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Citation: The Journal of Chemical Physics **79**, 3648 (1983); doi: 10.1063/1.446303 View online: http://dx.doi.org/10.1063/1.446303 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/79/8?ver=pdfcov Published by the AIP Publishing

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ESR spectrum of CIO (${}^{2}\Pi_{3/2}$) isolated in a CO₂ matrix

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(Received 7 January 1983; accepted 8 July 1983)

Upon isolation of ClO in a CO₂ matrix at 10 K, a highly anisotropic ESR spectrum is observed which is attributed to ClO. This might be the first observation of a neutral radical with a ${}^{2}\Pi$ ground state in a nonpolar matrix. Some of the structure discernible on the spectrum at 10 K may be related to ClO at different trapping sites. After annealing the sample at T > 45 K, the radical concentration diminishes and the g_{\perp} peak of the most prominent site splits into four peaks which may correspond to the hyperfine splitting of ClO. The spectrum can be explained by the following g and A tensors, $g_x = 1.889$, $g_y = 1.899$, $g_z = 2.66$ and $A_x = 111$ MHz, $A_y \le 20$ MHz, $A_z \le 55$ MHz. In a simple crystal field model these values are compared with molecular parameters of ClO deduced from gas phase spectra.

INTRODUCTION

A technique has been developed for the measurement of atmospheric free radicals in which matrix isolation is used for the stabilization of the radicals and electron spin resonance spectroscopy for their quantitative detection. The atmospheric radicals which have so far been observed by this method are NO_2 , HO_2 , and RO_2 .^{1,2} While the ESR spectra of these molecules are well known for different matrices, the extension of this technique to the detection of CIO—a radical which plays an important role in the chemistry of the stratosphere³—requires first the identification of the ESR spectrum of CIO in a matrix.

Matrix-isolated ClO has been observed in Ar matrices by its IR, Raman, and UV spectrum by Andrews and co-workers.⁴⁻⁶ Experiments of Rochkind and Pimentel⁷ and of Chi and Andrews⁴ also showed that ClO easily dimerizes in the matrix at the low ratios of matrix to radical molecules used in the IR work.

Although the ESR spectrum of ClO in the gas phase is well known^{8,9} the ESR spectrum of ClO in a molecular matrix has not until now been reported. A spectrum observed by Atkins *et al.*¹⁰ after photolysis of ClO₂ in H_2SO_4 and by Byberg¹¹ after irradiation of KClO₄ had at first been attributed to isolated ClO, but was later identified as the ClOO radical.^{12,13} For ClO in KClO₃ crystals g values had been identified after irradiation, but no analysis of the spectrum was given.¹⁴

The ESR spectrum of a diatomic radical with a ${}^{2}\Pi$ groundstate like CIO will depend strongly on the environment. Interaction with the surrounding crystal field may lift the degeneracy of the ${}^{2}\Pi$ orbital and thus lead to a partial quenching of the angular momentum around the molecular axis. No spectrum has been so far reported for the isolation of a neutral ${}^{2}\Pi$ radical in a nonpolar matrix. Previous attempts to observe NO in an argon matrix at 4 K and in a CO₂ matrix at 77 K were not successful.¹⁷ It is believed that the failure to observe resonance resulted from crystalline anisotropy of the matrix field which, in the case of a ${}^{2}\Pi$ state molecule, may be sufficient to smear out the resonance lines.

First experiments to trap ClO in a CO₂ matrix by de-

position at 77 K did not yield an ESR signal that could be related to ClO. However, upon deposition of ClO in CO₂ at 10 K a highly anisotropic spectrum became observable whose intensity was proportional to the ClO concentration in the deposition mixture. The large anisotropy of this spectrum points to a radical with an only partly quenched angular momentum, as expected for ClO. Annealing of the sample leads to a splitting of the g_1 peak of this radical which can be interpreted as the Cl hyperfine splitting of ClO. By the deposition at 10 K a diffusion and recombination of the radicals during the sampling process—can be prevented.

EXPERIMENT

ClO radicals are formed in a quartz flow system (Fig. 1) and are mixed with the CO_2 matrix gas. A part of



FIG. 1. Flow system for the trapping of ClO in CO_2 matrices.

0021-9606/83/203648-06\$02.10

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the gas stream is extracted through an orifice (0.3 mm diam) and the condensable gases are frozen onto a cold finger. During the deposition of the sample, the orifice is positioned at the upper edge of the ESR cavity and the gas phase concentration of the radicals Cl or ClO in front of the orifice can be measured quantitatively by ESR. After the sample has been collected, the flow system with the orifice is lowered and the cold finger with the sample can then be transferred into the ESR cavity.

The cold finger is a copper rod (8 mm diam) which is covered with a thin layer of gold. It is cooled to 10 K by a closed cycle He refrigerator (Air Products Type 208L). For the annealing experiments, the cold finger temperature was increased by a resistance heater. Temperature was measured with a gold-iron/chromel thermocouple and stabilized by an ADP temperature control unit from Air Products.

The ESR spectra are recorded with a Varian E-line century series 9 GHz ESR system with a 12 in. magnet and a Varian V 4535 large access cavity. The frequency was measured with a Systron Donner frequency counter. The magnetic field was measured with a NMR sonde from AEG. To increase the signal-to-noise ratio, the spectra are signal averaged on a Nicolet multichannel analyzer. The spectra were manipulated on a HP 9830 desk computer. Spectra simulations were done on a HP 9825 computer.

In order to ensure that the matrix ESR spectrum is independent of the ClO mode of formation, three gas phase reactions were used to produce the ClO radicals

$$k_{1}(298 \text{ K}) = 1.2 \times 10^{-11} \text{ cm}^{3} \text{ molecule}^{-1} \text{ s}^{-1}, {}^{18}$$

$$C1 + CIO_{2} - 2CIO, \qquad (2)$$

$$k_{2}(298 \text{ K}) = 5.9 \times 10^{-11} \text{ cm}^{3} \text{ molecule}^{-1} \text{ s}^{-1}, {}^{18}$$

$$C1 + C1_{2}O - C1O + C1_{2}$$

 $C_{1} + C_{1} + C_{1} + C_{1}$

$$k_3(298 \text{ K}) = 9.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$
.¹⁹ (3)

The chlorine atoms were formed from Cl_2 gas in a microwave discharge with He as a carrier gas. The ClO gas phase concentration was varied from 1×10^{12} to 4×10^{13} molecule cm⁻³ at a total pressure in front of the orifice of 3 Torr. The deposition velocity of CO_2 on the cold finger was 1.7×10^{17} molecule s⁻¹. The reaction time between the point of mixing and the orifice $t = 1.8 - 7.2 \times 10^{-2}$ s was long enough for the complete reaction of Cl to ClO via the fast reactions (1)-(3). To minimize the loss of Cl and ClO through wall reactions, the surfaces of the flow system were passivated with H_3PO_4 .

Decomposition of the ClO in the flow system was negligible. The reaction of ClO with O_3 is too slow $(k < 1 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ }^{18})$ to show any effect. In addition, the main gas phase destruction paths, the reaction of ClO with itself:

 $ClO + ClO \rightarrow Cl_2 + O_2$, (4a)

$$ClO + ClO - ClOO + Cl$$
, (4b)



FIG. 2. ESR spectrum following trapping of ClO, formed by $Cl+O_3$, in a CO_2 matrix at 10 K. Shown is the first derivative spectrum (lower curve) and its integration (upper curve). The broad spectrum with the peaks marked by g_{\parallel} and g_{\perp} is due to ClO. The sharp lines near g_e are OClO and NO₂ lines (ClO:OClO: NO₂ = 2300: 100: 1). The matrix to radical ratio is CO_2 : ClO = 3000: 1. The resonance field of the free electron is marked by g_e .

$$ClO + ClO - OClO + Cl$$
 (4c)

 $k_4 = 1-2.5 \times 10^{-14}$ cm³ molecule⁻¹²⁰ are slow enough that the loss of ClO in the flow system should be unimportant (<5%). However, trace amounts of the products ClOO and OClO of reactions (4b) and (4c) might be detected, since the matrix ESR spectra of these species are easily observed. Whereas the OClO concentration was the high enough to be detectable in the solid sample, the ClOO concentration was too low, because it quickly decomposes in the gas phase at low pressure ClOO - Cl + O₂.

 O_3 , required for reaction (1), was formed in a MW discharge of pure O_2 (Linde, grade 99.998%), O_3 is separated from the O_2 gas stream by condensation in a cold trap at 77 K and is stored on silica gel at 77 K.

OClO was made by reacting diluted sulfuric acid with KClO₃ in the presence of oxalic acid.²¹ Cl₂O was made by the reaction of Cl₂ with HgO at 196 K.²² For the experiments, a darkened glass flask was filled with 10 Torr of O₃, OClO, or Cl₂O. The flow rate of these gases was determined by the rate of pressure drop in the flask during the experiment. Cl₂ (Gerling, Holz, grade 99.8%), He (Messer Griesheim, grade 99.997%), and CO₂ (Messer Griesheim, grade 99.5%) were used without further purification.

RESULTS

The ESR spectrum that was observed after the trapping of ClO in a CO₂ matrix at 10 K is shown in Fig. 2. The spectrum is characterized by sharp lines near g_e , the g value of the free electron, and a broad spectrum which spreads over more than 1000 G.

The sharp lines are assigned to traces of OCIO and

NO₂. OCIO is formed in the gas phase recombination of ClO. NO₂ is formed from air impurities in the Cl_2 and He carrier gas entering the MW discharge where the Cl atoms are formed. OCIO and NO₂ contribute only a minor part of the total spin concentration in the sample. The absorption spectrum (upper curve in Fig. 2) shows that the broad ESR spectrum comprises by far the major part of the spins.

This broad spectrum was always observed when ClO radicals were trapped in a CO₂ matrix, regardless of the mechanism of formation of ClO. Conversely it was not observed when the products of a He, Cl₂ discharge were frozen out either alone or together with molecular oxygen. Further, the signal strength of this spectrum was proportional to the ClO gas phase concentration within the limit of experimental accuracy $(\pm 20\%)$. Also the shape of this spectrum corresponds to a radical with a cylindrically symmetric g tensor which is randomly oriented in the matrix. It is the form expected for the ESR spectrum of a matrix isolated radical with a ${}^{2}\Pi_{3/2}$ ground state. The g_{\parallel} and g_{\perp} factors can be identified as indicated in Fig. 2. They refer to g factors along and perpendicular to the molecular axis. Thus, all experimental evidence suggests that this broad ESR spectrum with $g_{ii} = 2.66$ and $g_{i} = 1.89$ should be attributed to ClO.



FIG. 3. Change of the ESR spectrum of a $Cl+O_3$ sample upon annealing. Measured at 10 K. After deposition at T=10 K and after annealing at 45 K for 10 h and 60 K for 5 h. The spectra are shown on the same scale.



FIG. 4. Interpretation of the g_{\perp} structure as hyperfine splitting due to a nuclear spin I = 3/2. Spectrum after annealing at 70 K (lower curve), calculated spectrum (upper curve). The parameters of the simulation are $g_x = 1.8888$, $g_y = 1.899$, $g_z = 2.66$ and $A_x = 110$ MHz, $A_y = 15$ MHz, $A_z = 50$ MHz. Line shape is a Lorentzian distribution with a halfwidth of 20 G.

ANNEALING

The annealing of the sample, at cold finger temperatures T > 45 K, leads to a decrease of the ClO signal (Fig. 3). This decrease of the ClO signal can be interpreted as the diffusion of ClO and the formation of diamagnetic (ClO)₂ consistent with the results of Chi and Andrews, ⁴ who after raising the temperature of the Ar matrix observed a decrease of the ClO line, while some of the (ClO)₂ lines increased.

In the present experiment, the OClO signal also increased upon annealing of the CO_2 matrix. This points to an additional chemical reaction in the matrix. So far, the experimental results favor the reaction ClO + ClO \rightarrow OClO + Cl analogous to the gas phase reaction.²³

In addition to a decrease in the signal strength, a change in the shape of the spectrum of the ClO spectrum was also observed. The change of the structure at the low field side of $g_{1} = 2.66$ and the high field side of $g_{1} = 1.89$ indicate that ClO is trapped on different sites in the matrix. These sites could have different diffusion characteristics.²³

Moreover, the linewidth of the ClO spectrum narrows after annealing and the g_1 peak of the most prominent trapping site ($g_1 = 1.89$) splits up into four peaks (Fig. 4). This splitting can be assigned to the hyperfine structure of a nuclear spin I = 3/2 like that of ³⁵Cl and ³⁷Cl the two natural isotopes of chlorine. This is clearly demonstrated by the comparison between the experimental spectrum and a computer simulation.

SPECTRUM SIMULATION

The simulated spectrum is determined for the Hamiltonian

$$\mathcal{\mathcal{C}} = \mu_{B} \cdot \mathbf{H} \cdot \mathbf{g} \cdot \mathbf{S} + \mathbf{S} \cdot \mathbf{A} \cdot \mathbf{I}$$

solved by first order perturbation.²⁴ The polycrystalline spectrum was generated according to the method described by Griscom *et al.*²⁵ The spectrum is best described by a Lorentzian line shape. The sharpening after the annealing can be reproduced by varying the linewidth.

The g value parallel to the molecular axis g_s is given by the position of the peak near H = 2500 G. Only an estimate can be given for the hyperfine structure term in this direction, because even after annealing of the sample at 77 K, no splitting of the peak was observable. The linewidth of the peak after annealing at 77 K indicates that $A_s \leq 55$ MHz.

The structure at $g_1 = 1.89$ which appeared after annealing at 60 K and was intensified after further warming to 77 K can be interpreted with the parameters of the line spectrum in Fig. 4. For the component with the larger hyperfine splitting (here characterized by x) g_x and A_x can be extracted as indicated from the measured spectrum.

The values of the y component are only roughly determined. It follows that the hyperfine structure term in this direction is much smaller than the x component $(A_y \ll A_x)$ and that g_y is larger than g_x . Table I shows the parameters which give the best simulation.

In the computation, it was taken into account that chlorine has two natural isotopes ${}^{35}Cl$ and ${}^{37}Cl$ with the ratio of 3:1. The values in Table I relate to ${}^{35}Cl$. The computation shows that a splitting due to the two isotopes of chlorine should not be expected at the observed linewidths. Also, the influence of the quadrupole interaction, which often complicates the interpretation of ESR spectra of chlorine containing radicals, cannot be observed in the present experiments.

g tensor

The parameters extracted from the matrix ESR spectrum can be compared with molecular parameters of CIO known from the gas phase spectra with the help of the theoretical description of ESR spectra of diatomic ²II radicals in solids. The dependence of the *g* values from the spin orbit coupling constant and the interaction with the surrounding crystal field, was derived by Kaenzig and Cohen²⁶ for the description of O₂ centers in alkali-halide crystals and has often been applied to the discussion of ESR spectra of diatomic ²II radicals like NO and O₂ for matrix isolated molecules as well as for molecules adsorbed on surfaces.

The energy levels of the upper molecular orbitals of

TABLE I. Magnetic parameters for 35 ClO trapped in a CO₂ matrix.

g tensor	A tensor (MHz)
$g_x = 1.889 \pm 0.002$	$A_{\rm x} = 111 \pm 6$
$g_{y} - g_{x} = 0.01 \pm 0.003$	$A_y \leq 20$
$g_{g} = 2.66 \pm 0.01$	A _g ≤ 55



FIG. 5. Schematic diagram of the upper molecular orbitals of ClO. Δ is the energy separation of the 3π orbitals caused by interaction with the surrounding crystal field. *E* is the excitation energy of a higher σ level.

ClO are schematically shown in Fig. 5. Through the asymmetric interaction with the surrounding crystal field, the 3π level is split into $3\pi_x$ and $3\pi_y$ by an energy Δ . The spin orbit interaction, characterized by λ , leads to a parital mixing of the 3π levels and an induced angular momentum around the molecular axis, the z axis. The ratio Δ/λ determines the difference of g_{\parallel} and g_{\perp} from g_{e} . Interaction with a higher σ level, with an energy difference E, causes the splitting of g_{\perp} in g_x and g_y . The principal values of the g tensor are given by

$$g_{x} = g_{e} \left(\frac{\Delta^{2}}{\lambda^{2} + \Delta^{2}}\right)^{V_{2}} - \frac{\lambda}{E} \left(-\left(\frac{\lambda^{2}}{\lambda^{2} + \Delta^{2}}\right)^{V_{2}} - \left(\frac{\Delta^{2}}{\lambda^{2} + \Delta^{2}}\right)^{V_{2}} + 1\right)$$

$$g_{y} = g_{e} \left(\frac{\Delta^{2}}{\lambda^{2} + \Delta^{2}}\right)^{V_{2}} - \frac{\lambda}{E} \left(+\left(\frac{\lambda^{2}}{\lambda^{2} + \Delta^{2}}\right)^{V_{2}} - \left(\frac{\Delta^{2}}{\lambda^{2} + \Delta^{2}}\right)^{V_{2}} - 1\right)$$

$$g_{z} = g_{e} + 2 \left(\frac{\lambda^{2}}{\lambda^{2} + \Delta^{2}}\right)^{V_{2}} I$$
(I)

where l is a correction of the orbital angular momentum around the molecular axis caused by the admixture of crystal field wave functions to the molecular wave function. For the free radical l equals 1.

From the g values given in Table I the values for $\Delta/\lambda, \lambda/E$, and l can be iteratively determined. They are $\Delta/\lambda = 2.8 \pm 2\%$, $\lambda/E = 8.4 \times 10^{-3} \pm 30\%$, and $l = 0.98 \pm 2\%$. With $\lambda = 318$ cm^{-19,27} we obtain $\Delta = 890$ and $E = 38\,000$ cm⁻¹. The g values for ClO in KClO₃ are given as $g_x = 1.9992$, $g_y = 2.0151$, $g_z = 2.166$.¹⁴ These give $\Delta/\lambda = 16.7$, $\lambda/E = 8.5 \times 10^{-3}$ and l = 1.37. If for the CO₂ matrix as well as for the KClO₃ matrix the spectrum is due to ClO, the Δ/λ values show that the angular momentum is quenched more strongly in KClO₃.

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$\langle r^{-3} \rangle_0^S = 2 \times 10^{25} \text{ cm}^{-3}$	$2\mu_B \frac{\mu_I}{I} \cdot \frac{8\pi}{3} \cdot \psi^2(0) = 14 \text{ MHz}$
$\langle r^{-3} \rangle_2^S = 1.88 \times 10^{25} \text{ cm}^{-3}$	
$\langle r^{-3} \rangle^{t} = 1.77 \times 10^{25} \text{ cm}^{-3}$	

The values for E are equal in the two surroundings. The high value for l in KClO₃ indicates that here ClO is not well described by the simple crystal field model. The value for E, the energy difference of the 3Π levels to an excited σ state, can be related to the excitation energy observed in gas phase ClO. The lowest Σ level that was observed by Basco and Morse²⁷ has an excitation energy of 54851 cm⁻¹ which is markedly higher than E for ClO in CO₂. Amano *et al.*²⁸ estimated an excitation energy of 31 000 cm⁻¹ for an effective Σ state of ClO from the analysis of the Λ splitting as observed in microwave spectra of ClO.

The Δ value for the most prominent trapping site for ClO in CO₂ is very small compared to the values for O₂⁻ in polar matrices such as water or alcohol.^{15,16} It is also small compared to the Δ value for O₂⁻ in the nonpolar matrix benzene. The smaller interaction with the crystal field leads, in addition to the higher spin orbit coupling constant for ClO, to a spectrum with a much greater anisotropy for ClO in CO₂ than those of O₂⁻ in different matrices.

The other trapping sites for ClO in CO₂ which disappear more rapidly upon annealing show an even smaller interaction. The site with the smallest Δ/λ value $(\Delta/\lambda = 0.63)$ leads to a broad peak around 1850 G corresponding to a g value $g_{\parallel} = 3.61$. The g value expected for the case of an unlifted degeneracy is $g_{\parallel} = 4$. The g_{\perp} feature for this site is already broadened beyond detection by the anisotropy in the crystal field interaction.²³

A tensor

The relation of the principal values of the hyperfine tensor for ClO in CO₂ as determined by the simulation of the spectra compare well with those of other ${}^{2}\Pi$ radicals like ${}^{16}O{}^{17}O{}^{-}$, 29 Se₂, and SSe³⁰ in alkali-halide crystals. In all cases A_x , the hyperfine term in the direction of the orbital of the unpaired electron, is greater than A_y the other perpendicular hyperfine term. Further A_x is greater than A_z , the hyperfine term along the bond axis, if not as in the case of Se₂ and SSe⁻ in KJ $g_{\parallel}-g_{e}$ is very large.

The nuclear hyperfine structure can be expressed in terms of the following Hamiltonian³¹:

$$\mathcal{H}_{HFS} = 2\mu_{B}\frac{\mu_{I}}{I} \left[\frac{\vec{L} \cdot \vec{I}}{r^{3}} + \left(\frac{3(\vec{I} \cdot \vec{r})(\vec{r} \cdot \vec{S})}{r^{5}} - \frac{\vec{I} \cdot \vec{S}}{r^{3}} \right) + \frac{8\pi}{3}\delta(r)\vec{I} \cdot \vec{S} \right]$$
(II)

The first term describes the interaction of the orbital angular momentum with the nuclear spin, the second is the dipole-dipole interaction of the electron spin with the nuclear spin, and the last term is the Fermi contact interaction. For this Hamiltonian, Zeller, Shuey, and Kaenzig²⁹ have derived the equations for the principal values of the hyperfine tensor for ¹⁶O¹⁷O⁻. Their equations for A_x, A_y , and A_z , slightly modified for the heteronuclear radical ClO, are

$$A_{x} = 2\mu_{B}\frac{\mu_{I}}{I} \left[\frac{8\pi}{3} \cos 2\alpha |\psi(0)|^{2} + \frac{1}{5} \cos 2\alpha \left\langle \frac{1}{r^{3}} \right\rangle_{0}^{5} + \frac{3}{5} \left(1 - \sin 2\alpha \right) \left\langle \frac{1}{r^{3}} \right\rangle_{2}^{5} \right]$$

$$A_{y} = 2\mu_{B}\frac{\mu_{I}}{I} \left[\frac{8\pi}{3} \cos 2\alpha |\psi(0)|^{2} + \frac{1}{5} \cos 2\alpha \left\langle \frac{1}{r^{3}} \right\rangle_{0}^{5} - \frac{3}{5} \left(1 - \sin 2\alpha \right) \left\langle \frac{1}{r^{3}} \right\rangle_{2}^{5} \right]$$

$$A_{z} = 2\mu_{B}\frac{\mu_{I}}{I} \left[\frac{8\pi}{3} |\psi(0)|^{2} - \frac{2}{5} \left\langle \frac{1}{r^{3}} \right\rangle_{0}^{5} + 2 \sin 2\alpha \left\langle \frac{1}{r^{3}} \right\rangle_{1}^{1} \right]$$
(III)

where $\sin 2\alpha$ is given by $\sin 2\alpha = [1 + (\Delta/\lambda)^2]^{-1/2}$, $\langle r^{-3} \rangle^l$, and $\langle r^{-3} \rangle_2^s$, $\langle r^{-3} \rangle_0^s$ represent the average of r^{-3} over the orbital momentum and two different spin momentum densities, respectively.²⁹

The difference $A_x - A_y$ yields an estimate for $\langle r^3 \rangle_2^s$. For $A_x = 110$ MHz and $-20 \le A_y \le 20$ MHz and

$$2\mu_B \frac{\mu_I({}^{35}\text{Cl})}{I} = 7.7 \times 10^{-24} \text{ cm}^3 \text{ MHz}$$
,³²

 $\langle r^{-3} \rangle_2^S = (1.8 \pm 0.3) \times 10^{-25} \text{ cm}^{-3}$ is obtained. This value agrees well with $\langle r^{-3} \rangle$ derived from the gas phase microwave³³ and gas phase EPR spectra⁹ (see Table II). Conversely the hyperfine parameters for the matrix isolated ClO can be calculated with the formulae III, the parameter Δ/λ derived from the g-factor analysis and the $\langle r^{-3} \rangle$ values derived from the gas phase work of Kakar et al.³³ shown in Table II.

With $\Delta/\lambda = 2.8$ the formulae III yield

 $A_x = 101$ MHz, $A_y = -16$ MHz, and $A_z = 40$ MHz.

These values agree quite well with the values derived from the measured spectrum, thus providing good support for the positive identification of the ClO ESR spectrum in a CO_2 matrix.

CONCLUSION

Both experiment and theory strongly support the identification of the observed spectrum as being due to ClO. The g and A tensors can be reasonably well described by the crystal field model for ²II radicals in solids by Zeller, Shuey, and Kaenzig²⁹ and the molecular parameters of ClO determined in the gas phase microwave³³ and ESR spectra.⁹ A weak π interaction between the linear CO₂ and ClO species might be responsible for the lifting of the orbital degeneracy of the ²II ground state of ClO.³⁴ The spectrum of ClO diminishes upon annealing, indicating diffusion and recombination of ClO. Further support for the identification may be obtained by the isolation of Cl¹⁷O.

For the detection of ClO in atmospheric samples, the sensitivity for the broad ESR spectrum of ClO in CO_2 is considerably less than for HO_2 and NO_2 . Therefore, the detection limit for ClO in an air sample of 10 nl would be about 1 ppb. The atmospheric samples are collected at 77 K. At this temperature the major constituents of the air, nitrogen, and the paramagnetic oxygen are not trapped thus providing an enrichment of the radicals on the cold finger. The annealing experiments indicate already that CO_2 is not an appropriate matrix to stabilize atmospheric radicals like ClO. Experiments to observe the ESR spectrum of ClO in a CO_2 matrix upon deposition at T > 50 K were not successful.

ACKNOWLEDGMENTS

We are grateful to H. W. Päetz for his help in the set up of the experiments and we thank him, Dr. D. Mihelcic and Professor D. H. Ehhalt for helpful discussions. This work was partially financed by the Bundesministerium für Forschung und Technologie under grant FKW 06.

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- $^{34}\mathrm{We}$ are grateful to one of the referees for this suggestion.