Effects of Cosmic Rays on Atmospheric Chlorofluorocarbon Dissociation and Ozone Depletion

Q.-B. Lu and L. Sanche
Group of the Canadian Institutes of Health Research in Radiation Sciences, Faculty of Medicine, University of Sherbrooke, Sherbrooke, Canada, J1H 5N4

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Data from satellite, balloon, and ground-station measurements show that ozone loss is strongly correlated with cosmic-ray ionization-rate variations with altitude, latitude, and time. Moreover, our laboratory data indicate that the dissociation induced by cosmic rays for CF_2Cl_2 and $CFCl_3$ on ice surfaces in the polar stratosphere at an altitude of ~15 km is quite efficient, with estimated rates of 4.3×10^{-5} and 3.6×10^{-4} s^{-1}, respectively. These findings suggest that dissociation of chlorofluorocarbons by capture of electrons produced by cosmic rays and localized in polar stratospheric cloud ice may play a significant role in causing the ozone hole.

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In the stratosphere, the major source of atmospheric ionization is cosmic rays [1]. The effects of cosmic rays on the Earth's climate have recently been explored: a strong correlation between the intensity of cosmic ray flux and global cloud coverage is found, and is suggested to be due to enhanced cloud nucleation by ions produced by cosmic rays [2,3]. However, the effects of low-energy electrons produced in large quantities ($\sim 4 \times 10^4$ MeV^{-1}) by cosmic radiation have not attracted much attention. The detected density of free electrons is very low, since most electrons produced by cosmic rays are captured by stratospheric molecules to produce negative ions, mainly O_2^- with a density of $\sim 5 \times 10^3$ cm^{-3} [1]. However, in the winter polar stratosphere at altitudes of ~15 km a strong polar vortex isolates a continent-size body of air, in which polar stratosphere clouds (PSCs) of several kms in thickness form at very low temperatures [4]. These PSCs consist of water ice or nitric acid/ice particles with a major composition of H_2O [4]. It is well known that low-energy electrons can be self-trapped (solvated) in H_2O ices with large trapping cross sections [5–7]. The physics and chemistry induced by cosmic rays can therefore be considerably different in PSCs than in the general stratosphere. Studies of electron transfer reactions for molecules adsorbed on ice surfaces may therefore be of significant interest. In this Letter, we examine such reactions within the context of ozone depletion.

The emission of chlorofluorocarbons (CFCs), mainly CF_2Cl_2 (CFC-12) and $CFCl_3$ (CFC-11), into the Earth's atmosphere is known to cause ozone depletion with the suggested release of chlorine atoms via solar photolysis [4]. It has long been known that the cross sections for dissociative electron attachment (DEA) to CFCs at electron energies near 0 eV, e.g., $e^- + CF_2Cl_2 \rightarrow Cl^- + CF_2Cl$, are 3–4 orders of magnitude higher than the corresponding photodissociation cross sections [8,9]. Nevertheless, DEA processes are not believed to be significant in the general atmosphere, because the electron transfer rate constants from O_2^- to CFCs are low (10^{-10} $cm^3\,s^{-1}$) [10]. However, the situation is different in the winter polar stratosphere due to the presence of PSC ices. It has recently been observed that negative ion yields in electron-stimulated desorption of CF_2Cl_2 are greatly enhanced by factors of 10^2 and 10^4 when CF_2Cl_2 is coadsorbed with polar water or ammonia ice on a surface, respectively [11]. This was first assigned to transfer of electrons, self-trapped in water or ammonia ice, to CF_2Cl_2 followed by DEA. Such a reaction occurring in PSCs could produce Cl^- ions that can create Cl atoms by photodetachment or react with other species on the ice surface to produce Cl_2 that then photodissociates to destroy ozone [12]. As with electrons trapped in O_2^-, however, fully solvated electrons in H_2O are expected to have small transfer rate constants to reaction with CFCs, due to their localization in deep traps. As shown in recent experiments, instead, it is electrons temporarily localized at precursors of the fully solvated state in polar ice that have a large probability of transfer to CF_2Cl_2, leading to a large enhancement of DEA to CF_2Cl_2 [13].

In this Letter, we show that a strong correlation exists between ozone depletion and the ionization rate of cosmic rays in the atmosphere. Moreover, our laboratory results lead to dissociation rates, induced by cosmic-ray ionization for CF_2Cl_2 and $CFCl_3$ on ice surfaces in the polar stratosphere at an altitude of ~15 km, of 4.3×10^{-5} and 3.6×10^{-4} s^{-1}, respectively. Based on these findings, we propose a new pathway leading to the formation of the ozone hole.

We first show the correlation between ozone depletion and cosmic-ray ionization rate by analyzing data obtained from satellite, balloon, and ground-station measurements.

(1) The altitude dependence of cosmic ray ionization rate shows a maximum intensity at an altitude of 15–18 km (Fig. 1a), due to the production of secondary particles causing multi-ionization [14]. Correspondingly, the ozone hole is observed in the polar stratosphere at 15–18 km in the early spring (Fig. 1b). Also shown in Fig. 1b is the available data for ozone loss over northern midlatitudes (40°–53° N) from 1979 to 1998, exhibiting two

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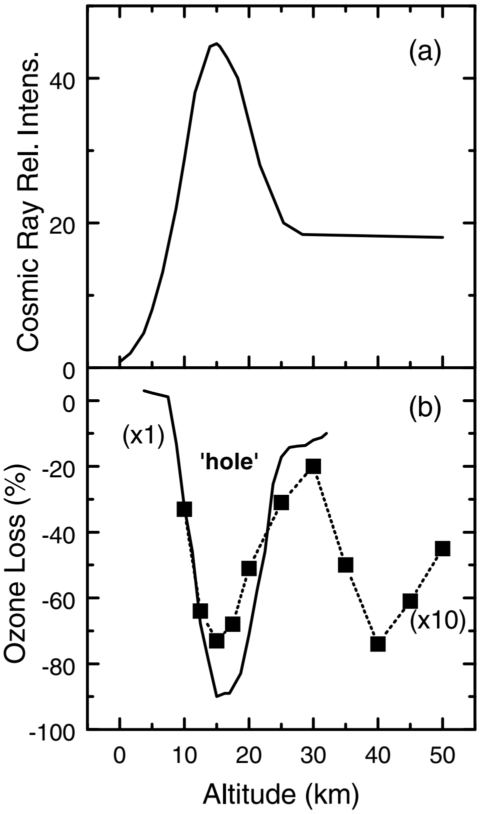


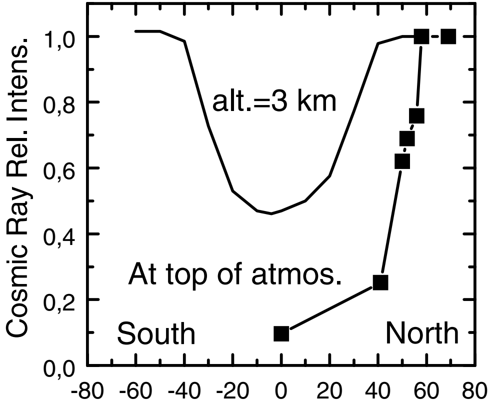
FIG. 1. (a) Cosmic-ray ionization-rate variation as a function of altitude (after Hayakawa [14]). (b) Dependence of ozone loss on altitude: The solid line is for the springtime ozone hole over Syowa, Antarctica, obtained by subtracting the altitude distribution curve of preozone hole (October, 1968–1980) from that of ozone-hole period (October, 1991–1997) (the curves from WMO Global Ozone Research and Monitoring Project–Report No. 44, p. 27); the squares represent the data for the altitude distribution of ozone loss per decade from 1979 to 1998 over northern midlatitudes (40°–53° N) (from Table I in [15]).

loss maxima in the upper (~40 km) and lower (~15 km) stratosphere, respectively [15]. No corresponding maximum exists at ~40 km in the ionization rate of cosmic rays (Fig. 1a), but the ozone loss maximum at this altitude agrees well with the photodissociation model calculation [15].

(2) The cosmic ray intensity has a strong latitude variation with maxima at the Earth's south and north poles due to geomagnetic field influences [14,16,17] (Fig. 2a). Correspondingly, the most severe ozone depletion also occurs at the polar stratosphere with high latitudes (Fig. 2b). The depletion over Antarctica is much larger than over Arctic in winter; this is generally attributed to the colder Antarctic stratosphere and the more stable Antarctic vortex [4], which produces more PSC ice particles. In contrast, the solar light intensity has a maximum at the geomagnetic equator and minima at the poles.

(3) The cosmic ray intensity has *an 11-year cycle,* in inverse phase to the solar activity cycle (Fig. 3a). Globally annual average ozone for a 13-year period (1979–1992), covering a full cosmic ray cycle, generally exhibits a corresponding variation: the lowest ozone concentration corresponds to the maximum of cosmic ray flux (Fig. 3b). The ozone level change is also determined by the rising rates of the stratospheric concentrations of CFCs and polar molecules (H_2O) (see below). This may result in the nonnegligible increase (~2%) in ozone loss from 1979 to 1982, in spite of the decreasing cosmic ray intensity in this period. However, if the mean value and the mean decreasing trend are removed, one can see that the ozone deviation is generally very close to that of cosmic ray flux (2%–3%).

(a) Latitude Effects of Cosmic Rays



(b) Ozone Loss vs Latitude

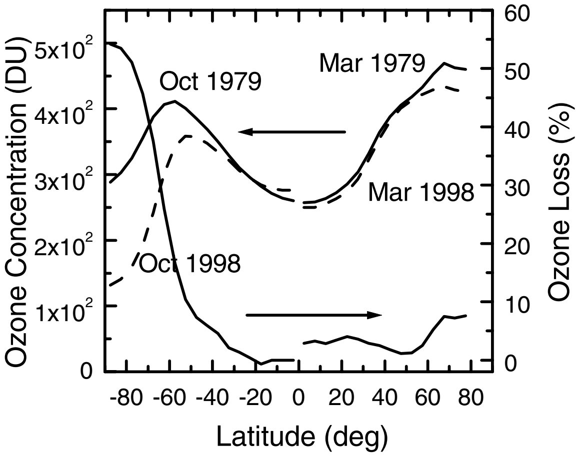


FIG. 2. (a) Cosmic-ray intensity as a function of latitude: the solid line reproduces data obtained at ~3 km from the sea level (after Pomerantz [16]); the solid squares are for the primary cosmic ray flux at the top of the atmosphere for northern latitudes (after Van Allen and Singer [17]). (b) Monthly average ozone concentrations in preozone hole (solid line for October 1979 for Antarctica and March 1979 for Arctic) and ozone hole period (dashed line for October 1998 for Antarctica and March 1998 for Arctic) and their difference (ozone loss) relative to the prehole value as a function of latitude (from NASA TOMS satellite database).

(4) The global concentration of CFC-12 measured by the CLAES instrument aboard the UARS satellite as a function of latitude also exhibits a strong depletion in the polar stratosphere: the upward bell shape of the CFC-12

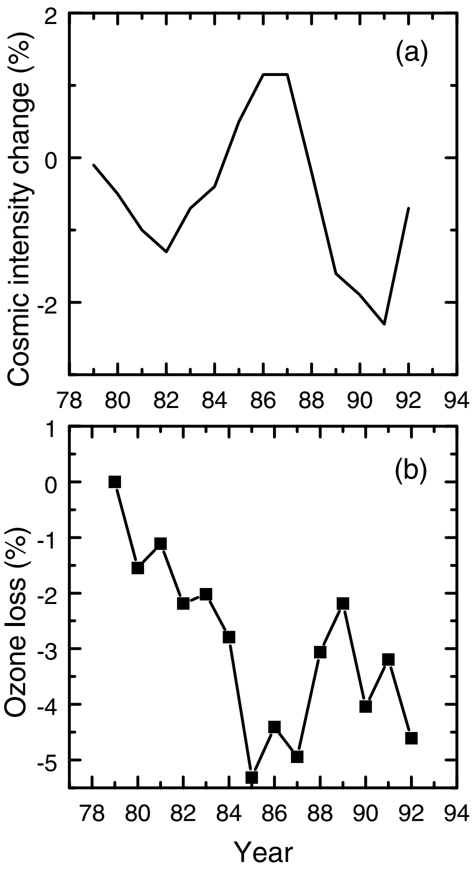


FIG. 3. (a) Variation of cosmic ray flux during the period of 1979–1992: the annual cosmic ray intensity is averaged from five station measurements, and the mean counting rate is subtracted (after Svensmark and Friis-Christensen [2]). (b) Annual average total ozone trend between 1979–1992 with latitudes from 0-65S; the data are normalized to the value of 1979 (from NASA TOMS satellite database).

distribution [18] generally corresponds to the downward bell of the cosmic ray intensity (Fig. 2a). Moreover, looking into the seasonal variations of the satellite images in closer detail, one can see that in March, the CFC-12 level in the polar stratosphere at altitudes between 16 and 20 km is higher ($\sim$360 pptv) over the fall Antarctica and is lower ($\sim$280 pptv) over the early spring Arctic. In contrast, an opposite phenomenon appeared in September: the CFC-12 concentration decreases to about 100 pptv in the early spring Antarctic stratosphere between 16 and 20 km, while it slightly rises to $\sim$320 pptv over the fall Arctic. These data indicate that CFCs are strongly destroyed in the winter polar stratosphere at altitudes below 20 km, although the destruction of CFCs over Arctic is much less than over Antarctic. Remarkably, it is dark (without sunlight but strongest cosmic rays) in the winter polar vortex over Antarctica and Arctic. Thus, we suggest that the depletion of CFCs may be related to cosmic radiation and the presence of PSCs in the winter polar stratosphere, but not to solar radiation.

We now calculate the dissociation rates induced by cosmic rays for CFCs physisorbed on H_2O ice in PSCs. The absolute DEA cross sections (σ) at $\sim$0 eV electrons for CF_2Cl_2 and $CFCl_3$ adsorbed on the surface of water ice have been measured to be $\sim 1.3 \times 10^{-14}$ cm^2 [13] and 1.1×10^{-13} cm^2 [19], respectively. These values are, respectively, 2 and 1 order of magnitude larger than the corresponding gaseous cross sections. These cross sections are measured at the sample temperature of 20 K, but it has been shown that the electron transfer rate from water ice to CFC molecules follows a non-Arrhenius relationship: $R(T) \propto \exp[-E_a/k_B(T - T_0)]$, with $E_a = 0.03$ eV and $T_0 = 224$ K [20]. From this relationship, we obtain $\sigma(190 \text{ K}) \simeq 10^3 \times \sigma(20 \text{ K})$ for the dissociation cross section at the stratospheric temperature of $\sim$190 K.

The rate, I, for the production of electrons by cosmic ray ionization is $\sim$45 cm^{-3} s^{-1} at an altitude of $\sim$15 km in the general stratosphere [21]. In the winter polar stratosphere, an estimate gives an ionization rate I on the surface of ice in PSCs of $45 \times \rho_{\text{ice}}/\rho_{\text{air}} \simeq 2.3 \times 10^5$ cm^{-3} s^{-1}, where ρ_{ice} and ρ_{air} are the densities of water ice and the air at the altitude of 15 km, respectively. As previously discussed [13], the lifetime of electrons localized at the precursor state of H_2O ice below 200 K should lie in the range of μs; here we take a value of 1 μs to obtain the precursor electron density $n(e_p^-)$ in PSC ice (i.e., 2.3×10^{-1} cm^{-3}). The electron-induced dissociation rate, R, of a CFC molecule on the surface of ice particles in a PSC is the product of σ at 190 K, $n(e_p^-)$ and the velocity $v(e_p^-)$ of electrons. For a precursor electron of 0.05 eV energy, R for CF_2Cl_2 is estimated to be $(10^3 \times 1.3 \times 10^{-14}\ \text{cm}^2) \times 2.3 \times 10^{-1}\ \text{cm}^{-3} \times 1.4 \times 10^7\ \text{cm}\,\text{s}^{-1} = 4.3 \times 10^{-5}\ \text{s}^{-1}$; the corresponding R for $CFCl_3$ is 3.6×10^{-4} s^{-1}. These estimates therefore indicate that in the winter lower stratosphere, electron-induced CFC dissociation on the surface of ice particles in PSCs by cosmic rays is very fast, with lifetimes of CFCs in the order of hours.

The enhanced effect for dissociation of CFCs on ice surfaces under polar stratospheric conditions should also occur for nearly all chlorine-containing species. This is because every chlorinated compound has a DEA resonance near 0 eV [8,9]. We have confirmed by experiments that the DEA cross section near 0 eV for HCl on the surface of H_2O ice is 2 orders of magnitude larger than the gaseous value [22].

Based on the above facts, we propose a new pathway contributing to the formation of the ozone hole. In ice particles of PSCs, low-energy electrons produced by high-energy particles created by cosmic rays experience inelastic scattering and rapidly reach subexcitation energies (a few tenths of an eV) [23]. Subsequently, subexcitation electrons rapidly become localized in precursor states of the fully solvated state in ice. Once a chlorine-containing molecule is adsorbed or trapped at the surface of ice, transfer of the precursor electron to the molecule has, according

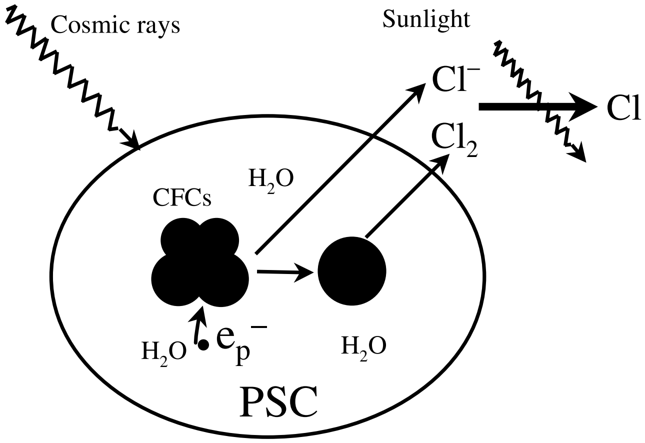


FIG. 4. Suggested scenario leading to ozone depletion: cosmic-ray radiation produces an electron in icy grains in dense polar stratospheric clouds, which becomes a precursor to the solvated electron. The electron in the precursor state breaks a CFC to produce a Cl^- ion, which exists either as free ion, or as Cl_2 formed in a reaction with other species on PSCs. Then, sunlight produces Cl atoms by photodetachment of Cl^- or photodissociation of Cl_2 to destroy O_3 via (Cl, ClO) reaction cycles.

to our measurements, a very high probability to occur and cause the dissociation of the molecule. This process is illustrated in Fig. 4. The resulting Cl^- ions can accumulate on surfaces of PSC ice particles or react with other species to produce Cl_2 in the winter polar stratosphere [12]. By photodetachment or photodissociation, Cl^- or Cl_2 can, respectively, be converted into Cl atoms that destroy O_3, upon the rise of sunlight in the spring.

According to our findings, the Cl^- yield (and thus the Cl yield) depends not only on the CFC concentrations in the stratosphere, but also on the densities of other molecular species, especially polar species such as H_2O. Because of the increasing emission of greenhouse gases (mainly CO_2) into the atmosphere, the sea ice in the Antarctic and the Arctic oceans is thinning. The concentration of H_2O in the lower stratosphere (16–20 km) has been observed to be increasing [24]. According to our suggestion, this may lead to more severe ozone depletion and a significant delay in the eventual recovery of the ozone hole.

In summary, we find that there exists a strong and straightforward correlation between ozone depletion (CFC destruction) and cosmic ray flux in both the latitude and altitude distributions, as well as in calendar year variations. Our laboratory measurements provide a sound physical basis for these observations. Our estimates indicate that electron-induced dissociation of CFCs in PSCs, due to cosmic ray radiation, is a very efficient process for destruction of CFCs in the lower polar stratosphere. These findings may offer a new scenario contributing to the formation of the ozone hole. A more complete discussion will be given in a forthcoming publication [19].

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