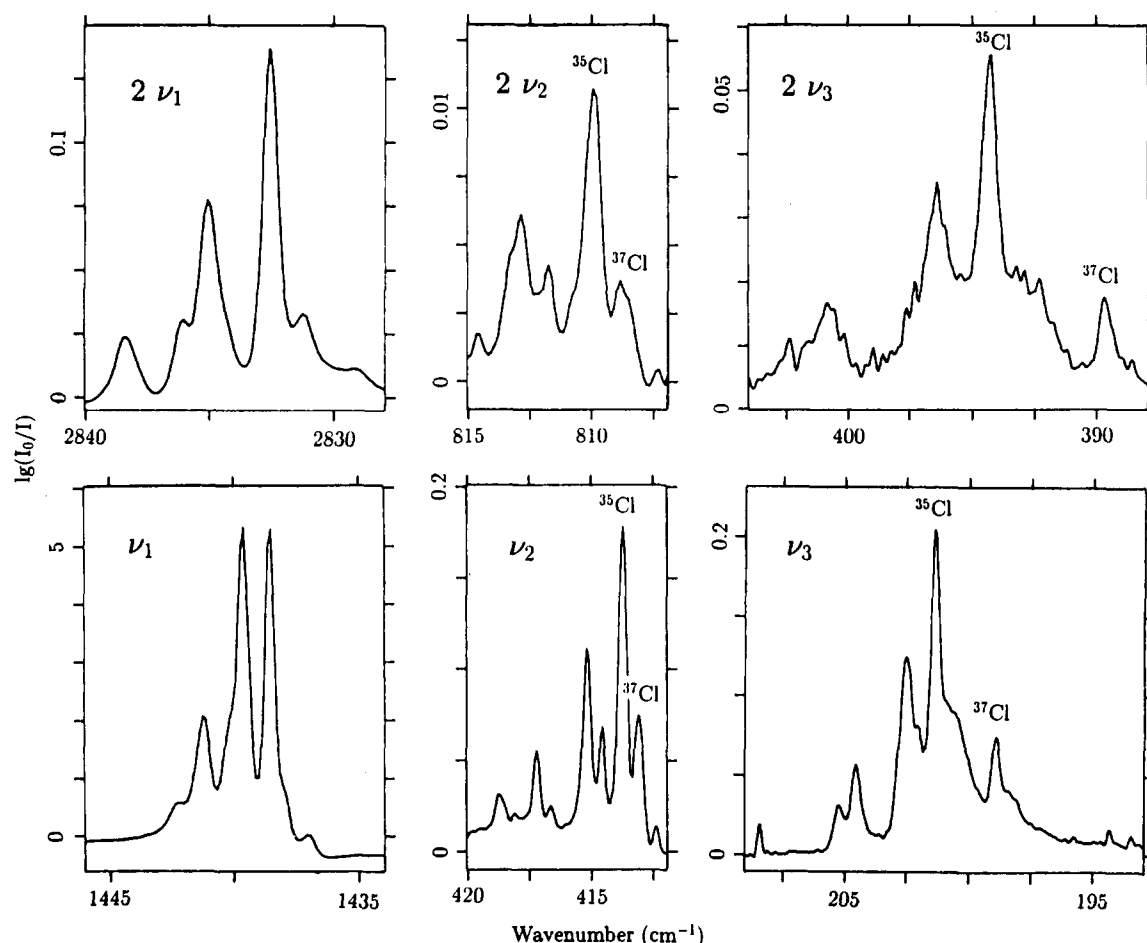


Figure 2. Infrared spectrum of the chlorine superoxide radical, ClOO (natural isotopic abundance), isolated in a neon matrix in the regions of the fundamentals and the first overtones. The most prominent band of each ³⁵/³⁷Cl isotopomer is indicated. Note the different absorbance scaling; the region of ν₁ was taken from another experiment with a smaller amount of matrix and scaled via the integrated absorbance of 2ν₁ in both experiments.

The ³⁵/³⁷Cl shifts increase from ν₃ (2.46 cm⁻¹) to 2ν₁ + ν₃ (2.74 cm⁻¹). This increase may be attributed to the ³⁵/³⁷Cl shift of ν₁, which was not observed directly. However, according to the force field calculation, this shift is only ~0.02 cm⁻¹ (Table XI); thus, a more important contribution may arise from differences in the matrix splittings or higher order anharmonic effects.

Anharmonic constants x_{ij} were calculated from the vibrations ν_i + ν_j⁵⁵ and are presented in Table IX together with values from ab initio calculations.²⁶ Values of x_{ij} calculated from combinations higher than ν_i + ν_j are slightly smaller (more negative), indicative of higher order anharmonic contributions. The agreement between experimental and calculated constants is good to excellent;

the average deviation (the sign of the difference was considered) is -1.4 cm⁻¹. No combination was observed involving ν₁ and ν₂; therefore, the ab initio value corrected by the average deviation was used as a rough estimate. Due to Fermi resonances (see above), experimental values of x₂₃ and x₃₃ are suggested to be upper and lower limits respectively, whereas x₂₂ presumably is unperturbed.

The resulting harmonic wavenumbers of ³⁵Cl¹⁶O¹⁶O are presented in Tables VII and VIII. For all other isotopomers, only a less complete set of anharmonic constants could be derived from overtones and combination bands. Therefore, the ratios ω_i/ν_i of ³⁵Cl¹⁶O¹⁶O were used to determine harmonic wavenumbers

TABLE VII: Harmonic and Anharmonic Fundamental Wavenumbers^a (cm⁻¹), Force Constants^b (10² N m⁻¹), and Structural Parameters^c (pm, deg) of XEO Compounds (X = -, F, Cl; E = C, N, O)

constant	CO ^d	NO ^d	OO ^d
ω/ν	2169.8/2143.3	1904.4/1876.1	1580.2/1556.4
f_R/R	19.019/112.83	15.955/115.08	11.766/120.75
	FCO ^e	FNO ^f	FOO ^g
$\omega_1/\nu_1 = \nu(\text{EO})$	/1861.6	1878.8/1843.5	/1488.9
$\omega_2/\nu_2 = \nu(\text{FE})/\delta$	/1026.1	775.5/765.8	/579.3
$\omega_3/\nu_3 = \delta/\nu(\text{F-EO})$	/627.5	522.9/519.9	/370.6
f_R/R	14.364/116.9	15.912/113.16	10.500/120
f_r/r	4.869/133.4	2.133/151.66	1.320/165
f_α/α	1.384/127.3	1.841/109.92	1.008/111.2
f_{Rr}	1.305/	1.902/	0.300/
f_{Ra}	0.380/	0.323/	0/
f_{ra}	0.286/	0.236/	0.027/
	CICO ^h	CINO ⁱ	CIOO ^j
$\omega_1/\nu_1 = \nu(\text{EO})$	/1876.7	1835.6/1799.7	1477.8/1438.6
$\omega_2/\nu_2 = \delta$	/570.1	603.2/595.9	432.4/413.7
$\omega_3/\nu_3 = \nu(\text{Cl-EO})$	/334.6	336.4/332.0	214.8/201.4
f_R/R	14.964/115.9	15.424/113.57	10.599/120.1
f_r/r	1.173/180.7	1.254/197.26	0.509/213.9
f_α/α	0.944/129.2	1.299/113.40	0.810/115.7
f_{Rr}	1.413/	1.440/	0.604/
f_{Ra}	0.026/	0.417/	0.294/
f_{ra}	0.122/	0.151/	0.032/

^a For the main isotopic species; for description of modes, see text. m_a : argon matrix. m_n : neon matrix. Gas-phase values elsewhere. ^b $R = r(\text{EO})$, $r = r(\text{ClE})$, $\alpha = \angle(\text{ClEO})$. ^c a, anharmonic; (a), partial harmonic correction; h, harmonic values. ^d e, r_e values; i, from ab initio calculations; r_0 values elsewhere. ^e Reference 43 (h, e). ^f Reference 44 (ν_3 : m_a , a). ^g Reference 45 (h, e); except wavenumbers from ref 46. ^h Wavenumbers from ref 47, ν_3 calculated from combination bands; force constants from ref 48; approximate r values from ref 49. See also text. ⁱ Reference 50 (m_a , (a), i); see also text. ^j Reference 51 (h, e); except harmonic wavenumbers from ref 52. ^k This work (m_n , h, i: ref 26); see text.

TABLE VIII: Comparison of Experimental Harmonic Wavenumbers (cm⁻¹), Equilibrium Structural Parameters (pm, deg), and Harmonic Force Constants (10² N m⁻¹) of ClOO with Values from ab Initio Calculations

constant ^a	exptl ^b	ab initio		
		CMRCI (3d 2f) ^c	AUMP2 6-31G* ^{d,e}	UCCSD 6-31G* ^e
ω_1	1477.8	1538.3	1836	1318.5
ω_2	432.4	403.2	467	537.9
ω_3	214.9	193.6	194	268.5
R	213.9	213.9	218.1	192.3
r	120.1	120.1	117.4	124.7
α	115.7	115.7	118.6	114.1
f_R	10.599	11.296	16.411	8.785
f_r	0.509	0.419	0.552	0.909
f_α	0.810	0.692	0.760	1.367
f_{Rr}	0.604	0.416	1.033	1.402
f_{Ra}	0.294	0.151	0.325	0.336
f_{ra}	0.032	0.002	-0.109	0.038

^a $R = r(\text{OO})$, $r = r(\text{ClO})$, $\alpha = \angle(\text{ClOO})$; deformation force constants normalized to 100-pm bond lengths. ^b This work; geometric parameters taken from ref 26, consistent with experimental data, see section d. ^c References 26, 53; for detailed description of basis set, see ref 26. ^d Reference 25. ^e Reference 54.

for all other isotopomers (cf. section b). Since anharmonic contributions to the vibrations of ClOO are relatively large, this procedure might be an additional source of small errors.

Suggesting monomeric OCIO to be completely converted into ClOO, the ratio of the strongest bands of both ClO₂ isomers was determined to be 5:4 ($\nu_1(\text{ClOO})/\nu_3(\text{OCIO})$).

(d) **Structure and General Valence Force Field of ClOO.** A reliable estimate of the structural parameters of ClOO can be obtained from ab initio calculations of ClOO.^{25,26} They can also

TABLE IX: Comparison of Experimental and ab Initio Anharmonic Constants of ³⁵Cl¹⁶O¹⁶O (cm⁻¹)

	experimental ^a	ab initio ^b
x_{11}	-22.2	-20.2
x_{12}	9 ^c	10.4
x_{13}	1.4	4.87
x_{22}	-8.8	-5.67
x_{23}	-11.1	-12.5
x_{33}	-4.3	-4.28

^a This work. ^b Reference 26. ^c Derived from ref 26; see section d.

TABLE X: Force Constants^a (10² N m⁻¹) and Potential Energy Distribution (PED)^b of ClOO

	force constants		PED		
	model I ^c	model II ^c	ν_1	ν_2	ν_3
f_R	10.599	10.087	1.03		0.05
f_r	0.509	0.487		0.18	0.89
f_α	0.810	0.833		0.86	0.15
f_{Rr}	0.604	0.031			-0.11
f_{Ra}	0.294	-0.311			
f_{ra}	0.032	0.030		-0.04	0.04

^a For definition of internal coordinates cf. Table VIII. ^b For model I, see section d. Only contributions ≥ 0.03 are presented. ^c $\nu_1(\text{Cl}^{16}\text{O}^{18}\text{O})$ ($\nu_1(\text{Cl}^{18}\text{O}^{16}\text{O})$) for model I and model II, respectively; see section d.

TABLE XI: Comparison of Measured^a Isotopic Shifts $\Delta\nu^b$ (cm⁻¹) with Those from Experimental Force Field Calculations^c

	$\Delta\nu(\text{Cl})$		$\Delta\nu(\text{O}_C)$		$\Delta\nu(\text{O}_T)$	
	obsd	calcd	obsd	calcd	obsd	calcd
ν_1	0	0.02	40.67	40.63	42.82	42.72
ν_2	0.66	0.65	16.50	16.42	6.71	6.60
ν_3	2.80	2.75	2.59	2.77	4.10	4.00

^a Including anharmonic correction, see force field section. ^b $\Delta\nu(\text{Cl}) = \nu(^{35}\text{Cl}^{16}\text{O}^{16}\text{O}) - \nu(^{37}\text{Cl}^{16}\text{O}^{16}\text{O})$, $\Delta\nu(\text{O}_C) = \nu(^{35}\text{Cl}^{16}\text{O}^{16}\text{O}) - \nu(^{35}\text{Cl}^{18}\text{O}^{16}\text{O})$, $\Delta\nu(\text{O}_T) = \nu(^{35}\text{Cl}^{16}\text{O}^{16}\text{O}) - \nu(^{35}\text{Cl}^{16}\text{O}^{18}\text{O})$. ^c Model I, cf. Table IX.

be deduced from harmonic wavenumbers of various isotopomers of ClOO. Unfortunately, not all of the data are known with sufficient precision (e.g., uncertainties of 0.03 cm⁻¹ in the isotopic shifts add up to an uncertainty of ca. 6 pm for the ClO bond length). However, ab initio structural parameters of ref 26 are compatible with our results with some small deviation for isotopic pairs involving ¹⁶O¹⁸O mixed isotopomers.

The ab initio structural parameters²⁶ of ClOO together with the harmonic wavenumbers were taken as input data to calculate a general valence force field with the program NORCOR⁴² (model I, cf. Table X). An alternate set of force constants was obtained when the assignments of $\nu_1(\text{Cl}^{18}\text{O}^{16}\text{O})$ and $\nu_1(\text{Cl}^{16}\text{O}^{18}\text{O})$ were exchanged (model II). Both models reproduced the experimental harmonic wavenumbers well with average deviations of ca. 0.06 and 0.07 cm⁻¹ for models I and II, respectively (Table XI). The force constants of both models show significant differences, but the potential energy distribution and the Cartesian displacement of the normal coordinates are very similar. Force constants of model I agree better with those of related compounds (cf. Table VII) and ab initio calculations (cf. Table VIII).

At present, model I is the preferred one. A knowledge of the rotational spectrum of ClOO would not only permit an improvement of its geometrical parameters, but it also could help to distinguish between models I and II via the centrifugal distortion constants. Their values (kHz) for model I (model II in parentheses) are: $D_N = 8.84$ (9.03), $D_{NK} = -69.5$ (-33.8), $D_K = 5334$ (4826), $R_5 = -6.10$ (-6.97), and $R_6 = -0.016$ (-0.015). The greatest deviation is observed for D_{NK} . This constant is almost the same as Δ_{NK} of Watson's A reduction. Comparison with

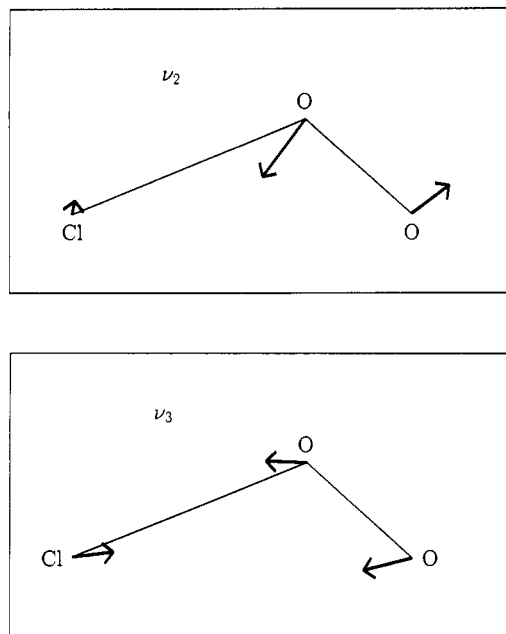


Figure 3. Cartesian displacement of the normal coordinates of ν_2 and ν_3 of ClOO. The vectors are lengthened for clarity.

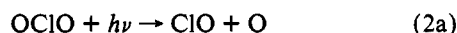
experimental values of Δ_{JK} or Δ_{NK} of FNO (−35.34),⁴⁵ FOO (−159.33),⁶⁰ and ClNO (−61.08)⁵¹ further support the preference of model I.

The ClO stretching force constant of ClOO is unusually small, about 85% smaller than that for a common ClO single bond (367 and 295 N m^{−1} for HOCl⁵⁶ and Cl₂O,⁵⁷ respectively). This parallels the very long ClO bond length, which, according to ab initio calculations,^{25,26} is about 25% longer than that of HOCl and Cl₂O, 168.9⁵⁸ and 169.6 pm,⁵⁷ respectively. For most of the XEO molecules, the XE stretching force constant is small, and the XE distance is large (cf. Table VII). It is noteworthy that for ClOO the ClO force constant is significantly smaller than the bending force constant, while for FCO it is opposite.

Despite the larger ¹⁶/¹⁸O shift of the terminal O atom ν_3 exhibits predominantly ClO stretching character. Taking into account the Cartesian displacement of the normal coordinate, ν_3 is a vibration of the Cl atom against the rest of the molecule (cf. Figure 3). This can be denoted as $\nu_3 = \nu(\text{Cl-OO})$. A similar situation occurred for ν_4 in ClClO₂.³¹ The vibration ν_2 is well described as a deformation mode (cf. Figure 3).

Considering the published force fields of XEO molecules (cf. Table VII), Cartesian displacements of the modes ν_2 and ν_3 of FNO, ClNO, and ClCO are very similar to ν_2 and ν_3 , respectively, of ClOO.⁵⁹ In ref 50, the assignments for ν_2 and ν_3 of ClCO were erroneously exchanged. For O₂F, the situation is slightly different; ν_2 and ν_3 both have ca. 50% bending and OF stretching character, respectively.^{48,59} It should be pointed out that the force constants of ref 49 fit neither the isotopic shifts⁴⁸ nor the more recently determined centrifugal distortion constants,⁶⁰ whereas those of ref 48 fit both sets of data quite well. Accordingly, force constants of ref 48 are presented in Table VII. The vibrations ν_2 and ν_3 of FCO show greater deviations: while ν_2 predominantly exhibits FC stretching character, ν_3 is well described as a bending mode.^{44,59}

(e) Isomerization of OCIO. The threshold for photodissociation of OCIO in the gas phase into O + ClO is 488 nm,⁶¹ and these are the predominant primary products of OCIO in the first electronic excited state.¹² Thus, the photoisomerization of matrix-isolated OCIO might proceed via the following reaction scheme:



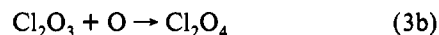
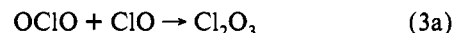
After photofragmentation of OCIO, the fragments recombine in

the matrix cage, and the excess energy is distributed in the phonon bath of the matrix. In the gas phase, no such stabilization of ClOO is possible, and Cl + O₂ would be formed because of the small Cl–OO dissociation energy (ca. 10–20 kJ mol^{−1}).²⁶ The formation of ClOO from matrix-isolated OCIO alternatively might proceed as an intramolecular rearrangement. According to ab initio calculations, low-lying electronic states ²A₁ and ²B₂, close to the ²A₂ state of OCIO, may be involved in these processes^{22,24,26} (additional calculations in this field are in progress⁶²). ClOO isolated in a neon matrix was completely decomposed within five minutes by irradiation of a Hg medium-pressure lamp using no filter. Cl + O₂ are the most likely products. Thus, at shorter wavelengths also the ClOO radical is excited sufficiently that after bond cleavage the Cl atom can escape from the matrix cage.

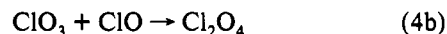
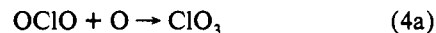
Besides ClOO, Cl₂O₄ was observed as a main byproduct from the photolysis of matrix-isolated OCIO with bands at 1293.2, 1277.6, 1040.2, 747.5, 652.1, 586.9, 565.3, and 514.6 cm^{−1} for the ³⁵Cl₂¹⁶O₄ isotopomer in a neon matrix.⁶³ Cl₂O₃ (ca. 1216.0, 1203.1, and 1060 cm^{−1}) and ClOCIO (ca. 997.5 and 989.1 cm^{−1}) were close to the limit of detection in a neon matrix but were clearly observable in an argon matrix with bands at 1226.8, 1213.5, 1200.7, 1060.5, and 1057 cm^{−1} for Cl₂O₃^{11,64} and those at 994.4 and 985.7 cm^{−1} for ClOCIO.⁶⁵ Bands of ClClO₂ around 1210 and 1035 cm^{−1} might coincide with those of Cl₂O₃ and be hidden by those of Cl₂O₄, respectively. Most of these absorptions were also present in the spectra of Arkell and Schwager, but the products could not be identified.¹⁶

An OCIO-OCIO van der Waals dimer is suggested to be the precursor of these byproducts. Three groups of bands (931.56, 930.70, 930.19, 928.00, 927.19, 926.69; and 925.44, 924.64, 924.07 cm^{−1}) in a neon matrix, close to $\nu_1(\text{OCIO})$ and exhibiting an approximate intensity ratio of 9:6:1 indicative for two equivalent Cl atoms, are most likely due to this dimer. In addition, bands assignable to the isotopomer containing only ³⁵Cl and ¹⁸O were observed at 892.25, 891.34, and 890.38 cm^{−1}. In the region of $\nu_3(\text{OCIO})$ absorption, features at 1104.14, 1102.76 and at 1197.99, 1197.13 cm^{−1} could be due to the OCIO dimer, but at present it is difficult to distinguish between very weak matrix splittings and bands due to the van der Waals dimer. No such feature was observed in the vicinity of $\nu_2(\text{OCIO})$. The formation of van der Waals dimers causes solid OCIO to be diamagnetic at low temperatures.¹⁰ For a valence bond study of the OCIO van der Waals dimer, cf. ref 66.

Several reaction schemes were discussed to describe the photochemical formation of Cl₂O₄ from gaseous OCIO at higher partial pressures. According to ref 11, the first step is the dissociation of OCIO to ClO + O with



or



being the subsequent steps. The formation of Cl₂O₄ due to the reaction of electronically excited OCIO with another OCIO molecule was excluded. Temperature-dependent investigations yielded indirect evidence for the formation of ClO₃;⁶⁷ thus, scheme 4 is at present the favored one. It is suggested that the formation of Cl₂O₄ in matrix proceeds analogously.

The formation of Cl₂O₃ affords escape of an O atom from the matrix cage. Formation of O₂ from OCIO-OCIO would favor formation of ClOCIO.

TABLE XII: Vibrational Wavenumbers (cm⁻¹) of the Chlorine Superoxide Radical, ClOO, Isolated in a Neon Matrix and Assignment^a

isotopomers								assignment
35/16/16	37/16/16	35/18/16	37/18/16	35/16/18	37/16/18	35/18/18	37/18/18	
4181.7								} 3ν ₁
4177.5								
3042.2								} 2ν ₁ + ν ₃
3040.34								
3036.91	3034.17							
2838.37		2764.31				2682.86		} 2ν ₁
2836.06		2762.09				2680.73		
2835.06		2761.13		2756.06		2679.46		
2832.56		2758.75		2753.58		2677.49		
2831.23				2752.60		2676.26		
2829.18						2674.41		
1836.3	1831.4?							} ν ₁ + 2ν ₃
1834.3								
1833.5								
1643.52						1557.4		} ν ₁ + ν ₃
1641.32	1638.76					1555.33	1552.69	
1442.25								} ν ₁ = ν(OO)
1441.24						1360.76		
1440.1						1359.7		
1439.63		1401.06		1399.04		1359.24		
1438.56		1400.02		1397.98		1358.19		
1437.9						1357.76		
1437.05						1356.82		} 2ν ₂
812.9	811.77					771.6	770.5	
809.93	808.7					768.7	767.5	
788.3								} ν ₂ + 2ν ₃
784.8	780.2							
614.0								} ν ₂ + ν ₃
611.21								
606.57						580.29		
604.03	601.23					577.81	574.7	
418.72	418.11					396.92		} ν ₂ = δ
417.20	416.64	401.85		411.14		395.47	394.87	
415.16	414.56	399.96	399.37	409.09	409.49	393.57	392.96	
413.73	413.09	398.62	397.99	407.59	406.96	392.19	391.54	
396.4								} 2ν ₃
394.29	389.70					383.60	378.88	
205.23								} ν ₃ + ν(Cl-OO)
204.52						198.85		
202.52						196.82		
201.38	198.92	199.1		197.78		195.83	193.25	

^a Cf. Table VI; the most prominent bands of each vibration and isotopomer are printed bold.

Additionally, the nature of various bands observed for each isotopomer and each vibration of ClOO will be discussed in this section. Arkell and Schwager observed bands at 1441, 407, and 373 cm⁻¹ for ³⁵Cl¹⁶O¹⁶O isolated in an argon matrix.¹⁶ The absorption at 1441 cm⁻¹ was accompanied by weaker features to the lower wavenumber side, the strongest one being at 1438 cm⁻¹. Absorptions at 1415 and 435 cm⁻¹ were assigned to a geometric isomer of ClOO as an intermediate, which could not possess C_{2v} symmetry because of the ¹⁸O pattern (1415.1, 1377.5, 1375.0, and 1336.7 cm⁻¹) of the strongest band. These absorptions decreased on annealing of the matrix or slowly on prolonged photolysis, whereas bands at 1441 cm⁻¹ mainly increased. An assignment of these bands to ClOO in an electronic excited state was excluded. In addition, in a nitrogen matrix bands of ClOO at 1424 and 1445 cm⁻¹ were detected and in an oxygen matrix at 1438 and 1442 cm⁻¹.¹⁶

Gole calculated low-lying electronic states of OCIO and ClOO by ab initio methods.²² He found four doublet states for ClOO: two ²A'' states corresponding to low-lying states ²A₂ and ²B₁ of OCIO, respectively, and two ²A' states related to low-lying states ²A₁ and ²B₂ of OCIO. It was suggested that ClOO is not formed in its ground electronic state ²A'' but in the ²A' state, which corresponds to the ²B₂ state of OCIO. Assuming this excited state to be long-lived, the absorption at 1415 and 435 cm⁻¹ might

be assigned to ClOO in this state. However, it was doubted that the matrix surroundings would stabilize this state for several minutes. Alternatively, a metastable geometric isomer of ClOO was discussed with slightly different bond angle and a very anharmonic OO stretching potential. Slow but spontaneous deactivation should yield the more stable ClOO molecule in its ground electronic state but excited in up to four quanta of ν₁. Thus, the group of bands near 1440 cm⁻¹ was assigned to a vibrational progression nν₁ → (n + 1)ν₁ (0 ≤ n ≤ 4).²²

We have reinvestigated the photoisomerization of OCIO isolated in an argon matrix. In comparison to neon matrix experiments, a simpler assembly was used. The main differences are described in the Experimental Section; photolysis times were longer by a factor of ca. 7. After 20 min of irradiation with a Hg medium-pressure lamp (λ ≥ 395 nm), nearly all of the matrix-isolated, monomeric OCIO was converted to ClOO with absorptions similar to those of Arkell and Schwager (ref 16, see above). Without further irradiation, no change in the spectrum appeared within 20 min. Thus, the absorptions at 1416.8 and 435.0 cm⁻¹ cannot be due to a species which deactivates spontaneously. Prolonged photolysis for another 2 h caused the bands at 1416.8 and 435.0 cm⁻¹ to decrease by one-third while features at 1442.5 and 408.3 cm⁻¹ increased by a factor of 1.5. This is similar to observations described in ref 16 but much slower despite the

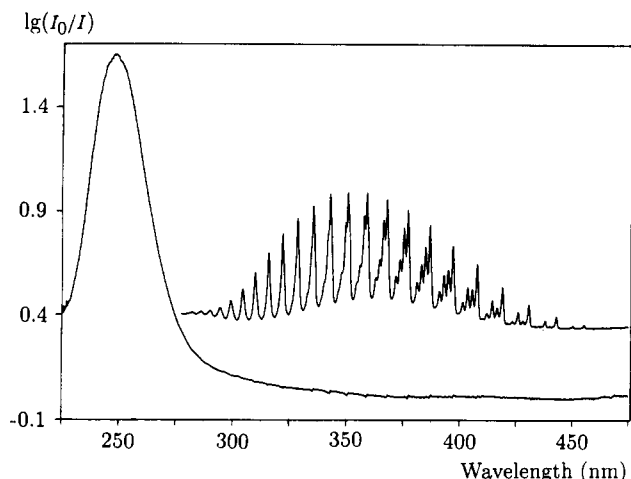


Figure 4. Ultraviolet spectrum of OCIO isolated in a neon matrix and of ClOO obtained from the same matrix upon photolysis. The OCIO spectrum has been shifted upward for clarity.

higher matrix temperature (ca. 15 K instead of 4 K). Use of cut-off filters at 320 or 280 nm did not increase this conversion. In addition, we have observed $2\nu_1$ at 2842.6 and 2787.4 cm⁻¹, respectively, which rules out the possibility that the bands around 1440 cm⁻¹ might be due to the vibrational progression mentioned above. Values of $x_{11} = -21.2$ and 23.1 cm⁻¹, similar to the neon matrix value (see section c) are incompatible with the assignment of a feature (e.g., very close to 1400 cm⁻¹ to $4\nu_1 \rightarrow 5\nu_1$; cf. Figure 6 of ref 22).

It seems more reasonable that each of the absorptions between ca. 1442 and 1415 cm⁻¹ is due to ν_1 of ClOO trapped in different

matrix sites. It is very likely that these species have slightly different geometric parameters, as observed for the more rigid OCIO (see section b) and presumably some small differences in the electronic spectrum. Species in metastable sites will be reoriented by annealing or irradiating the matrix. (Slight effects of reorientation have also been observed for ClOO isolated in a neon matrix.) The different ClOO species near 1415 cm⁻¹ and around 1440 cm⁻¹ may originate from OCIO in different matrix sites (cf. section a), because OCIO is converted much faster to a certain ratio of ClOO in various matrix sites than species in a given matrix site are reoriented. However, the initial ratio of ClOO species in different sites may also depend on the amount of excess energy available for reorientation of a ClOO molecule in the matrix.

(f) Electronic Spectra of Matrix-Isolated ClO₂ Isomers. UV-vis spectra of OCIO and ClOO isolated in a neon matrix were recorded in order to compare the intensities of both spectra and to determine the shape of the absorption curves relative to those in the gas phase.

Absorption cross sections of gaseous OCIO in its natural isotopic abundance were determined at 204, 296, and 378 K,⁷ and the vibrational⁸ and rotational structures⁶⁸ of the spectrum were analyzed. Recently, improved absorption cross sections of ClOO in the gas phase were reported.^{19,20}

The UV spectra of matrix-isolated OCIO and ClOO resemble those in the gas phase (cf. Figure 4), and all band positions at maximal band cross sections agree in both environments within the experimental error. The vibrational fine structure in the UV spectrum of OCIO isolated in a neon matrix is sharper than that in the gas phase,⁷ because rotational states and hot bands are not excited at 5 K. This directly affects the ratio of cross sections

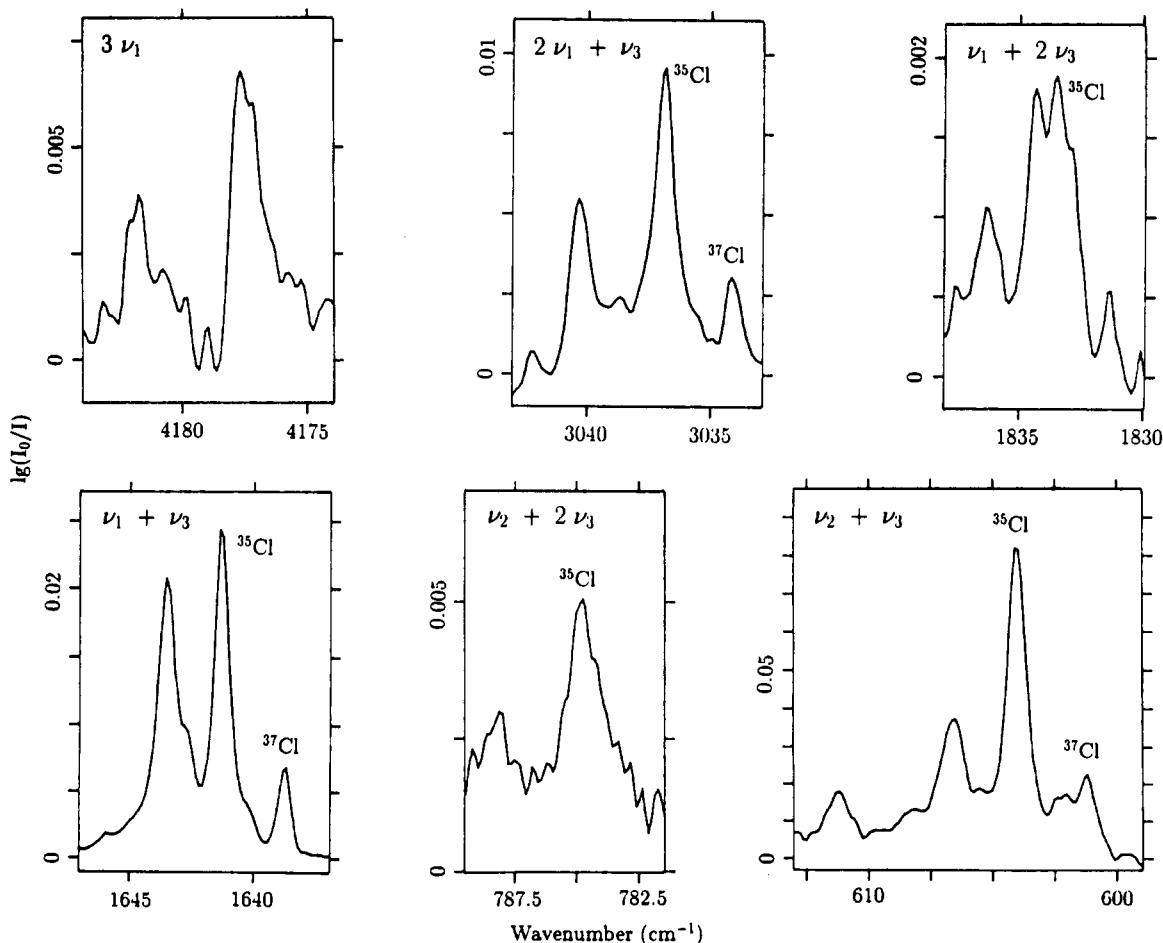


Figure 5. Infrared spectrum of the chlorine superoxide radical, ClOO (natural isotopic abundance), isolated in a neon matrix in the regions of various combination bands. Note the different absorbance scaling. The most prominent band of each ³⁵/³⁷Cl isotopomer is indicated.

$\sigma_{\max}(351\text{nm,OCIO})/\sigma_{\max}(247\text{nm,ClOO})$, which increases from 300 K (1:3, ref 7) to 5 K (2:3).

Appendix

Figure 5 shows all those observed vibrational bands of $\text{Cl}^{16}\text{O}^{16}\text{O}$ that are not included in Figure 2. The complete set of IR bands, including matrix splittings, is listed in Table XII. These data should be helpful for, for example, model calculations of the matrix host interactions which are large for the weakly bound molecule ClOO —even in neon matrix.

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