ASYMMETRICAL ClO₃: ITS POSSIBLE FORMATION FROM ClO AND O₂ AND ITS POSSIBLE REACTIONS

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Summary

An analysis of recent accurate experimental studies of Cl_2-photosensitized O_3 decomposition, in which O_3 disappearance and $OClO$ formation were directly monitored, suggests the possibility that the suppression of the quantum yield in the presence of O_2 may be due to the formation of asymmetrical chlorine trioxide ($ClO \cdot O_2$). Other intermediaries, such as Cl_2O_2, which may also form in the system are not thought to explain the observations. In addition to its capacity to oxidize, which it shares with other peroxo compounds, asymmetrical ClO_3 appears to undergo an interesting class of reactions in which the loosely bound O_2 adduct is relatively easily displaced by reactive atoms and radicals such as chlorine.

1. Introduction

The existence of chlorine atoms and ClO in the upper atmosphere of the Earth and the theoretical evidence that chlorine catalyzes the depletion of stratospheric ozone are now widely known. These findings have motivated us to analyze the observed suppression of quantum yield by the presence of O_2 in Cl_2-catalyzed O_3 decomposition, since O_2 is an important constituent of the stratosphere.

2. Background survey

2.1. Experimental data pertinent to Cl₂-photosensitized O₃ decomposition

The experimental results of most relevance are the following.

(1) In the absence of O_2 the quantum yield $-\Phi(O_3)$ for O_3 removal is high: greater than about 6 in the experiments of Norrish and Neville [1] and approximately 5.8 in those of Lin *et al.* [2] and Wongdontri-Stuper *et al.* [3].

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(2) Addition of O_2 suppresses $-\Phi(O_3)$. According to Norrish and Neville [1] a limiting value of 2 is attained at high O_2 pressures exceeding 600 Torr. These authors, however, inferred O_3 disappearance only indirectly. In later experiments, in which the O_3 concentrations were monitored directly, the quantum yield was found to decrease to 4.7 [2] or to 3.7 [3] depending upon the O_3 pressure and the light intensity.

(3) Notwithstanding these results, according to Wongdontri-Stuper *et al.* [3] an exceptionally low quantum yield ($-\Phi(O_3) \approx 1.7$) is attained when the O_3 pressure is very low (approximately 0.007 Torr) and the O_2 pressure is high (approximately 600 Torr).

In the present study we relied mainly on the data reported by Wongdontri-Stuper *et al.* [3] using UV spectroscopy. These data were preferred to those obtained by IR spectroscopy because they are in better accord with the unpublished results of Lin *et al.* [2] and because they are more comprehensive. Wongdontri-Stuper *et al.* [3] have also reported quantum yields $\Phi(OClO)$ for OClO formation. These provided useful constraints on our analysis.

2.2. Previous proposals for explaining the O_2 suppression of quantum yield

Norrish and Neville [1], who first discovered the phenomenon, have hypothesized that the reactions

$$Cl + O_2 + M \rightleftarrows ClOO + M$$

and

$$ClOO + O_3 \rightarrow ClO_3 + O_2$$
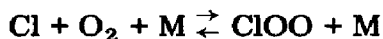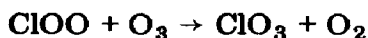
are responsible for the suppression of the quantum yield. According to Wongdontri-Stuper *et al.* [3] this mechanism would produce conflict with observed values of $-\Phi(Cl_2)$ in the presence of O_2. Rundel and Stolarski [4] suggest that the overall reaction

$$ClO + ClO + O_2 \rightarrow Cl_2 + O_2 + O_2 \tag{1}$$

proceeding with a rate coefficient of 2×10^{-33} cm^6 molecules^{-2} s^{-1}, constitutes the mechanism by which O_2 suppresses the quantum yield. However, since they have not identified the intermediary involved, their proposed mechanism is incomplete. Furthermore, reaction (1) alone cannot explain all known facts of the phenomenon. This will become clearer in Section 3.

3. The proposed theory

We propose that asymmetrical ClO_3 (asym ClO_3, $ClO \cdot O_2$) is formed in the reaction

$$ClO + O_2 + M \rightleftarrows Asym\ ClO_3 + M \tag{2}$$

and that it suppresses $-\Phi(O_3)$ by virtue of its capacity to react with ClO in the following manner:

$$\text{Asym } ClO_3 + ClO \rightarrow Cl_2 + O_2 + O_2 \tag{3a}$$

$$\rightarrow 2ClOO \tag{3b}$$

$$\rightarrow OClO + ClOO \tag{3c}$$

Channels (b) and (c) in the proposed reaction (3) are essential. These channels regenerate chlorine atoms by subsequent collisional disintegration of ClOO and keep the quantum yield as high as is observed even at high O_2 pressures. Channels (3b) and (3c) together must be comparable with channel (3a) at room temperature in order to sustain the observed behavior of $-\Phi(O_3)$ at higher O_2 pressures. Rundel and Stolarski [4] did not allow for these channels in their overall reaction (1). Consequently their mechanism would lead to $\Phi(O_3) = 2$ at high O_2 pressures, which contradicts observations.

In the experiments under consideration the Cl_2O_2 dimer [5, 6] is also an important intermediary and is efficiently formed by the reaction

$$ClO + ClO + M \rightleftarrows Cl_2O_2 + M \tag{9}$$

However, this dimer does not seem to be able to explain the observed behavior of $-\Phi(O_3)$. The product of the equilibrium constant K_9 ($= k_{9f}/k_{9r}$) and k_{10}, the rate constant of the reaction

$$Cl_2O_2 + M \rightarrow Cl_2 + O_2 + M \tag{10}$$

is only mildly dependent on O_2 or argon as the third body M [12]. In contrast, compared with the clear and pronounced effect of O_2 on $-\Phi(O_3)$, the effect of N_2 is at best only marginal. Furthermore, on the basis of the heat of formation $\Delta H_f(Cl_2O_2)$ of Cl_2O_2 [5], the reactions

$$Cl_2O_2 + O_2 \rightarrow ClOO + ClOO \tag{20}$$

$$\rightarrow ClOO + OClO \tag{21}$$

are both considerably endothermic. Consequently it is unlikely that, at room temperature, either reaction would be comparable with reaction (10) with $M \cong O_2$, as required by the observed $-\Phi(O_3)$. Hence these considerations argue against the Cl_2O_2 dimer being responsible for the suppression of the quantum yield $-\Phi(O_3)$ in the presence of O_2.

Reactions (3b) and (3c) are also endothermic; however, assuming that asym ClO_3 is only loosely bound, the energy deficits involved are significantly smaller and are probably comparable with the energy deficits in reactions (8b) and (8c) of Table 1, which are known to constitute a significant fraction of the total rate for reactions (8a), (8b) and (8c). In fact some endothermicity for the branches (3b) and (3c) is probably crucial for explaining the observed rapid drop of the quantum yield with decreasing temperature.

Atomic chlorine might react with asym ClO_3 in the following manner:

$$Cl + \text{asym } ClO_3 \rightarrow Cl_2O + O_2 \tag{5}$$

TABLE 1

Reaction scheme used in modeling observed quantum yields in experiments at room temperature

Reaction	Reaction number in text	Rate[a]	Source/comments
$ClO + O_2 + M \rightarrow Asym\ ClO_3 + M$	2f	$K_2 = k_{2f}/k_{2r} =$	Individually, k_{2f} and
$Asym\ ClO_3 + M \rightarrow ClO + O_2 + M$	2r	3.7×10^{-19}	k_{2r} are indeterminate.
$Asym\ ClO_3 + ClO \rightarrow Cl_2 + O_2 + O_2$	3a	5.0×10^{-15}	This study
$\rightarrow 2ClOO$	3b	4.0×10^{-15}	
$\rightarrow OClO + ClOO$	3c	5.0×10^{-16}	
$+ Cl \rightarrow Cl_2O + O_2$	5	1.2×10^{-10}	k_5 is not uniquely determined. It depends on the choice for k_{17}.
$Cl + O_3 \rightarrow ClO + O_2$	6	1.2×10^{-11}	Ref. 7
$ClO + O_3 \rightarrow ClOO + O_2$	7	1.5×10^{-19}	Refs. 2 and 3 and our unpublished analysis of the experimental data of ref. 1.
$ClO + ClO \rightarrow Cl_2 + O_2$	8a	3.7×10^{-15}	Total rate from refs. 6 and 8.
$\rightarrow ClOO + Cl$	8b	7.1×10^{-15}	Individual components
$\rightarrow OClO + Cl$	8c	4.0×10^{-16}	determined in this study.
$ClO + ClO + M \rightarrow Cl_2O_2 + M$	9f	3.0×10^{-32}	Ref. 5
$Cl_2O_2 + M \rightarrow ClO + ClO + M$	9r	4.0×10^{-18}	
$\rightarrow Cl_2 + O_2 + M$	10	1.0×10^{-20}	This study
$+ Cl \rightarrow ClOO + Cl_2$	11	1.0×10^{-11}	Ref. 5
$Cl + O_2 + M \rightarrow ClOO + M$	12f	1.7×10^{-33}	Ref. 5
$ClOO + M \rightarrow Cl + O_2 + M$	12r	3.1×10^{-13}	
$+ Cl \rightarrow Cl_2 + O_2$	14	5.0×10^{-11}	Ref. 9
$OClO + O_3 \rightarrow Asym\ ClO_3 + O_2$	15	3.0×10^{-19}	Ref. 10
$+ Cl \rightarrow 2ClO$	16	5.9×10^{-11}	Ref. 11
$2Asym\ ClO_3 \rightarrow Cl_2 + 3O_2$	17a	1.0×10^{-15}	This study
$\rightarrow 2ClOO + O_2$	17b	8.0×10^{-16}	
$\rightarrow OClO + ClOO + O_2$	17c	1.0×10^{-16}	
$Cl_2 + h\nu \rightarrow Cl + Cl$	18	I_a	Experimental data from ref. 3.
$ClO + OClO + M \rightarrow Cl_2O_3 + M$	19f		Not included in the fitting (see text).
$Cl_2O_3 + M \rightarrow ClO + OClO + M$	19r		

[a]Rate coefficients of bimolecular reactions are in units of cm^3 molecules^{-1} s^{-1} and those of three-body reactions are in units of cm^6 molecules^{-2} s^{-1}. I_a is in units of cm^{-3} s^{-1}.

Reaction (5) amounts to asym ClO_3 losing the adduct O_2 if it encounters an atomic or radical species for which ClO has a greater "affinity". Adduct displacement or "switching" reactions are quite commonplace with ionic clusters such as those encountered in the D-region ionosphere of the Earth [13]. It is possible that loosely bound neutral species such as asym ClO_3 may show the same tendency.

4. The numerical approach

Our "simulated" quantum yield was determined from the equation

$$\Phi(O_3) = \frac{d[O_3]}{dt} I_a^{-1} \tag{I}$$

where I_a is the rate of photon absorption per unit volume and

$$d[O_3]/dt = -\Sigma k_i[X_i][O_3] \tag{II}$$

where $[X_i]$ denotes the equilibrium concentration of the ith minor species X_i (such as Cl) and k_i is the rate coefficient of the relevant reaction. We numerically solved for $[X_i]$ assuming that the major species remained at their initial concentrations. In their experiments Wongdontri-Stuper *et al.* [3] allowed the trials to run until a significant fraction of the O_3 had been consumed. However, they found that the quantum yield remained constant throughout the trials. Thus our analysis, in which we assume that the concentrations of the major species remain constant at their initial values while the minor species are in equilibrium, is probably a reasonably good representation of what was actually measured. Finally, the rate constants of the assumed reactions were determined by the standard procedure of varying the values of the rate constants until the differences between the calculated and experimentally measured quantum yields were minimized in the least-squares sense.

5. Chemical reaction set

The reaction set which finally yielded a satisfactory fit to the data of Wongdontri-Stuper *et al.* [3] is listed in Table 1. Recently several reactions of this set have been subjected to very careful studies in independent experiments. Their rate coefficients, taken from the sources indicated in the table, were considered to be known and were held fixed in the fitting process. The postulated reactions (2), (3) and (5) have already been discussed. Reactions (17a), (17b) and (17c) are also new. The rate constants of these reactions were determined from the fitting process.

Cl_2O_3 may form in the system via reaction (19f). The stability of this species is, however, debatable. According to McHale and Von Elbe [14] this species has the structure $\begin{smallmatrix}O\\O\end{smallmatrix}>Cl—ClO$ and is only loosely bound. But, according to Cox *et al.* [5], Cl_2O_3 may be stable especially at lower temperatures (see also ref. 3). In view of the conflicting opinions expressed about the stability of Cl_2O_3, reactions (19f) and (19r) were not included in fitting the room temperature data. The absorption cross section of Cl_2 at 365 nm in conjunction with the values of I_a given by Wongdontri-Stuper *et al.* allow the light intensity to be estimated. From the known absorption cross sections of the species Cl_2O, ClO_2 etc. it was easily verified that photoprocesses were of secondary importance for these species; they were therefore neglected.

6. Results and discussion

In Tables 2 and 3 are shown the theoretically predicted values of
$-\Phi(O_3)$ and $\Phi(OClO)$ for the various individual experimental data points at
room temperature reported by Wongdontri-Stuper *et al.* [3]. The agreement

TABLE 2

Experimental data and calculated quantum yields for O_3 decomposition at 297 K

Cl_2 (Torr)	O_3 (Torr)	O_2 (Torr)	N_2 (Torr)	$I_a \times 10^{-13}$ (cm^{-3} s^{-1})	Quantum yield $-\Phi(O_3)$	
					Experimental	Calculated
11.6	0.007	640.0	—	0.050	1.70	1.77
11.6	0.032	640.0	—	0.050	2.50	2.76
11.3	0.076	640.0	—	0.050	2.90	3.16
11.6	0.141	640.0	—	0.050	3.80	3.38
11.6	0.345	640.0	—	0.050	4.70	3.62
11.6	0.314	540.0	—	0.050	4.40	3.63
11.6	0.153	85.0	—	0.050	4.60	4.25
11.6	0.009	—	—	0.050	4.70	5.75
11.6	0.010	—	—	0.016	4.80	5.80
11.6	0.018	—	—	0.050	6.10	5.78
11.0	0.041	—	—	0.048	5.80	5.81
3.1	0.065	—	—	0.014	5.80	5.86
11.6	0.117	—	—	0.050	6.40	5.83
10.7	0.145	—	—	0.046	6.10	5.84
11.6	0.171	—	—	0.050	5.70	5.85
11.2	0.179	—	—	0.049	7.00	5.85
11.6	0.403	—	—	0.050	6.70	5.90
11.6	0.155	—	100.0	0.050	5.90	5.61
11.6	0.165	—	680.0	0.050	5.60	4.69
8.6	0.048	—	—	3.200	5.50	5.27
3.3	0.112	—	—	1.230	5.60	5.72
11.1	0.482	—	—	4.100	6.20	5.73
5.9	1.320	—	—	0.980	5.64	5.88
5.3	2.200	—	—	1.260	5.47	5.92
6.9	2.330	—	—	0.180	5.10	6.09
6.0	2.330	—	—	0.160	6.30	6.11
6.2	2.410	—	—	0.430	5.60	6.00
6.7	2.410	—	—	0.460	5.40	6.00
6.5	2.570	—	—	3.000	5.71	5.88
5.9	2.640	600.0	—	0.980	3.80	3.71
6.5	2.800	—	—	0.580	5.02	6.00
6.3	2.960	—	—	0.160	6.30	6.19
5.8	3.030	—	—	1.950	6.05	5.92
6.8	3.110	—	600.0	1.000	4.72	4.92
6.8	3.270	—	—	1.130	5.54	5.97
5.3	3.270	—	—	3.300	6.27	5.90
6.1	3.660	—	600.0	1.000	4.72	4.94
6.2	3.730	—	—	3.900	5.78	5.90
6.1	5.450	600.0	—	1.000	3.71	3.78
6.2	5.760	600.0	—	2.100	3.65	3.75

TABLE 3

Experimental data and calculated quantum yields for OClO formation at 297 K

Cl_2 (Torr)	O_3 (Torr)	O_2 (Torr)	N_2 (Torr)	$I_a \times 10^{-13}$ (cm^{-3} s^{-1})	Quantum yield Φ(OClO) Experimental	Calculated
7.8	3.42	–	–	4.34	0.069	0.101
6.9	3.40	–	–	3.84	0.130	0.102
12.9	3.81	–	–	7.19	0.082	0.101
12.8	4.08	–	–	7.12	0.085	0.101
16.8	4.66	–	545.0	9.38	0.062	0.076
13.7	5.48	630.0	–	7.67	0.073	0.090
13.4	5.91	–	–	7.47	0.125	0.101
14.1	5.95	630.0	–	7.08	0.088	0.091
13.4	5.95	–	–	7.47	0.120	0.101
14.0	5.97	630.0	–	7.81	0.079	0.091
13.1	6.38	–	–	7.30	0.090	0.101
13.8	6.87	–	545.0	7.71	0.100	0.076
13.9	7.08	630.0	–	7.76	0.073	0.091
13.0	7.90	–	–	7.28	0.130	0.101
13.0	7.93	630.0	–	7.45	0.089	0.091
14.3	7.94	–	–	7.99	0.091	0.101
13.6	8.01	–	–	7.58	0.115	0.101
13.0	8.21	–	–	7.28	0.087	0.101
13.2	8.91	–	–	7.39	0.082	0.101
13.2	9.41	630.0	–	7.39	0.112	0.092
13.4	9.57	–	–	7.47	0.120	0.101
14.9	9.61	630.0	–	8.32	0.077	0.092
14.0	10.30	–	–	7.84	0.111	0.101
15.2	10.50	–	545.0	8.49	0.071	0.076
16.1	10.70	630.0	–	9.01	0.068	0.092
14.2	11.30	–	–	7.91	0.081	0.101
13.0	11.40	–	–	7.28	0.087	0.101
13.5	12.50	–	545.0	7.55	0.086	0.076

between the predicted and observed quantum yields appears to be quite satisfactory and root mean square errors attain low values of 0.526 and 0.02 for $-\Phi(O_3)$ and Φ(OClO) respectively, reflecting in large measure the apparent scatter inherent in the data itself.

6.1. Reaction between ClO and ClO

A possible pressure effect on the reaction ClO + ClO → Cl_2 + O_2 has been explicitly incorporated through reactions (9f), (9r) and (10) and through reactions (2f), (2r) and (3a). The rate constant k_8 of reaction (8), ClO + ClO → product, should therefore correspond to the low pressure regime. In our studies we took k_8 to be slightly less than half the value recommended by Watson [7]. This was done at the suggestion of Watson [8] in view of recent results of Cox et al. [5]. The magnitude of k_{8c} was determined from Φ(OClO) and then k_{8a} and k_{8b} were tuned with reference to $\Phi(O_3)$ data.

Branching ratios $k_{8a}:k_{8b}:k_{8c}$ at room temperature obtained in this study are in excellent agreement with those obtained by Wongdontri-Stuper *et al.* [3]. Since identical experimental data are being used, this agreement can be considered to be a confirmation of the approaches adopted in these studies. Unfortunately there is a considerable difference of opinion among chemical kineticists about the importance of the molecular channel. This subject matter has been discussed in detail by Wongdontri-Stuper *et al.* [3].
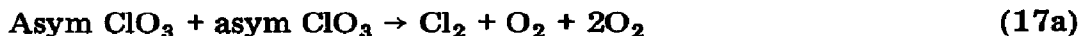
6.2. Role of asym ClO_3

The effectiveness of the postulated asym ClO_3 intermediary in suppressing the O_3 dissociation should jointly depend upon K_2 ($= k_{2f}/k_{2r}$) and k_3. With the given observational data, neither K_2 nor k_3 can be determined independently of each other. Our approach therefore was to estimate k_3 and then to adjust the equilibrium constant K_2. We used the simplest estimate, $k_3 \approx k_8$, and adjusted K_2 and the individual branches (3a), (3b) and (3c). In this attempt k_{3b} was adjusted mainly with the help of the $\Phi(OClO)$ data and k_{3a} and k_{3c} were tuned with reference to $-\Phi(O_3)$ values.

Our results suggest that the ClOO channel in reaction (3) is reduced by about a factor of 2 compared with the corresponding channels in reaction (8). The possible inequality $\Delta H_f(\text{asym } ClO_3) < \Delta H_f(ClO)$ could lead to the more unfavorable endothermicities in reactions (3b) and (3c). Reaction (3a) was, however, inferred to be relatively faster than reaction (8c). This contrasting behavior, of k_{3a} on the one hand and of k_{3b} and k_{3c} on the other, suggests that reactions (3b) and (3c) proceed through a transition state which is different from that involved in reaction (3a). It is reasonable to assume that reactions (3b) and (3c) are atom abstraction reactions involving linear transition states, whereas reaction (3a) involves a transition state of the type invoked by King *et al.* [15] to explain interhalogen formation.

An equilibrium constant K_2 with a value of 3.7×10^{-19} cm^3 molecules^{-1} was derived for reaction (2). This value is dependent upon the choice for k_3 because the observational data are sensitive only to the product K_2k_3 and not to individual K_2 or k_3 values. If k_3 is actually faster than assumed, then K_2 would be correspondingly smaller, and vice versa.

6.3. Reactions between two asym ClO_3 species

$$\text{Asym } ClO_3 + \text{asym } ClO_3 \rightarrow Cl_2 + O_2 + 2O_2 \qquad (17a)$$

$$\rightarrow ClOO + ClOO + O_2 \qquad (17b)$$

$$\rightarrow ClOO + OClO + O_2 \qquad (17c)$$

These reactions were included in the model as a possible explanation for the observation that $-\Phi(O_3)$ remains high even at O_2 pressures as high as 1500 Torr [2, 16]. At such high pressures a large fraction of ClO would exist as asym ClO_3 in our model and reactions (17b) and (17c) have the potential to

sustain the reported high $-\Phi(O_3)$. Inclusion of reactions (17a) and (17b) were also useful in understanding the low O_3 pressure data of Wongdontri-Stuper *et al.* [3]. This portion of the data (see Section 6.4) suggest that reactions (17a), (17b) and (17c) proceed at a rate about five times slower than that of the reactions between asym ClO_3 and ClO. This appears to be consistent with expectations.

6.4. Low O_3 pressure data

Data points for extremely low O_3 pressures are quite intersting inasmuch as, in these cases, O_2 was able to depress the quantum yield to values below 2. They suggest that there must be some reaction(s) which converts the active chain carriers, chlorine atoms and ClOO, into stable terminal species before they have a chance to react with ozone. One of the reactants in this reaction must also require the presence of O_2. Out of several possibilities tried, only reaction (5) (*i.e.* Cl + asym $ClO_3 \rightarrow Cl_2O + O_2$) succeeded in explaining the observation. We therefore feel that reaction (5) could be an important component of the possible chemistry of asym ClO_3. It suggests that the loosely bound O_2 adduct in asym ClO_3 can be easily displaced by reactive atoms and radicals.

7. Summarizing remarks and conclusions

It appears that the formation of an asym ClO_3 intermediary and its reactions with ClO might be responsible for the suppression of $-\Phi(O_3)$ by O_2. Other intermediaries, such as the Cl_2O_2 dimer, which may form in the system are not thought to explain the observations. The O_2 adduct which is loosely bound to ClO in asym ClO_3 seems to be easily displaceable by atoms and radicals such as chlorine.

Acknowledgments

References

1 R. G. W. Norrish and G. H. J. Neville, *J. Chem. Soc.*, (1934) 1864.
2 C. L. Lin, S. Jaffe and W. B. DeMore, unpublished results, 1976.
3 W. Wongdontri-Stuper, R. K. M. Jayanti, R. Simonaitis and J. Heicklen, *J. Photochem.*, *10* (1979) 163.
4 R. D. Rundel and R. S. Stolarski, *J. Geophys. Res.*, *81* (1976) 5759.
5 R. A. Cox, R. G. Derwent, A. E. J. Eggleton and H. J. Reid, *J. Chem. Soc.*, *Faraday Trans. I*, *75* (1978) 1648.
6 W. G. Alcock and G. C. Pimental, *J. Chem. Phys.*, *48* (1968) 2373.
7 R. T. Watson, *J. Phys. Chem. Ref. Data*, *6* (1977) 871.
8 R. T. Watson, personal communication, 1979.
9 R. D. Ashford, N. Basco and J. E. Hunt, *Int. J. Chem. Kinet.*, *10* (1978) 1233.
10 J. W. Birks, B. Shoemaker, T. J. Leck, R. A. Borders and L. J. Hart, *J. Chem. Phys.*, *66* (1977) 4591.
11 P. P. Bemand, M. A. A. Clyne and R. T. Watson, *J. Chem. Soc.*, *Faraday Trans. I.*, *69* (1973) 1356.
12 H. S. Johnston, E. D. Morris, Jr., and J. V. den Bogaerde, *J. Am. Chem. Soc.*, *91* (1969) 7712.
13 L. Thomas, *Radio Sci.*, *9* (1974) 121.
14 E. T. McHale and G. Von Elbe, *J. Phys. Chem.*, *72* (1968) 1849.
15 D. L. King, D. A. Dixon and D. R. Herschbach, *J. Am. Chem. Soc.*, *96* (1974) 3328.
16 W. B. DeMore, personal communication, 1976.