JOURNAL

OF THE AMERICAN CHEMICAL SOCIETY

VOLUME 89, NUMBER 24 NOVEMBER 22, 1967

Physical and Inorganic Chemistry

Matrix Infrared Study of the ClOO Radical[1]

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Received March 13, 1967

Abstract: The photolysis of OClO in an argon matrix at 4°K has produced the ClOO radical. The radical in argon has fundamental infrared absorptions at 1441, 407, and 373 cm^{-1}. Parallel work using O^{18}-substituted OClO gave isotopic infrared absorptions which were in excellent agreement with calculated values obtained from the normal coordinate analysis. The radical has also been produced by photolysis of Cl_2 in normal and isotopically substituted oxygen matrices at 4°K. Other evidence suggests that a second species exists, which is believed to be a structural isomer of the ClOO radical, and which has fundamental infrared absorptions at 1415 and 435 cm^{-1} in argon at 4°K.

The existence of the ClOO radical as a reactive intermediate in the gas-phase photolysis reactions of Cl_2 with O_2 was suggested by Porter and Wright.[2,3] They made calculations of potential curves for this radical using the methods of Eyring and Polanyi. Benson and Buss[4] estimated that ClOO is thermodynamically more stable than its isomer OClO by 4 kcal/mole, and that the bond dissociation energy D(Cl–OO) = 8 ± 2 kcal. Inconclusive attempts were made to trap this radical at 77°K after its half-life was estimated to be from 10^3 to 10^6 sec at that temperature.[5] In a recent reinvestigation of the mechanism of halogen monoxide formation, the reaction scheme[2] which requires the existence of ClOO was supported.[6] The present low-temperature matrix study describes the production of the ClOO radical and its identification by infrared spectroscopy.

Experimental Section

The low-temperature infrared cell, Beckman IR-9 spectrophotometer, and high-pressure mercury arc used in this work have been described previously.[7] For the experiments requiring infrared observations from 200 to 400 cm^{-1}, the cell was equipped with CsI optics, and spectra were run on a Perkin-Elmer Model 621 infrared spectrophotometer. Valves were installed on the cell so that it could be moved under vacuum at 4°K to the latter spectrometer.

In all runs the gas mixtures were produced by simultaneous deposition from two manifolds, and flow rates were adjusted to give the desired matrix to reactant ratio (M/R). The N_2 and O_2 (Matheson, research grade), Ar (Airco minimum purity 99.997%), and Cl_2 (Matheson, high purity; Airco, research grade) were used without further purification. The labeled O_2 was 99.5% O^{18} (Bio-Rad Laboratories, Richmond, Calif.) and the D_2O was 98% O^{18} (Yeda Research and Development Co., Rehovoth, Israel). Unlabeled ClO_2 was synthesized by the chlorination of sodium chlorite (reagent grade, City Chemical Corp., New York, N. Y.). Chlorine dioxide, labeled with O^{18}, was synthesized by reacting ClF_3 (Matheson, 98%) with D_2O^{18}. The labeled ClO_2 was separated from the side products ClO_2F, ClO_3F, and HF by vacuum-line fractionation. The two purified samples had an approximate isotopic distribution of 20:62:18, respectively, and 11:41:48, respectively, of the isotopic forms ClO^{16}_2, $O^{16}ClO^{18}$, and ClO^{18}_2, according to infrared analysis. Ultraviolet irradiations were made using either filter 1 (water, 2200–9000 A), filter 2 (aqueous $NiSO_4$ solution, 2200–3500 and 4500–5900 A), or filter 3 (aqueous $CuSO_4$ solution + Corning No. 5970, 3650 A).

Two series of matrix reactions were made. The first series was based on the photolysis of Cl_2–O_2 mixtures (O_2:Cl_2, 40:1) in which the oxygen served as a reactive matrix. A deposition rate of 0.2 mmole/min was used, and deposition times ranged from 2.5 to 25 min. Irradiation periods were from 35 to 92 min using filters 1 or 2. The second series of runs involved the photolysis of ClO_2 in several

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[1] This work was supported by the Research and Technology Division, AFSC, Edwards, Calif., under Contract AF 04(611)-11389.

[2] G. Porter and F. J. Wright, *Z. Electrochem.*, **56**, 782 (1952).

[3] G. Porter and F. J. Wright, *Discussions Faraday Soc.*, 14, 23 (1953).

[4] S. W. Benson and J. H. Buss, *J. Chem. Phys.*, 27, 1382 (1957).

[5] S. W. Benson and K. H. Anderson, *ibid.*, 31, 1082 (1959).

[6] G. Burns and R. G. W. Norrish, *Proc. Roy. Soc.* (London), **A271**, 289 (1963).

[7] A. Arkell, R. R. Reinhard, and L. P. Larson, *J. Am. Chem. Soc.*, **87**, 1016 (1965).

Table I. Summary of Runs. Photolysis of OClO in a Matrix at 4°K

Run no.	Matrix	M/R	OClO used, μmoles	Photolysis: Time, min	Photolysis: Filter	Spectra taken: IR-9	Spectra taken: PE-621	Table and/or figure
1	Ar	40	88	10	2	X		III
2	O_2	40	88	10	2	X		III
3	Ar	200	22	10	2	X		III
4.1	Ar	400	22	0.5	3	X		III
4.2				10	2	X		
5	Ar	400	22	0.03–25	3	X		1
6	Ar	400	22	1.5	3	X		2
7	N_2	400	22	0.5	3	X		3
8	Ar	400	22 (50% O^{18})	0.5–30	3	X		IV
9	Ar	400	67	12–36	None		X	V, 4
10	Ar	200	90	10	2	X	X	VI, 5
11	Ar	200	90 (80% O^{18})	10	2	X	X	VI, 5

matrices at matrix to reactant ratios (M/R) of 40 to 400 (Table I). The deposition rate was 0.2 mmole/min, and deposition times ranged from 95 to 142 min. Irradiation times ranged from several seconds to 36 min. In several runs, after irradiation and recording of the spectra using the Beckman IR-9, the cell was sealed off and moved to the Perkin-Elmer 621 location for extension of the spectral observations down to 200 cm^{-1}. The cell was then allowed to warm up at the latter location for recording of background spectra. In one run, the entire photolysis sequence was carried out at the Perkin-Elmer 621 location using an unfiltered, high-pressure mercury arc source (Hanovia, 100 w, SH 616A). This procedure allowed spectra to be recorded before and after photolysis. Parenthetical values next to absorptions which appear throughout the text refer to intensity (log I_0/I).

Results

Photolysis of Cl_2, O_2 Mixtures. Initial attempts to observe the Cl + O_2 reaction were made using an argon matrix (Cl_2:O_2:Ar, 1:1:40 and 1:4:40) but only a very small band was observed at 1440 cm^{-1} after photolysis. By using oxygen as the matrix (O_2:Cl_2, 40:1), the size of the band at 1440 cm^{-1} was increased sufficiently for further study using isotopic substitution. By using a 50:50 mixture of $O^{16}{}_2$ + $O^{18}{}_2$ for the matrix, a 92-min photolysis (filter 2) produced the absorptions summarized in Table II. In addition to the known absorptions for ozone and α-oxygen,[8] new bands were observed at 1440, 1399, and 1358 cm^{-1}. As shown in Table II the positions of these new bands are in complete agreement with the values predicted for isotopically substituted O–O stretching vibrations. The absence of any other absorptions related to the 1440-cm^{-1} band suggested that if the 1440-cm^{-1} absorption was the O–O stretching vibration of the ClOO radical, then the other absorptions (ClO stretch and ClOO bend) were either too weak to be observed or they were outside the spectral range of our observations. It became evident that a much more efficient source of the species producing the 1440-cm^{-1} absorption would be required to complete the spectral observations. Subsequent work showed that the Cl_2 + O_2 system and the Cl_2 + O_3 system[9] would be unsatisfactory in this respect.

Table II. Absorptions[a] Produced during the Photolysis of Cl_2 in $O^{16}{}_2$, $O^{18}{}_2$ (50:50 mixture)[b] Matrix at 4°K

ν_{obsd}	Absorbance × 10^3	ν_{calcd}	Vibrational assignment
1550	23	...	$O^{16}O^{16}$ (α-$O^{16}{}_2$)
1463	16	1465[c]	$O^{18}O^{18}$ (α-$O^{18}{}_2$)
1440	21	...	$O^{16}O^{16}$ (ClOO)
1399	12	1399[d]	$O^{16}O^{18}$
1358	20	1358	$O^{18}O^{18}$
1035 (1033)[e]	39	1034[e]	$O^{16}O^{16}O^{16}$ (O_3, ν_3)
1022 (1020)	37	...	$O^{16}O^{16}O^{18}$
1002 (1000)	9	1000	$O^{16}O^{18}O^{16}$
1013 (1010)	6	1010	$O^{18}O^{16}O^{18}$
988 (986)	32	...	$O^{18}O^{18}O^{16}$
979 (976)	27	975	$O^{18}O^{18}O^{18}$

[a] In cm^{-1}. [b] The $O^{18}{}_2$ (99.5% O^{18}) was from Bio-Rad Laboratories, Richmond, Calif. [c] B. C. Cairns and G. C. Pimentel, *J. Chem. Phys.*, **43**, 3432 (1965). [d] Calculated using "diatomic molecule" approximation. [e] From unpublished observations and a normal coordinate analysis of ozone.

Photolysis of OClO. Initial work with OClO indicated that it would be a good source for photolytic production of the 1442-cm^{-1} absorption. As shown in Table III, a series of runs was made to determine if the band at 1442 cm^{-1} was related to any of the other absorptions in the spectrum down to 450 cm^{-1}. Comparison of runs 1 (Ar matrix) and 2 (O_2 matrix) showed that the absorption at 1442 cm^{-1} in the O_2 matrix was reduced to about one-tenth its normal size in an argon

Table III. The Effects of Increasing Dilution (M/R) on the Photolysis[a] of OClO in a Matrix at 4°K

Absorptions, cm^{-1}	Run no. 1	2	3	4.1	4.2	Assignments
564	0.023[b]	0.013[c]	0.003	0.001	...	Class I
586	0.011[b]	...	0.002	0.002	0.002	Class I
638	0.048[b]	0.013	0.004	...	...	Class I
648	0.160[b]	0.036	0.017	0.008	0.008	Class I
702	...	0.015	...	...	...	O_3
995	...	...	...	0.007	...	Class III
1037	0.076[b]	0.302	0.009	0.005	0.003	O_3
1215	...	...	...	0.002	...	Class III
1228	...	...	...	0.002	...	Class III
1258	0.010[b]	0.006	...	...	...	Class I
1279	0.090[b]	0.025	0.013	0.007	0.008	Class I
1290	0.103[b]	0.029	0.014	0.007	0.008	Class I
1415	...	...	...	0.230	0.010	Class III
1438	0.070	0.088	0.087	0.112	0.075	Class II
1442	0.420	0.043	0.473	0.486	0.537	Class II
1458	0.027[b]	0.020	...	...	...	Class I
2110	...	0.013	...	...	...	O_3

[a] Photolysis time in all runs except 4.1 was 10 min (BH6, $NiSO_4$ filter). [b] Absorptions still present after diffusion (4–45–4°K). [c] Intensity = log I_0/I.

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(8) B. C. Cairns and G. C. Pimentel, *J. Chem. Phys.*, 43, 3432 (1965).

(9) Unpublished work has shown that photolysis of Cl_2–O_3–Ar mixtures at 4°K gave very small yields of the same species produced in the Cl_2 + O_2 work.

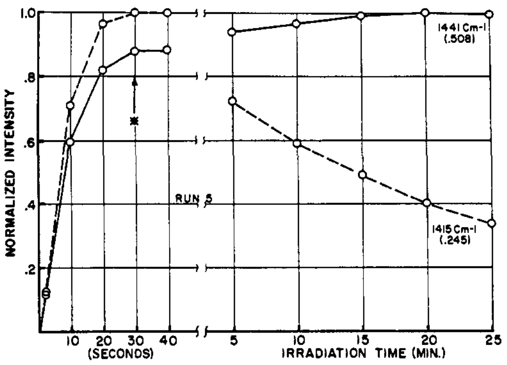

Figure 1. The effects of prolonged irradiation on absorptions in the 1400–1460-cm^{-1} region (argon matrix at 4°K): - - - -, 1415 cm^{-1} (0.245); ———, 1441 cm^{-1} (0.508); *, all OClO gone after 30-sec irradiation.

matrix. In addition, the larger absorption at 1438 cm^{-1} in the O_2 matrix suggested that the 1438-cm^{-1} band may represent an oxygen perturbation of the absorption at 1442 cm^{-1}. When the sample in run 1 was diffused (4–45–4°K) the characteristic band broadening and shifting (1-2 cm^{-1}) were observed. However, it should be noted that all bands except 1438 and 1442 cm^{-1} survived the diffusion operation. Run 2, which showed the appearance of two new absorptions at 702 2110 cm^{-1}, established that these absorptions as well as the one at 1037 cm^{-1} can be assigned to ozone. In runs 3 and 4 ($M/R = 200$ and 400, respectively) it was apparent that the increased dilution favored the formation of the species responsible for the absorption at 1442 cm^{-1} at the expense of other compound formation. A comparison of runs 1, 3, and 4.2 showed that there were three classes of absorptions. Class I absorptions, which included all absorptions except those in the 1400–1450-cm^{-1} region, decreased with increasing dilution and can most probably be assigned to photolysis products from aggregated OClO. It should be noted that the class I absorptions in run 3 have all decreased to a greater extent compared to run 1 than that warranted by the smaller amount of OClO used in run 3. The two class II absorptions, 1438 and 1442 cm^{-1}, both increased with increasing dilution suggesting that these derived from monomeric OClO. The four class III absorptions at 995, 1215, 1228, and 1415 cm^{-1} were easily distinguished from all other absorptions by their appearance only when short photolysis times (2 to 40 sec) were used, and by their subsequent photolytic sensitivity. A comparison of 4.1 and 4.2 indicated that the observed increase in the absorbance of the 1442-cm^{-1} band most probably derived from the simultaneous decrease in the absoption at 1415 cm^{-1} and possibly also from 1438 cm^{-1} and the remaining class III absorptions. To further test this observation and to establish the decay-growth pattern of the 1415- and 1442-cm^{-1} absorptions, a series of three runs (5–7) was made. In run 5, which is shown in Figure 1, irradiation for 30 sec, using the BH6–filter 3 combination, caused all of the OClO to disappear and absorptions at 995 (0.003), 1415 (0.245), 1438 (0.100), and 1441 cm^{-1} (0.448) to appear. Subsequent irradiation showed the gradual loss of 1415 and 995 cm^{-1} accompanied by further increase in 1441 cm^{-1}. The absorption at 1438 cm^{-1} remained constant at 0.100 throughout the irradiation, indicating that the observed decrease in the 1438-cm^{-1} band in run 4 can be attributed to the use of filter 2 in the latter run. There was also no change in a very small absorption at about 1460 cm^{-1}. The effects of warming were observed in run 6 as shown in Figure 2. After loss of OClO and formation of absorptions (cm^{-1}) at 995 (0.009), 1415 (0.226), 1438 (0.110), 1441 (0.614), and about 1460 (0.011), the sample was allowed to warm slowly from 4°K. The most rapid decrease in the 1415-cm^{-1} band and increase in the 1441-cm^{-1} band occurred between 4 and 5°K. Beyond that, in the 5 to 20°K region, there was a steady, but slower, loss of the 1415-cm^{-1} absorption with a similar but opposite change in the 1441-cm^{-1} band. Above 20°K both absorptions decreased steadily with the 1415- and 1441-cm^{-1} absorptions disappearing at 36.5 and 46°K, respectively. The intensity of the band at 995 cm^{-1} remained essentially constant in the 5 to 20°K range. The 1438-cm^{-1} absorption paralleled the observed changes in the 1441-cm^{-1} band. The 1460-cm^{-1} absorption increased from 0.011 at 4°K to 0.036 at 42°K which suggested that it may be associated with ClOO aggregation. In run 7, shown in Figure 3, a nitrogen matrix was used and several differences were immediately noted. First, the principal absorptions at 1415 and 1441 cm^{-1} in argon were perturbed to 1424 and 1445 cm^{-1}, respectively, in nitrogen. Second, the relative intensities of the absorptions in nitrogen are nearly the reverse of those found in argon: N_2, 1424 (0.526) and 1445 cm^{-1} (0.271), whereas Ar, 1415 (0.226) and 1441 cm^{-1} (0.488). This suggests that the N_2 matrix may be providing a stabilizing effect on the formation of the

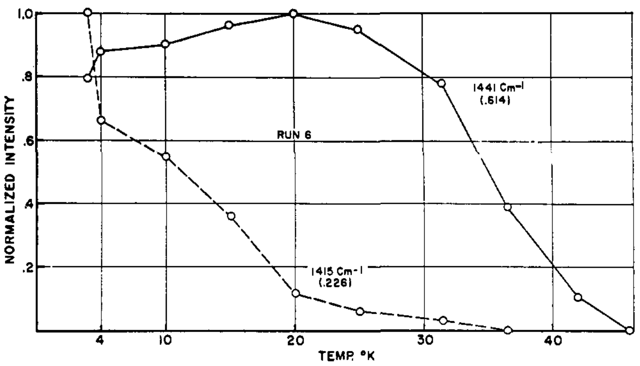

Figure 2. The effects of warming on the absorptions in the 1400–1460-cm^{-1} region in an argon matrix at 4°K: - - - -, 1415 cm^{-1} (0.226); ———, 1441 cm^{-1} (0.614).

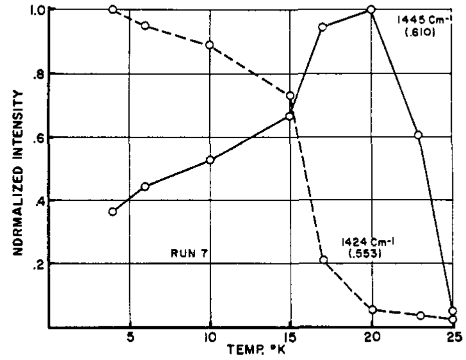

Figure 3. The effects of warming on the absorptions in the 1400–1460-cm^{-1} region in a nitrogen matrix at 4°K: - - - -, 1424 cm^{-1} (0.533); ———, 1445 cm^{-1} (0.610).

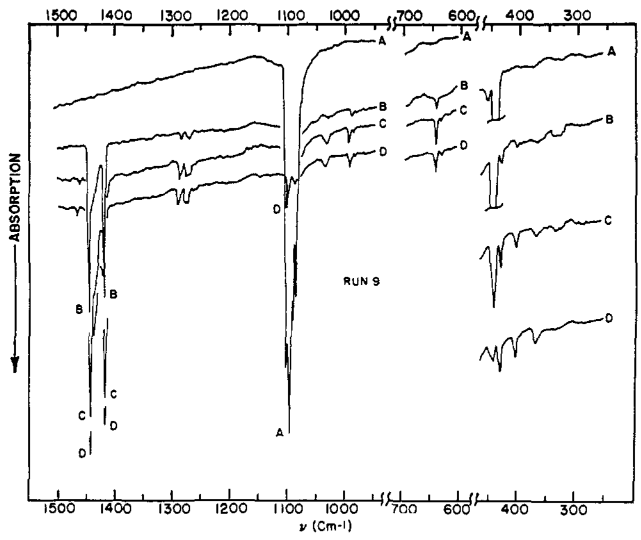

Figure 4. Growth study of the absorptions in the 250–1500-cm^{-1} region produced by photolysis of OClO in argon at 4°K.

1424-cm^{-1} species. Although a small absorption near 995 cm^{-1} was produced, the results from run 6 had already shown this absorption to be unrelated to the band at 1415 cm^{-1}, and its thermal behavior in this run was not followed. No absorption was found at 1438 cm^{-1} in run 7 and the behavior of the absorption near 1460 cm^{-1} was similar to that found in the previous run (run 6).

Run 8, using OClO (50% O^{18}), was made to determine if the 1415-cm^{-1} absorption was produced by a species containing oxygen. This sample of OClO contained an approximate isotopic distribution of 20:62:18 of the forms O^{16}ClO^{16}, O^{16}ClO^{18}, and O^{18}ClO^{18}, respectively. The small amount of OClO used in this run precluded observation of any absorptions other than those found in the 1300–1450-cm^{-1} region. As shown in Table IV a short-term photolysis (0.5 min) produced two sets of four absorptions each, with intensity ratios which paralleled the isotopic distribution in the parent OClO. The observed splitting established that the 1415-cm^{-1} absorption also contained oxygen, as had been previously established for the 1441-cm^{-1} absorption in the Cl$_2$–O$_2$ (O^{18}) work. The observation of a quartet for each of these species confirmed that the proposed triatomic molecules contain an unsymmetrically substituted O–O linkage. Additional photolysis (30 min) caused the 1415-cm^{-1} quartet to decrease and the 1441-cm^{-1} quartet to increase, in agreement with the observations made in run 5.

Table IV. Absorptions (cm^{-1}) Produced by Photolysis of OClO (~50% O^{18}) in Ar at 4°K

ν_{obsd}	ν_{calcd}[a]	Absorbance × 10^3 0.5 min[b]	 30.5 min[b]	Vibrational assignment
1440.8		29	41	O^{16}O^{16} (ClOO)
1402.3 1400.1	1400.2	58	73	O^{16}O^{18}
1360.9	1358.4	18	24	O^{18}O^{18}
1415.1		22	6	O^{16}O^{16} (ClOO*)[c]
1377.5 1375.0	1375.2	44	11	O^{16}O^{18}
1336.7	1334.2	22	3	O^{18}O^{18}

[a] Calculated by "Diatomic molecule" approximation. [b] Photolysis time. [c] The designation ClOO* refers to an intermediate form of the ClOO radical.

Because no other absorptions were found in the region down to 450 cm^{-1} which could be assigned as fundamental absorptions of the 1441-cm^{-1} species, it was necessary to extend the spectral observations to the region below 450 cm^{-1}. This was accomplished by modifying the infrared cell so that it could be moved at 4°K to a second location having a Perkin-Elmer 621 available for use. Although temporary temperature-measuring and pumping facilities were also installed, the Perkin-Elmer 621 location gave very limited operational flexibility. The most serious deficiency was the difficulty involved with running sequential irradiations. This problem was overcome by the use of a portable ultraviolet source (Hanovia SH 616A, 100 w) at the Perkin-Elmer 621 location. The use of this much weaker source was possible only because of the ease with which OClO undergoes photochemical isomerization. Using this procedure, run 9 was made to establish the existence of absorptions below 450 cm^{-1} and to determine their relationship with the other absorptions in the spectrum. The results of this run are shown in Figure 4 and summarized in Table V. As shown in Figure 4, the spectrum before photolysis (spectrum A) showed no absorptions in the 250–1500-cm^{-1} region other than those assignable to OClO. Subsequent sequential irradiations totalling 36 min showed the loss of OClO, the growth of the principal absorptions at 1415 and 1441 cm^{-1}, and the growth of three new absorptions in the region below 450 cm^{-1} at 435, 407, and 373 cm^{-1}. The relationship of these three absorptions to the other absorptions in the spectrum can be more readily seen in the summary of all absorptions from run 9 given in Table V. Of the 13 absorptions produced during photolysis, only three of those grew consistently throughout the irradiation. These three absorptions, which are at 373, 407, and 1441 cm^{-1}, were therefore considered to be the three fundamentals of the ClOO radical. In contrast, the absorbances of the absorptions at 1415 an 435 cm^{-1} levelled off at 24 min of irra-

Table V. Photolysis[a] of OClO in Ar at 4°K

Absorptions cm^{-1}	Photolysis times (min) 0	 12	 24	 36	Assignments
373	...	0.006	0.009	0.015	ClOO
407	...	0.008	0.017	0.024	ClOO
435	...	0.010	0.028	0.029	ClOO*
448	0.362[b]	0.230	0.071	0.018	OClO
564	...	...	0.004	0.001	?
586	...	...	0.009	0.002	?
648[c]	...	0.018	0.031	0.025	?
940[d]	0.194	0.100	0.045	...	OClO
995[c]	...	0.011	0.020	0.019	?
1037	...	0.010	0.012	0.014	O$_3$
1100[d]	0.819	0.660	0.258	0.053	OClO
1279[c]	...	0.014	0.022	0.023	?
1290	...	0.015	0.030	0.025	?
1415	...	0.326	0.649	0.650	ClOO*
1441[c]	...	0.370	0.796	0.920	ClOO
1458	...	...	0.013	0.017	(ClOO)$_n$

[a] Photolysis using an unfiltered Hanovia SH 616 (100 w) high-pressure mercury ultraviolet source. [b] Intensity, log I_0/I. [c] Doublet. [d] Quartet.

diation and stayed essentially constant through 36 min of irradiation. Although the absorption at 1279 cm^{-1} showed a similar behavior, it had already been shown in run 4.1 (Table III) that the absorption at 1279 cm^{-1} was not related to the 1415-cm^{-1} band. In addition, it was found in run 10 that the intensities of the three absorptions were 435 (0.005), 1279 (0.093), and 1415 cm^{-1} (0.095). A comparison of these values with those found in run 9 (Table V) readily showed that the 1279-cm^{-1} absorption was also not related to the 435-cm^{-1} band and therefore remained unidentified. On the basis of these observations and the data obtained in the decay-growth studies in runs 5–7, and the isotopic data in run 8, the absorptions at 435 and 1415 cm^{-1} were assigned as an intermediate (designated $ClOO^*$) in the formation of the ClOO radical. The absorptions at 564, 586, 648, and 1290 cm^{-1} appeared to be related but remained unidentified. The intensity of the 1290-cm^{-1} absorption indicated that it probably was not the first overtone of the 648-cm^{-1} band. The doublet at 995 cm^{-1} had the characteristic splitting and intensity relationship of $Cl^{35}O$, $Cl^{37}O$ stretching vibrations. Although the growth of this doublet was somewhat similar to the growth of the bands at 435 and 1415 cm^{-1}, it was found in run 6 that the behavior of the 995-cm^{-1} doublet, on warming from 5 (0.009) to 20°K (0.011), was quite different from the behavior of the 1415-cm^{-1} absorption (decreased from 0.150 to 0.026) in the same temperature range. No data were obtained which would exclude a possible relationship between the 995-cm^{-1} doublet and the absorption at 435 cm^{-1}. Finally, the absorption near 1460 cm^{-1} was assigned to ClOO aggregation primarily on the basis of its behavior during warm-up in run 6.

Parallel runs 10 and 11 were made for the specific purpose of determining the positions of the O^{18}-substituted absorptions of the three ClOO fundamentals. In run 10, as shown in Figure 5 (spectrum A), the photolysis of OClO in Ar produced the absorptions at 373, 407, and 1440.8 cm^{-1} with complete loss of the OClO absorptions.[10] A parallel run was made (run 11) in which the OClO consisted of a mixture of $O^{16}ClO^{16}$,$O^{16}ClO^{18}$, and $O^{18}ClO^{18}$, 11:41:48, respectively. Photolysis of this mixture caused complete loss of all OClO absorptions with production of the absorptions shown in Figure 5 (spectrum B). As expected from the results of run 8 (Table IV), the absorption at 1440.8 cm^{-1} split into a quartet with absorptions at 1440.8 and 1360.9 cm^{-1} and an equal intensity doublet at 1402.3 and 1400.1 cm^{-1} (Figure 5, spectrum C). In addition the absorption intensity ratio of 13:40:47 was almost identical with the predicted ratio (11:41:48) for this starting material. In the region below 420 cm^{-1} the two absorptions at 407 and 373 cm^{-1} were split into four bands at 400, 391, 385, and 360 cm^{-1} plus an unresolved shoulder at about 407 cm^{-1}. Although the intensity ratio of the four bands in the 407–385-cm^{-1} region coud not be measured accurately, it can be seen that a marked qualitative similarity exists with the ratio found in the O–O stretching region. A summary of the absorptions from runs 10 and 11 is given in Table VI together with the values calculated from the force constants obtained by normal coordinate analysis. The spurious absorptions in run 10 at 1420 and 1432 cm^{-1}, which were not previously observed, were believed to be perturbations of the 1441-cm^{-1} band due to site effects and/or matrix defects. Matrix defects may have been enhanced in this run through a combination of conditions involving reactant concentration and sample thickness.

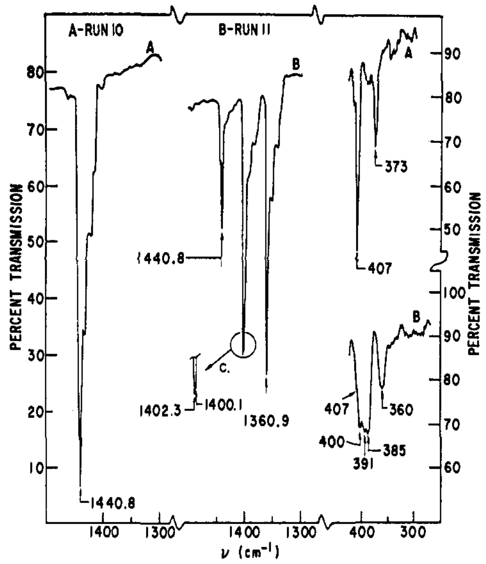

Figure 5. Absorptions produced by ultraviolet irradiation at 4°K (10 min, BH6, $NiSO_4$ filter). (A) $O^{16}ClO^{16}$ in Ar (M/R = 200). (B) $O^{16}ClO^{16}$:$O^{16}ClO^{18}$:$O^{18}ClO^{18}$ (11:41:48) in Ar (M/R = 200). The region below 420 cm^{-1} was recorded on a Perkin-Elmer 621 (scale expansion 5×). (C) Slow scan of the doublet near 1400 cm^{-1} (enlarged 1.5×).

Table VI. Principal Absorptions (cm^{-1}) Produced by Photolysis of OClO[a] in Ar at 4°K

ν_{obsd}	ν_{calcd}[b]	Vibrational assignments[c]	
1440.8	1441.9	ν_1	$ClO^{16}O^{16}$
407	406	ν_2	
373	372	ν_3	
1402.3	1402.6	ν_1	$ClO^{16}O^{18}$
400	401	ν_2	
...	...	ν_3	
1400.1	1400.1	ν_1	$ClO^{18}O^{16}$
391	393	ν_2	
...	...	ν_3	
1360.9	1359.5	ν_1	$ClO^{18}O^{18}$
385	385	ν_2	
360	361	ν_3	

[a] In a series of runs the O^{18} content ranged from 0 to 80% (M/R = 200). [b] k_{OO} = 9.654 mdynes/A, k_{OCl} = 1.290 mdynes/A, k_{OOCl} = 1.038 mdynes A/rad^2, $k_{OCl-OOCl}$ = 0.545 mdyne/rad, k_{OO-OCl} = 0.070 mdyne/A. The calculated values have an average frequency discrepancy of 0.9 cm^{-1}. [c] All data pertain to Cl^{35} only.

Discussion

The ClOO Radical. By analogy with other known matrix reactions in which FO_2[11,12] and HO_2[13] were produced from $F + O_2 \rightarrow FO_2$ and $H + O_2 \rightarrow HO_2$, it was expected that Cl atoms should react with O_2 to give the radical ClOO. Therefore the weak absorption observed at 1440 cm^{-1} during the photolysis of $Cl_2 + O_2$ mixtures was tentatively assigned to the O–O stretching vibration

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(10) Under conditions of higher resolution and a scan speed of 0.8 cm^{-1}/min, the band at 407 cm^{-1} was observed on the IR-9.

(11) A. Arkell, *J. Am. Chem. Soc.*, **87**, 4057 (1965).

(12) R. D. Spratley, J. J. Turner, and G. C. Pimentel, *J. Chem. Phys.*, **44**, 2063 (1966); P. N. Noble and G. C. Pimentel, *ibid.*, **44**, 3641 (1966).

(13) D. E. Milligan and M. E. Jacox, *ibid.*, **38**, 2627 (1963).

of ClOO. Subsequent isotopic work with $Cl_2 + O_2$ (50% $O_2{}^{18}$) gave observed absorptions (Table I) which further supported this assignment. It should be noted that the absorbance of the 1399-cm^{-1} absorption, which was assigned to the $O^{16}O^{18}$ stretch of the ClOO radical, was much larger (Table I) than would be expected from a starting mixture containing less than 1% $O^{16}O^{18}$ as molecular oxygen. In addition, the formation of ozone was not expected from the range of ultravioet radiation used. The apparent exchange reaction to form $O^{16}O^{18}$ substituted ClOO and the formation of ozone can be explained if it is assumed that higher oxides of chlorine are involved as reactive intermediates. Thus photolysis of these intermediates as shown in (3–5) could produce the

$$Cl + O_2 \longrightarrow ClOO \tag{1}$$

$$ClOO + O_2 \longrightarrow ClO_4 \tag{2}$$

$$ClO_4 \longrightarrow ClO_3 + O \tag{3}$$

$$ClO_3 \longrightarrow ClOO + O \tag{4}$$

$$ClO_3 \rightleftharpoons Cl + O_3 \tag{5}$$

$$O + O_2 \rightleftharpoons O_3 \tag{6}$$

ozone directly as in (5) or indirectly as in (3), (4), and (6). Photolysis of the ozone, reverse of (6), or reaction of the ozone with chlorine[9] atoms, reverse of (5), would provide the means for isotopic exchange and ultimate formation of $O^{16}O^{18}$-substituted ClOO.

The very weak absorptions produced in the $Cl_2 + O_2$ work and the absence of any other absorptions related to the 1440-cm^{-1} band prompted the search for a more efficient method of producing ClOO. This was found in the photochemical isomerization of OClO. A dilution study, summarized in Table III (runs 1, 3, and 4.2), showed that all observed bands were unrelated to the principal absorption at 1442 cm^{-1}. The other absorptions were either identified as ozone (1037 cm^{-1}), tentatively identified as an O_2 perturbation of 1442-cm^{-1} band (1438 cm^{-1}), or remained unidentified as did the absorptions at 995, 1215, and 1228 cm^{-1}, and the remaining class I absorptions.

The extension of the spectrum down to 250 cm^{-1} and a growth study (Figure 4, Table V) showed that two new bands at 407 and 373 cm^{-1} were most probably related to the absorption at 1441 cm^{-1}. Subsequent isotopic work (Figure 5, Table VI) caused the 407-cm^{-1} absorption to split into four bands at 407, 400, 391, and 385 cm^{-1}, and caused the 373-cm^{-1} band to shift to 360 cm^{-1}. The assignment of the 407-cm^{-1} quartet to ν_2 (Cl–O stretch) and the 373-cm^{-1} doublet to ν_3 (ClOO bend) was made primarily on the basis of similar isotopic shifts observed for the O–F stretching and OOF bending modes of the O_2F radical.[12] In addition, Noble and Pimentel[12] later showed that the 585-cm^{-1} doublet (O–F stretch) could be resolved into the required quartet for a bent OOF molecule. Their work also showed that the unresolved central feature in the O–O stretching region was commensurate with the splitting predicted by their revised normal coordinate analysis. In contrast, the central feature in the O–O stretching region for ClOO was resolved with an observed spacing of about 2 cm^{-1}. It was also of interest that the Cl–O stretching quartet (407, 400, 391, and 385 cm^{-1}) had a less pronounced central spacing (9 cm^{-1}) than the central spacing (18 cm^{-1}) observed for the O–F stretching quartet (584, 581, 563, and 560 cm^{-1}) of the O_2F radical. Aside from these minor differences the two radicals, O_2F and O_2Cl, appear to be quite similar from a structural standpoint.

Structure and Force Constants for ClOO. The calculation of force constants and isotopic frequencies was made using an IBM 1620 computer. The program, which was based on equations derived by Cross and Van Vleck,[14] was written so that an iterative procedure could be used to minimize the sum of the squares of the differences between the observed and calculated frequencies. Provision was made for variation of any or all of the three principal force constants and for testing the effectiveness of the three interaction force constants either individually or in various combinations. The assumed molecular parameters used in the calculations were $r_{OO} = 1.23$ A, $r_{OCl} = 1.83$ A, and $\alpha_{OOCl} = 110°$. The choice of these values was based on a consideration and adjustment of the molecular parameters found in molecules[15,16] such as O_2F_2 and Cl_2O. Using the ten observed frequencies for ClOO, shown in Table VI, the force constants listed in footnote *b* (Table VI) were obtained. The over-all agreement between observed and calculated isotopic frequencies (average difference = 0.9 cm^{-1}) affords the final confirmation that the observed infrared spectrum belongs to the ClOO radical.

The observation of a quartet in both the O–O and Cl–O stretching regions demonstrates the nonequivalence of the two oxygens and confirms that the ClOO molecule has a Cl–O–O structure. A comparison of the principal force constants of ClOO and related molecules is shown in Table VII. The position of the O–O stretching frequency and its respective stretching force constant indicate that the O–O bond in ClOO is quite similar to that found in O_2F.[11,12] It is also evident that the Cl–O bond in ClOO is much weaker than the corresponding bond in Cl_2O.

Table VII. Comparison of the Principal Force Constants of ClOO and Related Molecules

Molecule	k_{O-O}, mdynes/A	k_{O-X}, mdynes/A	k_{bend}, mdynes A/rad^2	Ref
OO	11.4	. . .	. . .	*a*
ClOCl	. . .	2.75	1.32	*b*
FOO	10.5	1.32	1.01	*c*
ClOO	9.7	1.29	1.04	This work
HOO	6.1	6.46	0.84	13

[a] G. Herzberg, "Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules," D. Van Nostrand Co., Princeton, N. J., 1950. [b] M. M. Rochkind and G. C. Pimentel, *J. Chem. Phys.*, **42**, 1361 (1965). [c] P. N. Noble and G. C. Pimentel, *ibid.*, **44**, 3641 (1966).

The indication of a very weak Cl–O bond is in agreement with the statement by Benson and Buss[4] that the Cl–OO bond energy may be about 8 kcal. They also point out that if *D*(Cl–OO) is 8 kcal, then ClOO is thermodynamically more stable than OClO by 4 kcal. This, of course, is in accord with our observation of a rapid and complete conversion of OClO to the more photolytically stable ClOO. The photochemical isomerization of OClO in inert matrices at 4°K is in

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(14) P. C. Cross and J. H. Van Vleck, *J. Chem. Phys.*, 1, 350 (1933).

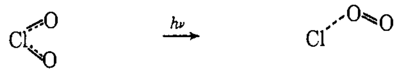
(15) R. H. Jackson, *J. Chem. Soc.*, 4585 (1962).

(16) R. H. Jackson and D. J. Millen, *Proc. Chem. Soc.*, 10 (1959).

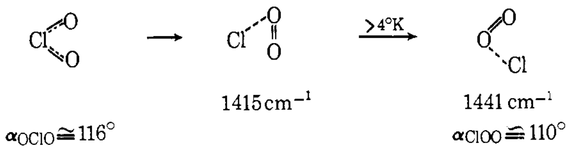
marked contrast to the results observed on the photolysis of this compound in the gas phase[17] or in a hydrocarbon glass at 77°K,[18] that is, formation of the ClO radical. This difference in the observed products may be explained by a consideration of the "cage effect."[19] In the gas phase or in hydrocarbon glasses, the oxygen atom produced in the photolysis step may easily escape from the site of the primary decomposition. However, in inert matrices at 4°K, recombination of the generated ClO + O, followed by rapid deactivation, permits the accumulation of ClOO.

The Intermediate ClOO Radical (ClOO*). The evidence which supports the existence of an intermediate in the formation of the ClOO radical consists primarily of observations made in the O–O stretching region. Specifically, these observations demonstrate that the formation of the absorption at 1415 cm^{-1} is favored by short photolysis times (≤ 30 sec), by the use of a 3650-A transmission filter during photolysis, and by using nitrogen instead of argon as the matrix (the 1415-cm^{-1} band in Ar shifts to 1424 cm^{-1} in a nitrogen matrix). The decay of the 1415-cm^{-1} absorption and growth of the 1441-cm^{-1} absorption was observed either by additional photolysis beyond 30 sec (Figure 1) or by warming the matrix above 4°K (Figure 2). It is of interest to note that in the thermal conversion the decay-growth process started as soon as the liquid helium container became empty and the temperature indicator showed approximately 5°K. The decay of the 1424-cm^{-1} absorption and growth of the band at 1445 cm^{-1} in a nitrogen matrix was also observed by warming the matrix above 4°K (Figure 3). The indication of certain structural similarities between this intermediate (ClOO*) and the ClOO radical was shown in run 8 (Table IV). The observation of a quartet in the 1415- to 1437-cm^{-1} region with isotopic spacing nearly identical with that found for the O–O stretch of the ClOO radical showed that this intermediate was basically quite similar to its relatively more stable counterpart. This similarity was the presence of a relatively short, unsymmetrically substituted O–O linkage in both species. Finally, the tentative assignment of the absorption at 435 cm^{-1} as ν_2 (Cl–O stretch) of ClOO* was regarded as reasonable on the basis of the similar growth behavior of the 435- and 1415-cm^{-1} absorptions in run 9 (Table V). No evidence of a bending frequency could be found for ClOO* which suggests that it is either coincident with the ClOO bending frequency at 373 cm^{-1}, too weak to be observed, or below the 250-cm^{-1} limit of these observations. In view of the unusually low thermal stability of ClOO* it should also be noted that its observed photochemical conversion to ClOO may have been purely thermal in nature and resulted from the slight heating effect which accompanies photolysis.

Although several explanations regarding the character of ClOO* have been considered, only one of them withstands the test of all observations. The possibility of ClOO* being an excited electronic state of ClOO was ruled out because of the long half-life ($\sim$4 min at 20°K) found for ClOO*. Also ruled out was the possibility that ClOO* was the symmetrical form of ClOO. This form would have given only three isotopic O–O stretching vibrations instead of the observed quartet. The explanation which seems most probable is that ClOO* is a structural isomer[20] of ClOO. In this case the rigid matrix at 4°K prevents the newly formed ClOO* from attaining the interatomic distances and angle estimated for the ClOO radical. In going from the parent compound, OClO, to the ClOO radical three major structural changes must occur: the Cl–O bond must lengthen,



the O–O distance must shorten, and the ClOO angle must increase by almost 80°. It is most probably this large change in the relative positions of the three atoms which is restricted by the rigid matrix cage. Thus, an intermediate structure (ClOO*) is produced, having a compressed ClOO angle, but which probably requires only slight rotation of the molecule in the cage to allow the ClOO angle to increase and attain the more stable ClOO structure.



Diffusion of Chlorine Atoms. One other observation was made during the warm-up studies (Figures 2 and 3) which may be related to the diffusion of chlorine atoms. It was found that the disappearance of ClOO radical in both N_2 and Ar matrices started at about 20°K. This suggests that ClOO is subject to photolysis by the infrared radiation from the spectrophotometer, as shown in (7), but merely recombines at temperatures below

$$ClOO \underset{<20^\circ K}{\overset{h\nu}{\rightleftarrows}} Cl + O_2 \xrightarrow{>20^\circ K} 0.5Cl_2 + O_2 \qquad (7)$$

20°K. However, above 20°K the generated chlorine atoms escape the cage and combine to give Cl_2. Although 20°K is too low a temperature to consider the loss of ClOO by diffusion of the molecule, as shown in (8), it is not too low a temperature to consider the loss

$$ClOO \xrightarrow{>40^\circ K} (ClOO)_n \qquad (8)$$

of ClOO by photolysis and diffusion of the generated chlorine atoms.[21,22] It should also be noted that the loss of ClOO, which appears to start at 20°K (Figures 2 and 3), is complicated by the production of ClOO from ClOO* in the 4–20°K range. In the absence of ClOO* the loss of ClOO as shown in (7) or its possible loss as shown in (9) would account for the unpredictable ap-

$$ClOO + ClOO \xrightarrow{\Delta} Cl_2 + 2O_2 \qquad (9)$$

pearance of the 1460-cm^{-1} band which was assumed to be due to ClOO aggregation.

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[17] F. J. Lipscomb, R. G. W. Norrish, and B. A. Thrush, *Proc. Roy. Soc.* (London), **A235**, 455 (1956).

[18] I. Norman and G. Porter, *ibid.*, **A230**, 399 (1955).

[19] G. C. Pimentel in "Formation and Trapping of Free Radicals," A. M. Bass and H. P. Broida, Ed., Academic Press Inc., New York, N. Y., 1960.

[20] Conformational isomerism as a direct result of restricted rotation by a rigid matrix was first observed and discussed by G. C. Pimentel, *J. Am. Chem. Soc.*, **80**, 62 (1958).

[21] M. E. Jacox and D. E. Milligan, *J. Chem. Phys.*, **43**, 866 (1965), discuss the diffusion of chlorine atoms at 14°K.

[22] M. M. Rochkind and G. C. Pimentel, *ibid.*, **46**, 4481 (1967), have observed absorptions at 1428 and 1438 cm^{-1} which, they proposed, were due to the O–O stretch in ClOO.

Acknowledgment. The authors wish to thank Drs. W. F. Brown and W. E. Crockett for the development of the computer program used in the normal coordinate analysis. We are also indebted to Mr. G. H. Post for his help with the experimental portion of the work.

Matrix Infrared Spectra of HOBr and HOCl[1]

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Received April 21, 1967

Abstract: The photolysis of mixtures of Ar–HX–O_3 at 4°K has produced the species HOBr (ν_1 3590, ν_2 1164, ν_3 626.0 cm^{-1}) and HOCl (ν_1 3581, ν_2 1239, ν_3 729 cm^{-1}). The use of the isotopic starting materials HX, DX, and $O^{16,18}{}_3$ produced data which have been used to calculate potential functions of these molecules.

The infrared spectrum of hypobromous acid, HOBr, has not been observed previously. That of hypochlorous acid was observed in the gas phase by Hedberg and Badger.[2] In this paper we present infrared studies of various isotopically substituted HOX species synthesized by photolysis of Ar–HX–O_3 mixtures at 4°K.

Experimental Section

The low-temperature infrared cell and its associated equipment have been described elsewhere.[3] Sample irradiations of up to 40 min were made using a high-pressure mercury arc (General Electric BH6). An elliptical spun aluminum reflector was used to focus the light from the arc onto the sample through an aqueous $NiSO_4$ solution filter (2200–3500 and 4500–5900 A). The filter (5-cm quartz cell) contained 100 g of $NiSO_4 \cdot 6H_2O$/l. of water. The infrared spectra were recorded from 4000 to 400 cm^{-1} on a Beckman IR-9 spectrometer. The estimated resolution and frequency accuracy was ±1 cm^{-1} for runs using isotopic substitution and ±2 cm^{-1} for all others.

All gas blends were prepared by standard manometric procedure using matrix to reactant ratios (M/R) of 40 for blends of HX (DX) in argon. Gas mixtures with ozone were produced by simultaneous deposition from two manifolds. Flow rates were adjusted to give M/R values between 25 and 40 for ozone in argon. The two reactant gas streams were not permitted to converge until just prior to deposition on the liquid helium cooled CsBr window. No unusual reactivity between the hydrogen halides and the CsBr window was observed. The HX (DX) blends were made up and deposited from a glass manifold covered with aluminum foil. Fluorolube grease was used on all stopcocks, and gas pressures were monitored by use of a pressure transducer gauge, the diaphragm of which was coated with Teflon. Ozone was deposited from an all metal manifold. In a typical run about 4.5 mmoles of blended material was deposited in 40 min at 4°K.

The following chemicals were used without further purification: argon (Airco, minimum purity 99.997%), H_2 and Cl_2 (Airco, research grade), O_2 (Matheson, research grade), D_2 (Matheson, 99.5% minimum isotopic purity), HCl (Matheson, 99% minimum purity), HBr (Matheson, 99.8% minimum purity), $O_2{}^{18}$ (Bio-Rad Laboratories, 99.5% O^{18}), and D_2O (General Dynamics Corp., 99.7%). Deuterium bromide was synthesized by the reaction of Br_2 and red phosphorus moistened with D_2O. The products were passed through a tower of red phosphorus and trapped in a liquid nitrogen cooled trap. The DBr was degassed and a midfraction used in making up blends. Deuterium chloride was synthesized by photolyzing mixtures of Cl_2 with excess D_2. The noncondensable gases at liquid nitrogen temperature were pumped off, and the DCl was separated from any unreacted Cl_2 by distillation from a −140° trap to a −196° trap. A midfraction of this material was used in matrix runs. Ozone and isotopically labeled O_3 were made by discharging O_2, with a Tesla coil, in a liquid nitrogen cooled Pyrex tube.

Results and Discussion

All the vibrational frequencies produced in the 4000–400-cm^{-1} range after photolysis of various mixtures of isotopically substituted reactants except those assigned to the various isomers of water are presented in Tables I and II. Figure 1 shows all bands produced in a typical run with an Ar:HBr:O_3 (50% O^{18}) ratio of 40:1:1. The spectrum, after deposition (B), contains bands assignable to the various isomers of ozone and those as-

Table I. Observed and Calculated[a] Vibrational Frequencies (cm^{-1}) of Hypobromous Acid from Ar–O_3–HBr Experiments Employing Isotopic Substitution

Ar–$O^{16}{}_3$–HBr	Ar–O_3 (50% O^{18})–HBr	Ar–$O^{16}{}_3$–DBr	Ar–O_3 (50% O^{18})–DBr
...	(3579) 3580	...	(2636) 2637
3589	(3591) 3590	2652	(2653) 2652
...	(1162) 1162	...	(848.6) 848.5
1164	(1165) 1162	854.0	(853.8) 853.9
...	(598.0) 597.8	...	(593.9) 593.8
626.0	(625.8) 626.0	621.8	(621.4) 621.5

[a] Values in parentheses calculated from force constants given in Table III.

Table II. Observed and Calculated[a] Vibrational Frequencies (cm^{-1}) of Hypochlorous Acid[b] from Ar–O_3–HCl Experiments Employing Isotopic Substitution

Ar–$O^{16}{}_3$–HCl^{35} [c]	Ar–O_3 (50% O^{18})–HCl^{35}	Ar–$O^{16}{}_3$–DCl^{35}	Ar–$O^{18}{}_3$–DCl^{35}
...	(3570) 3570	...	(2630) 2630
3578	(3581) 3581	2647	(2647) ...
...	(1236) 1237	...	(906) 906
1239	(1240) 1239	911	(911) ...
...	(702) 701	...	(702) 702
728	(728) 729	728	(728) ...

[a] Values in parentheses calculated from force constants given in Table III. [d] Gas-phase vibrational frequencies for HOCl at 3626, 1242, and 739 cm^{-1} and DOCl at 2674, 911, and 739 cm^{-1} are reported in ref 2. [c] Bands assignable to O–Cl^{37} were observed in only two cases: $HO^{16}Cl^{37}$, 723 cm^{-1}, and $HO^{18}Cl^{37}$, 695 cm^{-1} (calculated 723 and 696 cm^{-1}).

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(1) This work was supported by the AFRPL, Research and Technology Division, AFSC, Edwards, Calif., under Contract AF 04(611)-11389.

(2) K. Hedberg and R. M. Badger, *J. Chem. Phys.*, 19, 508 (1951).

(3) A. Arkell, R. R. Reinhard, and L. P. Larson, *J. Am. Chem. Soc.*, 87, 1016 (1965).