Electron attachment explodes Freon molecules: New possibilities for removing Freons from the atmosphere

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It is suggested that Freon molecules could be destroyed by the attachment of electrons from the plasma of a discharge produced in the troposphere (< 10 km). Experiments demonstrate that this destruction actually occurs. Microwave treatment of the atmosphere to protect the ozone layer from Freons is discussed in detail. Some preliminary experiments described here demonstrate a pronounced destruction of Freons in a microwave discharge.

The appearance of Freons in the atmosphere is one of the greatest menaces to the ozone layer. Since the Freons are chemically inert, they pass through the atmosphere into the stratosphere, to heights of 15–20 km, i.e., to the region of the ozone layer. There, the Freons are destroyed by uv light from the sun. They form radicals containing chlorine, which in turn begin to annihilate the ozone in chain reactions (up to 10^5 cycles) such as $Cl + O_3 \rightarrow ClO + O_2$, $ClO + O \rightarrow Cl + O_2$ (Ref. 1, for example).

If this disintegration occurred in the troposphere (below 10 km), the radicals would be blocked; they would be carried down by rain and thus would not reach the ozone layer. However, the Freons are not destroyed at these heights, since there is no uv light there. On the other hand, in specifically this region we could make use of the large electron affinity of Freon molecules. This affinity is so large that it is greater than

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the dissociation energy; the attachment of even a slow electron would result in an explosion of the Freon molecule. These attachment cross sections are so large as to be comparable to the gas-kinetics cross sections.[2,3] In some cases an electron can be "torn out of" a negative ion by a Freon molecule. There will be enough energy to cause dissociation, because most negative ions have a small binding energy.

It can thus be suggested that by producing large numbers of electrons and negative ions one could annihilate Freon molecules in a region of interest in the atmosphere.

There are a variety of ways to produce electrons, plasmas, and negative ions in discharges of various types. These discharges range from glow discharges, brush discharges, and streamers to high-current discharges in dc, quasisteady, pulsed, rf, and microwave fields. They could be laser discharges. They could be discharges which result from bursts of ionizing radiation, and of highly ionizing radiation, and of uv light which accompany such discharges and which form ionization halos.[4]

For an isolated electron the probability (w_{eF}) for a collision with a Freon molecule may be small, because of the low density of Freon molecules, $n_F \simeq 10^9$ cm^{-3}, and also because of the short electron lifetime with respect to attachment to other molecules (primarily oxygen): $\tau_e \approx 10^{-7}$ s, $w \simeq n_F \sigma v_e \tau_e \simeq 10^{-6}$. In many cases, however, electrons do not attach to other molecules, for any of the following reasons: These other molecules have small electron affinities, which render the attachment reversible; the electrons and the gas are heated in the discharges; metastable states of molecules and atoms are excited; and radiation from the discharge causes photodetachment of electrons. The electrons are thus lost primarily through recombination over times $\tau_r \simeq (\alpha_r n_e)^{-1} \simeq 10^{-3}$ s, having had time to participate in dissociative attachment to Freons (the latter molecules being destroyed in the process). We should also point out that the electron lifetimes in several discharges are longer because of various electron production mechanisms (e.g., associative ionization).

Let us take a closer look at microwave discharges, since it is a fairly simple matter to produce them at heights of 5–10 km. At such heights they would not cause any damage to the ozone layer (as discharges in the stratosphere would[5,6]), because they would be washed down by a rain of nitrogen oxides. Because of the sophisticated level of microwave technology and the high efficiency of existing microwave sources, this possibility looks completely feasible. The situation is particularly promising when we note that there are good possibilities for initially reducing the breakdown threshold, by means of various seeds, probing spheres, balloons, kites, and other simple devices. Microwave discharges have the further advantage over other plasma production methods (in particular, those which would employ entities that float in the air) that the height and volume of the air being treated can easily be changed.

Gas discharges can form nitrogen oxides, but only in amounts small in comparison with industrial amounts, and the harm to the ozone layer would be negligible, since the discharges are produced in the troposphere, and the by-products are washed down. Essentially none of these by-products reach the ozone layer (in contrast, the discharges in the stratosphere which are being planned for producing a plasma mirror[5] would cause direct harm to the ozone layer[6,7]).

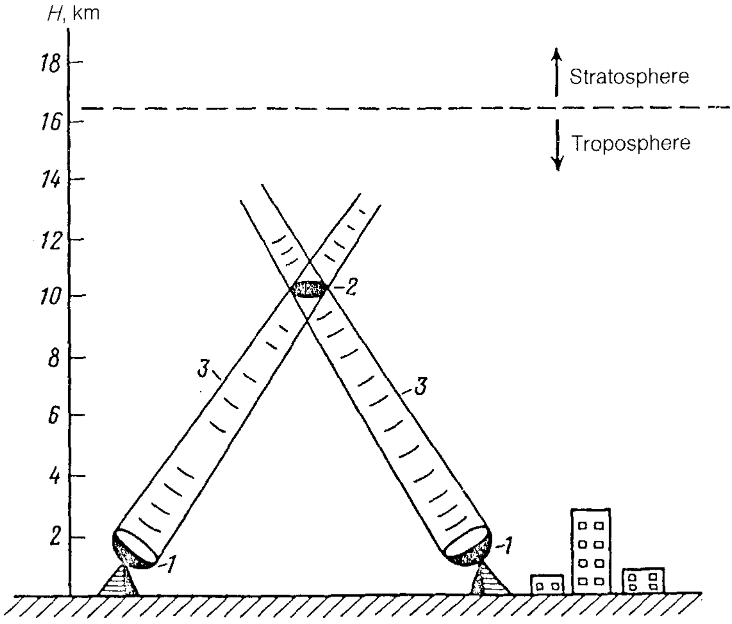

FIG. 1. Schematic diagram of a microwave method for removing a Freon impurity from the atmosphere. *1*—Ground-based antenna; *2*—microwave discharge; *3*—beam of microwave radiation.

Figure 1 illustrates the production of a localized discharge in a region of the atmosphere which requires treatment. The ground-based antennas form one converging microwave beam or several beams which intersect each other. The beam or beams would be focused at the desired height H. These would be intense pulsed microwave beams. The treatment consists of irradiating the volume of interest by a pulse train for a comparatively short time, corresponding to the time scale for the destruction of Freon molecules. As an example, we will go through an estimate for a height of 10 km. It is a simple matter to show (Ref. 8, for example) that, for a single microwave beam with a convergence angle $\sim 10^{-3}$ rad, the electron density in the breakdown wave is $\bar{n}_e \simeq 10^{10}$ cm^{-3}. For two beams one could achieve $\bar{n}_e \sim 10^{11}$ cm^{-3} or more, depending on the relative orientation of the electric vectors of the beams.[8]

If the critical breakdown field of air is exceeded by a factor of 1.5–2, the pulse length required to reach the specified plasma density would be 40–150 ns, and the radiation intensity would be 200–400 kW/cm^2. The specific energy deposition in the gas would be $\sim 10^{-4}$ J/cm^3. The pulsed radiation power required, if centimeter-range radiation is used, would be 20–40 GW.

Under the assumption $\bar{n}_c \gg n_{F_0}$ (where n_{F_0} is the initial density of the Freon molecules), we can easily estimate the relative change in the number of chlorofluorocarbon molecules which are destroyed in dissociative-attachment events in the recombining plasma:

$$n_F/n_{F_0} \simeq (1/\bar{n}_e)^\gamma/(1/\bar{n}_e + \alpha_r t)^\gamma,$$

where $\gamma \equiv k_D/\alpha_r$, k_D is the dissociative-attachment constant (which is on the order of 3×10^{-8} cm^3/s for $CFCl_3$), and α_r is the recombination coefficient. Setting $\alpha_r = 10^{-7}$ cm^3/s and $\bar{n}_e \simeq 10^{12}$ cm^{-3}, we find that if the recombination decay is maintained, then about 40% of the initial number of Freon molecules will have dissociated by a time 200 μs after the microwave pulse ends. If CF_2Cl_2 is treated, the same result will be achieved by irradiating a selected volume of the atmosphere by a train of five or six microwave pulses.

On the other hand, the low concentration of Freons in the troposphere means that the energy cost of destroying a single Freon molecule would be fairly high: tens of keV per molecule.[1)] Even at such a high cost, however, it would be possible to destroy several tens of metric kilotons of Freons in the troposphere over the course of a year at an average cw microwave power of about 10 GW. If there are local accidental releases of large masses of Freons, and if their concentration increases by a factor of 10^5–10^6, even a nonequilibrium microwave discharge in subcritical fields,[9] with an energy deposition $\sim$0.1 J/cm^3, could apparently be used successfully.

We have carried out a laboratory modeling of the removal of a Freon impurity from air by a localized microwave discharge. Figure 2 is a schematic diagram of the apparatus which we used. The microwave radiation (with a wavelength of 2 cm) is focused into a metal housing. The transverse dimension of the focus is 2.5 cm. The maximum intensity of the microwave radiation at the focus is 30 kW/cm^2. The length of the microwave pulse is 10–30 μs. The repetition frequency is 2 Hz. For convenience in the experiments and in the analysis of the results, the gas was enclosed in a 1-liter quartz chamber. The chamber was evacuated to high vacuum and then filled with a mixture of air and Freon 12. The working pressure of the mixture was varied over the range 10–500 Torr. The Freon partial pressure was varied over the range 3–150 Torr.

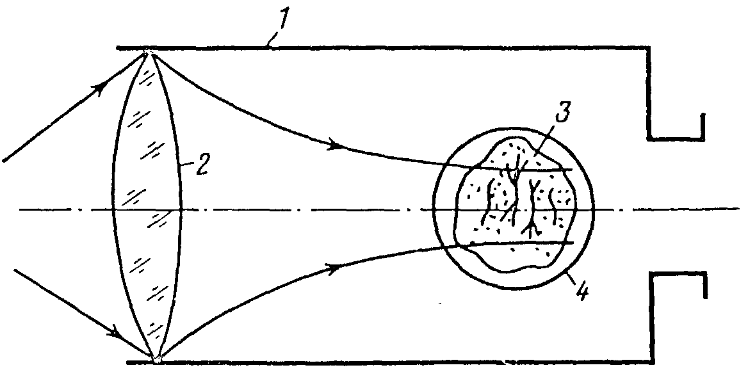

FIG. 2. Schematic diagram of a laboratory experiment to model the method proposed here for purifying the atmosphere. *1*—Metal housing; *2*—quartz lens, which shapes a converging microwave beam; *3*—microwave discharge; *4*—quartz chamber.

The Freon concentration was measured before and after the gas was irradiated with the train of microwave pulses. Figure 3 is a representative plot of the Freon concentration versus the irradiation time. The experimental estimate of the expendi-

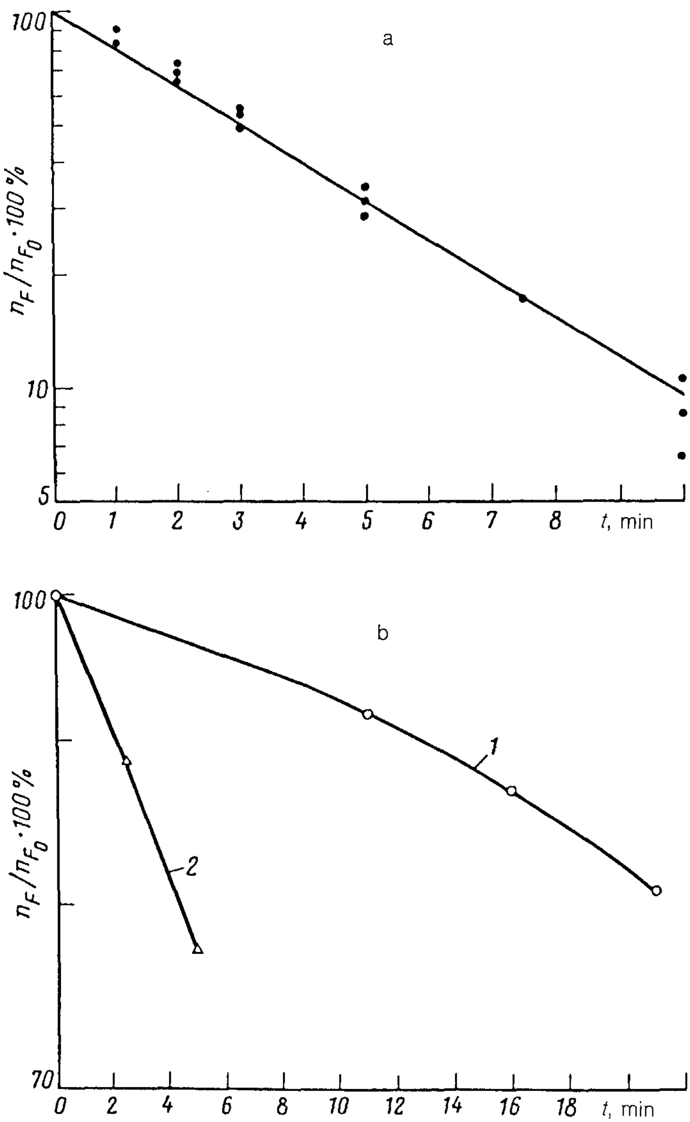

FIG. 3. Concentration of Freon molecules (CF_2Cl_2), divided by the initial value of this concentration, in a gas mixture irradiated by a train of microwave pulses versus the irradiation time. The pulse repetition frequency is 2 Hz; the pulse length is 30 μs; and the microwave power in the pulse is 325 kW. a—Freon in air, with a total pressure $p = 100$ Torr, and with a Freon partial pressure $p_{F_0} = 3.3$ Torr; b—Freon in air (1) or argon (2), with $p = 250$ Torr and $p_{F_0} = 1.7$ Torr.

ture of energy on the destruction of the Freon is ~1 keV/molecule. The experimental results can be explained in a consistent way in terms of the development of dissociative detachment in the plasma after the discharge. However, we do not rule out the possibility of a further destruction of the Freons by electron impact and by uv light from the discharge. The basic result of this analysis and these experiments, i.e., the conclusion that a microwave discharge has a pronounced effect on the Freon concentration, shows that more-detailed research on this method and an implementation of this method would be worthwhile. Purifying the atmosphere would be necessary even if the production of Freons were brought to a complete halt, since a very large amount of Freon has already accumulated in the atmosphere, and it will continue to enter the ozone layer in unacceptable amounts for a long time (~100 yr).

[1)]The disintegration of the Freons could apparently also be promoted by chemical reactions involving long-lived excited oxygen, produced in a discharge or by the photolysis (stimulated by a source of uv light) of a small part of the background ozone in the troposphere ($n_{O_3} \simeq 10^{12}$ cm^{-3}). This process might substantially reduce the amount of energy required.

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