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# **The Role of Low-Energy ( $< 20$ eV) Electrons in Atmospheric Processes**

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## 1.0 Introduction

The literature on atmospheric atomic and molecular processes is, perhaps unsurprisingly, heavily populated with photochemical studies. The iconic example is the photon-induced dissociation of chlorofluorocarbons, leading to the formation of chlorine atoms that catalyze the destruction of stratospheric ozone.[1] By comparison, the literature on electron-induced atmospheric processes is more limited,[2] particularly for processes induced by low-energy (< 20 eV) electrons. Yet, the ionosphere, a significant component of earth's atmosphere, is characterized by the presence of a high density ( $10^2 - 10^6 \text{ cm}^{-3}$ ) of thermal (< 1 eV) free electrons.[3] Bombardment of earth's upper atmosphere by sunlight (vacuum ultraviolet (VUV) (6.2 – 12.4 eV) but not visible light), solar wind particles (energetic electrons and protons), magnetospheric particles, and cosmic ray particles (high-energy protons and atomic nuclei), causes ionization that results in the production of copious numbers of low-energy secondary electrons.[4] While secondary products such as excited species and ions produced from the high-energy radiation interacting with molecules cause some radiation damage, it is the low-energy secondary electron-molecule inelastic collisions that are thought to be the primary driving forces in a wide variety of radiation-induced chemical reactions.[4]

Low-energy electron-induced processes (excitation, dissociation, and ionization) in the terrestrial atmosphere may influence a wide range of complex phenomena, including chemical reactions. Recent results of radio- and gamma-emission measurements conducted during thunderstorms suggest that lightning initiation in earth's atmosphere may be mediated by low-energy electrons produced by cosmic rays.[5] The role of cosmic rays in initiating lightning showers has now become an area of active research.[6] According to a recent hypothesis, [7-10]

the subject of significant current controversy,[11, 12] low-energy electrons produced by cosmic rays, in addition to UV-VIS photons from the sun, interact with chlorofluorocarbons to produce chlorine atoms that subsequently destroy ozone in the Antarctic. Dissociative electron attachment (DEA) to  $\text{NaHCO}_3$  and  $\text{NaCO}_3$  has been identified as a possible source of free Na atoms in the sporadic (sudden) sodium layers (SSL) found in earth's upper atmosphere.[13] Low-energy electrons produced by the interaction of cosmic rays with molecules present in the earth's atmosphere may contribute to enhanced aerosol nucleation, the first step in cloud formation. This cosmic-ray-induced cloud-formation mechanism is a subject of active research because this process may influence global warming.[14]

A number of important extraterrestrial atmospheric processes are also thought to be mediated by low-energy electrons. Dissociative electron attachment to HCN has been identified as the first step in the production of heavy ( $m/z \sim 10,000$ ) negative ions detected by the Cassini Plasma Spectrometer in the upper atmosphere of Titan.[15] Low-energy electron-induced enhanced production of  $\text{H}_2\text{O}_2$  is postulated to have implications for life and habitability on Mars.[16]

Following a brief introduction to the vertical structure of earth's atmosphere and the ionosphere, we present in this chapter an overview of low-energy ( $< 20$  eV) electron-induced processes relevant to terrestrial and extraterrestrial atmospheric processes.

## **2.0 Vertical Structure of Earth's Atmosphere**

Earth's atmosphere is generally divided into four layers based on how the temperature changes with height (Figure 1.0). The troposphere, the bottom layer extending up to  $\sim 10$  km in altitude, is characterized by a temperature decrease with height increase. Because this first layer contains the preponderance of atmospheric mass, particularly the majority of atmospheric water

vapor, the troposphere is the region largely responsible for Earth's weather. The stratosphere (10–50 km altitude), the second layer, still contains appreciable concentrations of many of the major tropospheric gases, but also includes the ozone layer (~25 km altitude) which absorbs ultraviolet radiation from the sun. The temperature in the stratosphere generally increases with increasing height. Except for the occasional polar stratospheric clouds, also known as nacreous clouds, the stratosphere is generally devoid of clouds. The mesosphere (50–80 km altitude) is characterized by temperature decrease with increasing height. This third layer is arguably the least-studied of the layers due to its altitude being too high for most planes and too low for satellites.[17] The temperature in the fourth layer, the thermosphere, increases with height to values that exceed 1000 °C.

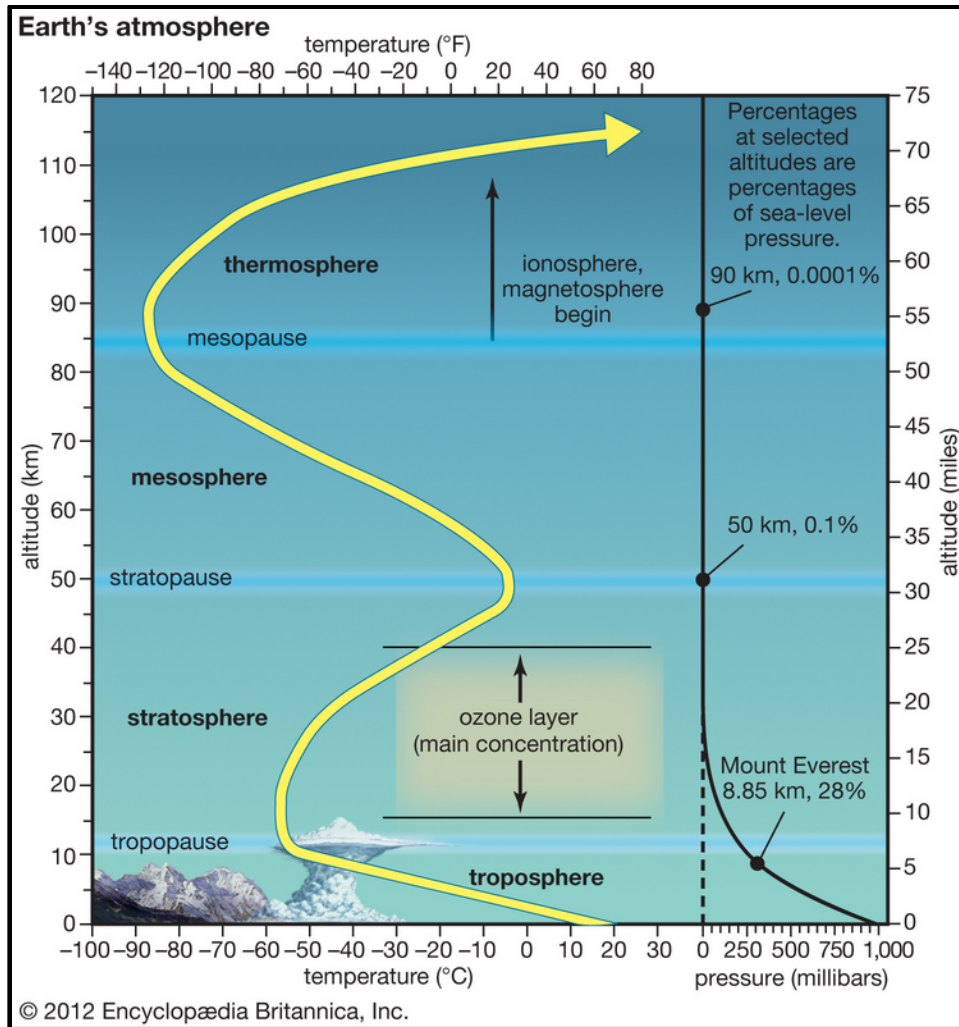


Figure 1.0  
Vertical structure of earth's atmosphere[18]

The ionosphere (60–300 km altitude), the electrically conducting region of the mesosphere and thermosphere, plays an important role in the propagation of radio waves and the formation of auroras. Based on the ion density, which is equal to the electron density, the ionosphere is further subdivided into three regions. The D layer at altitudes of 60 to 85 km, the lowest ionospheric region, is situated in the mesosphere. The D region disappears during night time because the relatively high pressures allows for the attachment of electrons to molecules to form negative ions such as  $\text{CO}_3^-$  and  $\text{NO}_3^-$ . [3] Photo detachment effectively competes with this process during daytime. The D-region is characterized by an electron density of  $10^2 - 10^3$

$\text{cm}^{-3}$ . [19] The E-region with an electron density of  $\sim 10^5 \text{ cm}^{-3}$ , spans the altitudes between 85 and 140 km. The formation of this region is mediated by soft x-rays and EUV ( $\lambda < 100 \text{ nm}$ ) from the sun. The E-region vanishes at night because of the fast reaction between electrons and the positive ions of oxygen and nitrogen. The dominant molecular ions in this region are  $\text{NO}^+$  and  $\text{O}_2^+$ . [3] The F-layer, the uppermost portion of the ionosphere observed at altitudes above 140 km, is characterized by an electron density that can exceed  $10^6 \text{ cm}^{-3}$  at some locations. [17] While the lower region of the F layer disappears at night, the higher region persists throughout the night. [3]

### **3.0 Auroral Emissions Driven by Low-Energy Electron-Induced Vibrational Excitation**

The aurora borealis and aurora australis emissions, displays of shimmering bands and filaments of light in the night sky, result from collisions between atoms/molecules in the earth's upper atmosphere and energetic magnetospheric/solar wind particles mostly consisting of electrons. [20] For example, the most distinctive green color at 557.7 nm in the auroral emissions results from excited oxygen atoms at an altitude of 90 to 150 km undergoing a forbidden transition from  $^1\text{S}$  to  $^1\text{D}$ . Calculations suggest that  $\sim 30\%$  of this auroral feature is due to direct electron impact. [21] Auroral emissions in the UV region have been attributed to radiative decay following electron impact electronic excitation of molecular nitrogen. [22]

Low-energy (1–3 eV) electrons are hypothesized to play an important role in infrared auroral emissions. [23] Previously such emissions were attributed exclusively to chemiluminescence from vibrationally excited NO produced by the reaction of excited O and N atoms. The newly proposed mechanism involves electron capture by NO to form a temporary negative ion (TNI) which subsequently undergoes, within 10–100 femtoseconds, autodetachment to form a vibrationally excited NO molecule. [23] Because the formation of the TNI is a resonance process, the vibrational excitation cross section at energies below 5 eV for NO is

enhanced, as shown in Figure 2.0. Statistical equilibrium calculations suggest that over 30% of the infrared auroral emissions can be attributed to photon emission near 5  $\mu\text{m}$  from the low-energy electron-induced vibrationally excited NO.[23] Complete agreement between calculations and rocket measurements, however, has not yet been achieved.[24]

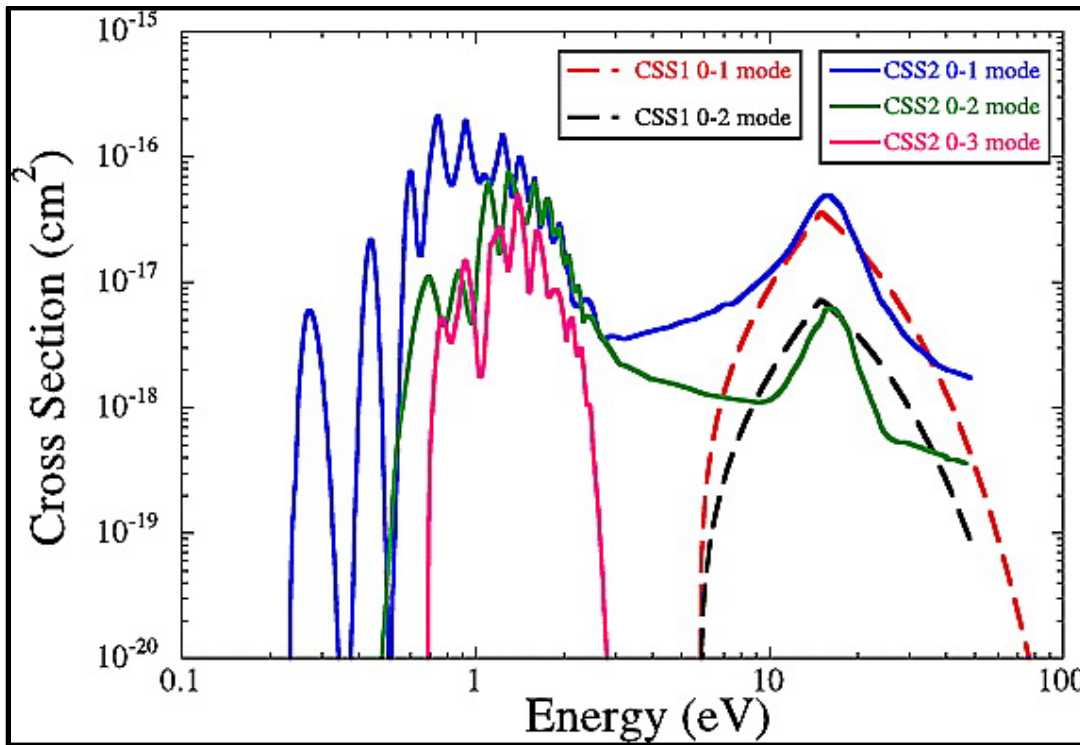


Figure 2.0  
Vibrational excitation cross section as a function of incident electron energy. Results which take into account the formation of the TNI are labeled CSS2 and are shown as solid lines.[23]

#### 4.0 Role of Low-Energy Electrons in Triggering Lightning

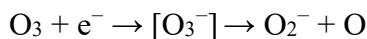
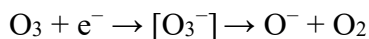
Electrical breakdown in the atmosphere is a prerequisite for lightning flash, an electrical discharge between a thundercloud and Earth.[25] It has been long known that the measured electric fields in thunderclouds are about ten times smaller than that required for electrical breakdown.[26] Although statistical analysis of cosmic ray showers do not support “relativistic runaway electron avalanche” mechanism initiating lightning,[6] results of radio and gamma



emission measurement conducted during thunderstorms suggest that lightning initiation in earth's atmosphere is triggered by "runaway breakdown" which is mediated by an avalanche of low-energy secondary electrons produced by cosmic rays.[5] In addition to cosmic rays, studies indicate that high speed solar wind particles, consisting mostly of energetic electrons and protons, increase terrestrial lightning rates, which is estimated to be about 100 times per second.[27] This enhanced triggering of lightning by solar wind particles is also likely due to the cascade of low-energy secondary electrons producing "runaway breakdowns" similar to those produced by cosmic rays. A recent publication, however, notes that "processes leading to the initiation of lightning flashes are still not fully understood." [28]

### **5.0 Low-Energy Electron-Induced Production of Negative Ions in the Ionosphere**

Dissociative electron attachment to ozone (O<sub>3</sub>) present in the D-region of the ionosphere yields the anions O<sup>-</sup> and O<sub>2</sub><sup>-</sup>. [29]

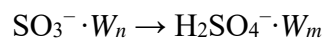
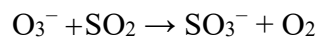
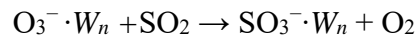
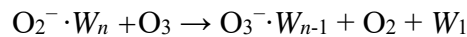


These oxygen anions react with ozone to yield the ozone negative ion (O<sub>3</sub><sup>-</sup>) which subsequently reacts with CO<sub>2</sub> and NO to produce the three most important negative ions in the atmosphere (CO<sub>3</sub><sup>-</sup>, NO<sup>-</sup> and NO<sub>3</sub><sup>-</sup>). [30]

### **6.0 Enhanced Aerosol Nucleation Induced by Low-Energy Electrons?**

A preponderance of evidence indicates that global warming is driven by the release into the atmosphere of greenhouse gases such as carbon dioxide during the burning of fossil fuel. Although experiments to simulate aerosol nucleation, conducted in the Cosmics Leaving Outdoor Droplets (CLOUD) chamber at CERN, the European Organization for Nuclear Research, suggest that cosmic rays enhance cloud formation, [31] the extent to which this

phenomenon may influence global warming remains uncertain.[32] Up to 50% of the global cloud condensation nuclei may derive from nucleation of aerosol particles.[33] While changes in the sun's brightness are not thought to contribute more than 10% to global warming in the twentieth century,[34] the changes in solar activity influence the flux of cosmic rays reaching the earth's surface. A controversial hypothesis, put forward at the turn of the twenty-first century, suggests a correlation between global temperatures and solar activity.[14] According to this proposition, increased solar activity in the past several decades contributed to a cosmic ray flux reduction which in turn caused an increase in global temperatures because of a decrease in cloud formation.[14] The attachment of cosmic-ray induced low-energy secondary electrons to molecular oxygen is thought to produce  $O_2^-$  which attracts water molecules ( $W_n$ ) to yield the  $O_2^- \cdot W_n$  complex. This step is posited to enhance the production of sulfuric acid aerosol particles via the following mechanism:[35]



Although ionizing radiation has been recently shown to produce large ( $> 50$  nm) cloud condensation nuclei (CCN),[36] a multiple regression analysis of temperature and galactic cosmic ray (GCR) flux suggests that “there is little empirical evidence that links GCR to the recent global warming.”[37] A recent study found no significant correlation between global albedo, the fraction of the incident light that is reflected by a surface, and cosmic rays.[38] More recent experiments conducted in CLOUD at CERN also suggest that cosmic rays have little influence on the formation of sulfuric acid-dimethylamine clusters thought to be important for

cloud formation.[39] Nevertheless, the role of cosmic ray-derived low-energy electron-induced aerosol nucleation remains an active area of research.[40]

## **7.0 Chlorofluorocarbon dissociation by low-energy electrons: Implications for the ozone hole?**

According to a hypothesis proposed at the turn of the 21<sup>st</sup> century, low-energy electrons produced by cosmic rays, in addition to UV-VIS photons from the sun, interact with chlorofluorocarbons (CFCs) to produce chlorine atoms that subsequently destroy ozone in the Antarctic. Chlorofluorocarbons are man-made chemicals which were commonly used in refrigerants and aerosol sprays starting in the late 1920s.[41] Most common among the CFCs are CFC-11 (CFCl<sub>3</sub>) and CFC-12 (CF<sub>2</sub>Cl<sub>2</sub>). Commercial and domestic use of CFCs led to their release into the atmosphere where they are a major culprit in the formation of the ozone hole in the stratosphere. The weak carbon-halogen bonding in CFCs allow for facile release of halogen atoms which subsequently destroy ozone.[1] Due to their strong impact on stratospheric ozone, the use of CFCs was targeted for elimination by the Montreal Protocol which called for signing nations to halt use of several CFCs (including CFC-11 and CFC-12) by 1996.[42] CFCs, initially replaced by hydrochlorofluorocarbons (HCFCs), have more recently been replaced by hydrofluorocarbons (HFCs) which have much lower ozone depletion potentials than CFCs and HCFCs, and contain no chlorine which dominates ozone processing.[43] However, despite reduction in their use and release to the atmosphere, CFCs remain as the leading cause of ozone depletion because of their long lifetimes in the atmosphere (of the order of 50 to 100 years).[43]

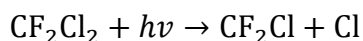
### **7.1 Depletion of Ozone: Photochemical Mechanism**

*Stratospheric Reactions:*

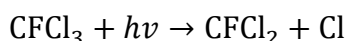
The traditionally accepted explanation for ozone depletion is that solar-produced UV photons (predominantly for wavelengths in the range of 175 – 220 nm [44]) lead to the dissociation of CFC molecules into a halogen and a free radical. This is the first step in a self-sustaining chain reaction which involves the processing and resulting destruction of O<sub>3</sub> initiated by the released halogen atom.

In 1974, Molina and Rowland proposed the following mechanism for O<sub>3</sub> depletion in the stratosphere starting from CFC<sub>13</sub> and CF<sub>2</sub>Cl<sub>2</sub> molecules:[45]

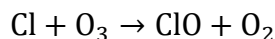
Production of free halogen atom:



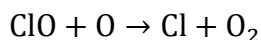
and



Depletion of ozone:

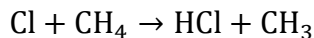


Formation of free halogen atom:

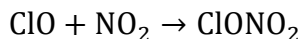


The final step in this reaction releases the Cl atom to react with another O<sub>3</sub> molecule which allows for a continuation of the ozone depletion cycle.

While the reactions delineated above show the fundamental pathway for ozone depletion, other reactions also play an important role in determining the concentration of stratospheric ozone. Other molecules present in the stratosphere, such as methane (CH<sub>4</sub>) and nitrogen dioxide (NO<sub>2</sub>), can, at least temporarily, halt the depletion cycle by incorporating Cl into less reactive molecules such as HCl and ClONO<sub>2</sub> (chlorine nitrate) through the following gas-phase reactions:[45, 46]



and



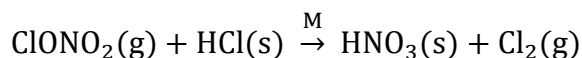
In the absence of additional factors, these termination reactions alone should ensure that CFCs do not lead to the observed dramatic effect on ozone as the reactive Cl is removed from the ozone-depletion chain and incorporated into fairly inert molecules.

*Polar Stratospheric Clouds:*

Ozone depletion undergoes a yearly cycle during which depletion is most pronounced in polar springs (e.g., Antarctica during the September through early November months).[47] Researchers have tied the cyclical changes to a combination of processes which start with the Antarctic winter.

With the onset of winter, temperatures within the stratosphere drop, leading to the formation of polar stratospheric clouds (PSCs). These clouds contain both water ices as well as nitric acid trihydrate (NAT) particles which consist of water and nitric acid in a molar ratio of 3:1.[48] The formation of  $\text{HNO}_3 \cdot 3\text{H}_2\text{O}$  ices are particularly important as these clouds remove nitrogen from atmosphere which can otherwise be used to remove Cl from the ozone-depletion chain through the creation of inert compounds.

Within these clouds, heterogeneous reactions, mediated by an additional molecule/particle (M), lead to the release of reactive  $\text{Cl}_2$  from the inert HCl and  $\text{ClONO}_2$  compounds:[48-50]



Laboratory experiments emulating PSC conditions have successfully reproduced the above heterogeneous reaction. The experiments also indicate that purely gas phase reactions without

mediating particles (e.g., particles comprising PSCs) are insignificant pathways for Cl<sub>2</sub> formation.[51-53]

In addition to the formation of PSCs at the beginning of winter, a polar vortex also forms. A polar vortex is a cyclone which forms due to diminished polar sunlight leading to stratospheric radiative cooling. High velocity winds of order 100 m/s are produced by this polar cooling because of the resulting pressure gradient between the cool polar region and the warmer mid-latitude.[48] The Coriolis effect causes the winds to form a vortex around the pole. This polar vortex acts to isolate the atmospheric content inside the vortex from that outside, trapping PSCs, reactants, and products within the vortex core. The Cl<sub>2</sub> molecules released through heterogeneous reactions are contained within the vortex core near the pole.

As the polar spring arrives (beginning of September for Antarctica) and PSCs vanish, solar UV radiation returns to the poles and photodissociates Cl<sub>2</sub> releasing single Cl atoms which can once again start the ozone depletion cycle for air trapped within the polar vortex. By late spring (~ November for Antarctica), the polar vortex begins to disappear as the polar stratosphere begins to warm and the atmospheric air previously contained within the polar vortex is dispersed through the atmosphere. While the ozone is depleted most notably by Earth's poles during winter months, the overall depletion is felt extensively as the initially localized ozone depletion results in extended-latitude ozone thinning with atmospheric mixing after polar vortexes disappear.

## **7.2 Depletion of Ozone: Cosmic Ray Driven Electron (CRE) Mechanism**

Cosmic rays interacting with matter create large numbers of low-energy electrons. This phenomenon occurs within earth's atmosphere, where it is estimated that cosmic rays create  $\sim 4 \times 10^4$  electrons per MeV.[54] After Rowland and Molina's 1974 study pointing to CFC-led

depletion of the ozone, the majority of research focused on photodissociation of CFCs. However, studies also began on electron interactions with CFCs.

Gas-phase experiments show that low-energy electrons can release chlorine from CFC-11 and CFC-12. Thus, the first step needed in initiating the ozone-depletion cycle can be started by UV photons or low energy electrons. Specifically, in irradiating  $\text{CFCl}_3$  and  $\text{CF}_2\text{Cl}_2$  molecules with low energy electrons ( $< 10$  eV), Illenberger et. al. find DEA resonances associated with  $\text{Cl}^-$  formation at 0 eV for  $\text{CFCl}_3$  and 0.55 eV for  $\text{CF}_2\text{Cl}_2$ . [55] The associated DEA cross-sections for  $\text{Cl}^-$  formation are determined to be  $9.5 \times 10^{-15} \text{ cm}^2$  and  $1.1 \times 10^{-16} \text{ cm}^2$  for  $\text{CFCl}_3$  and  $\text{CF}_2\text{Cl}_2$  respectively. [55] These cross-sections are impressively  $\sim 2$  to 6 orders of magnitude larger than UV-absorption cross-sections of  $10^{-18} \text{ cm}^2$  at 175 nm to  $10^{-20} \text{ cm}^2$  at 220 nm for both  $\text{CFCl}_3$  and  $\text{CF}_2\text{Cl}_2$  compounds at room temperature. [56] These initial gas phase studies show that low-energy electrons will readily dissociate CFCs and release  $\text{Cl}^-$  which can then shed the excess electron and initiate the ozone-depletion cycle. Furthermore, the studies show that CFCs can potentially be dissociated more readily by electrons than by UV photons. However, while cosmic rays produce large numbers of secondary electrons in the stratosphere, the actual density of free electrons ( $\sim 10^3$  per  $\text{cm}^3$  near 85 km and under 10 per  $\text{cm}^3$  below 60 km [57, 58]) is small since neutral molecules such as  $\text{O}_2$  readily absorb free electrons to become negative ions. [59]

#### *Initial Cosmic-Ray-Driven Electron Mechanism*

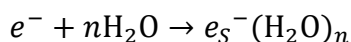
In 1999, Lu and Madey studied dissociation yields of  $\text{Cl}^-$  from low-energy electron-induced reactions of  $\text{CF}_2\text{Cl}_2$  coadsorbed with condensed polar and nonpolar gases on a Ru(0001) substrate at 25 K, using electron-stimulated desorption ion angular distribution (ESDIAD) measurements. [8] The low-energy electrons in these experiments were produced by bombarding

the Ru(0001) substrate with 250 eV electrons. Lu and Madey found that when CF<sub>2</sub>Cl<sub>2</sub> is coadsorbed with polar gases (such as H<sub>2</sub>O and NH<sub>3</sub>), Cl<sup>-</sup> yield is enhanced by factors of ~10<sup>2</sup> (for H<sub>2</sub>O) to ~10<sup>4</sup> (for NH<sub>3</sub>) as compared to when CF<sub>2</sub>Cl<sub>2</sub> is coadsorbed with nonpolar gases such as Xe, Kr, and Ar.[8]

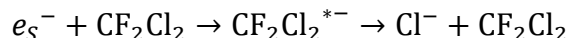
The difference in Cl<sup>-</sup> yields between the polar and nonpolar media was initially attributed to solvation of the secondary electrons in the polar media. The solvation process involves the reorienting of polar molecules in response to the presence of a free electron, ultimately leading to the electron being trapped within a Coulomb potential created by surrounding polar molecules. In polar liquids, this process may appear obvious as molecules can easily move and respond to local forces. However, even in polar ices, solvation can also occur [60] where the relatively weak intermolecular dipole-dipole forces will still allow for molecular reorientation in the presence of the electron. Such solvation is not expected for condensed nonpolar media.

Lu and Madey proposed that the solvated electron ( $e_s^-$ ) in a condensed polar medium, such as water, could then tunnel through the polar media onto CF<sub>2</sub>Cl<sub>2</sub> creating a vibrationally excited negative ion (CF<sub>2</sub>Cl<sub>2</sub><sup>\*-</sup>), which would subsequently dissociate:[8]

Electron solvation:



Dissociation of CF<sub>2</sub>Cl<sub>2</sub>:

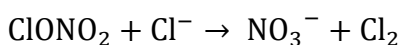


This last step releases Cl<sup>-</sup> and so indicates a potential pathway for electron-initiated CFC dissociation to start the ozone depletion chain. Furthermore, Lu and Madey estimated dissociation cross-sections for CF<sub>2</sub>Cl<sub>2</sub> coadsorbed with H<sub>2</sub>O to be ~1 × 10<sup>-14</sup> cm<sup>2</sup> and for NH<sub>3</sub>



to be  $\sim 6 \times 10^{-12} \text{ cm}^2$ . [7] These cross-sections are  $10^2$  to  $10^4$  times larger than the gas-phase DEA cross-section for  $\text{CF}_2\text{Cl}_2$ .

Based on these experiments (showing very large dissociation cross-sections for  $\text{CF}_2\text{Cl}_2$  coadsorbed with polar media), Lu and Madey suggested a new possible pathway for ozone depletion which begins with cosmic rays from outer space. Cosmic rays interact with the atmosphere creating large numbers of low-energy electrons. During the polar winter, these low-energy electrons become solvated within the polar media comprising the polar stratospheric clouds. The solvated electrons then tunnel into CFCs adsorbed on these PSCs, leading to CFC dissociation and  $\text{Cl}^-$  release. In addition,  $\text{Cl}^-$ , which remains adsorbed on PSCs, can also react with inert chlorine nitrate ( $\text{ClONO}_2$ ) to produce reactive  $\text{Cl}_2$ : [61]



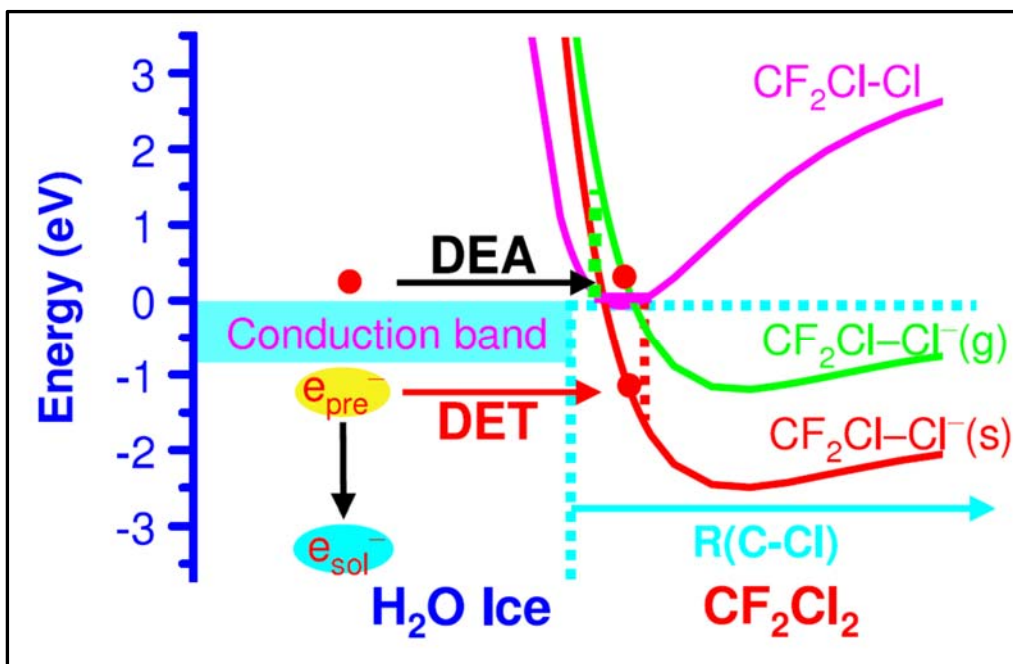
With the onset of polar spring and the return of solar photons,  $\text{Cl}^-$  and  $\text{Cl}_2$  are converted to  $\text{Cl}$  atoms and the ozone-depletion cycle begins once again.

#### *Refining Cosmic-Ray-Electron Mechanism*

These initial experiments by Lu and Madey [7] motivated, but did not unambiguously demonstrate, the role of low-energy electrons in the dissociation of  $\text{CF}_2\text{Cl}_2$  in polar media. Subsequent low-energy electron transmission (LEET) measurements between 0 and 10 eV with 40 meV resolution show that adsorption to polar media such as  $\text{H}_2\text{O}$  and  $\text{NH}_3$  enhances DEA dissociation of  $\text{CF}_2\text{Cl}_2$  by near 0 eV electrons. [62] Furthermore, these measurements were used to conclude that it is short-lived presolvated electrons, rather than fully solvated electrons, which are responsible for the large DEA cross-section of  $\text{CF}_2\text{Cl}_2$  adsorbed on polar media. [62]

Presolvated electrons are partially trapped electrons and are precursor states to solvated electrons. A presolvated electron has near-vacuum energy and can be thought of as an excited

state of the solvated electron. When  $\text{CF}_2\text{Cl}_2$  is adsorbed on condensed polar media such as  $\text{H}_2\text{O}$ , the potential energy curve for the negative ion  $\text{CF}_2\text{Cl}_2^-$  is shifted downward in energy by  $\sim 1$  eV compared to the gas phase curve due to a polarization potential created by the  $\text{H}_2\text{O}$  film (see Figure 3).[59, 62] The near 0 eV DEA resonance for  $\text{CF}_2\text{Cl}_2$  can be accessed by near but sub-zero-energy electrons such as presolvated electrons. The process of a presolvated electron attaching itself to  $\text{CF}_2\text{Cl}_2$  adsorbed on condensed polar media is called dissociative electron transfer (DET). Solvated electrons are well bound in their Coulomb trap and are unable to initiate the DEA process for  $\text{CF}_2\text{Cl}_2$ . LEET measurements have helped determine that a similar process occurs for  $\text{CFCl}_3$ . [63]

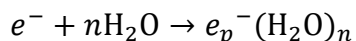


**Figure 3:**

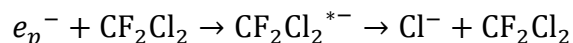
Figure taken from [59]. The potential energy curves are shown for  $\text{CF}_2\text{Cl}_2$  (violet), gas phase  $\text{CF}_2\text{Cl}_2^-$  (green), and  $\text{CF}_2\text{Cl}_2^-$  adsorbed on  $\text{H}_2\text{O}$  ice (red). The potential energy curve for  $\text{CF}_2\text{Cl}_2^-$  adsorbed on  $\text{H}_2\text{O}$  ice is lowered compared to the gas phase  $\text{CF}_2\text{Cl}_2^-$ . This allows presolvated electrons with near-vacuum level energies to attach to and dissociate  $\text{CF}_2\text{Cl}_2$ . Fully solvated electrons are well-bound to the  $\text{H}_2\text{O}$  ice and cannot attach to  $\text{CF}_2\text{Cl}_2$ .

The refined CRE mechanism is summarized in Figure 4. The outline is the same as for the initially proposed mechanism involving solvated electrons, but is updated for presolvated electrons ( $e_p^-$ ):

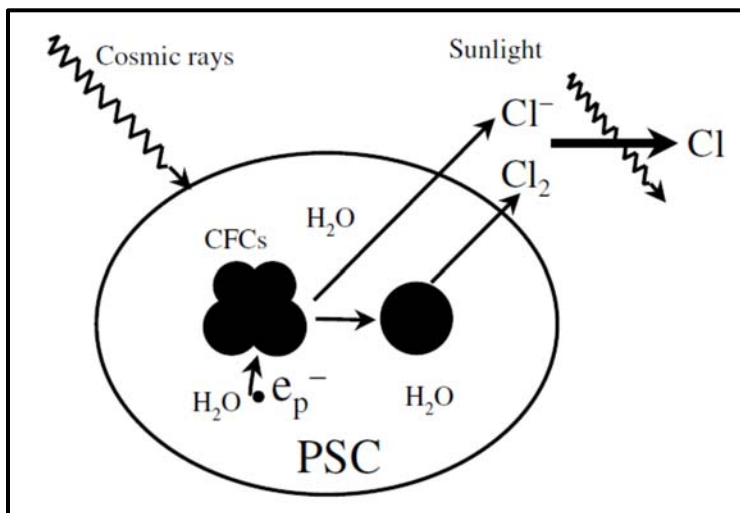
Electron presolvation:



Dissociation of  $\text{CF}_2\text{Cl}_2$ :



Given the large number of electrons produced by cosmic rays, the large DEA cross-sections for CFCs adsorbed on polar media compared to UV gas-phase absorption cross-sections, and the link to PSCs which helps to explain the yearly cyclical ozone depletion, the CRE mechanism illustrates a possible additional pathway to ozone depletion besides the traditional photochemical explanation.



**Figure 4:**

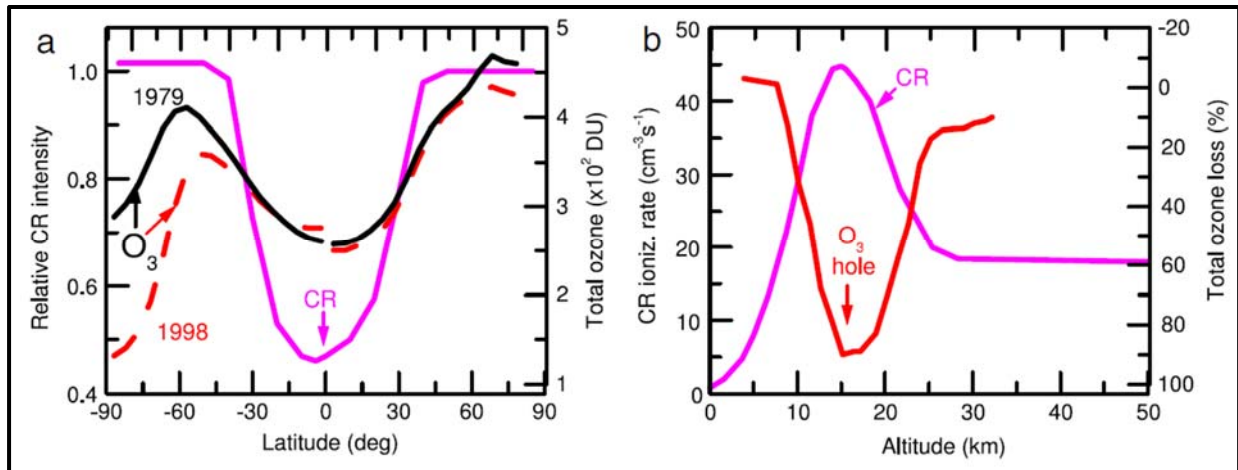
Figure taken from [54] illustrating the main components of the CRE mechanism by which CFCs are dissociated and Cl atoms are released to start the ozone depletion chain.

### 7.3 Additional Evidence for CRE Mechanism and Questions:

While the fundamental experimental work examining electron-induced reactions of CFCs adsorbed on ices are not of debate, the relative importance of these reactions in ozone depletion compared to the photochemical mechanism are.

#### *Additional Evidence for the CRE Mechanism*

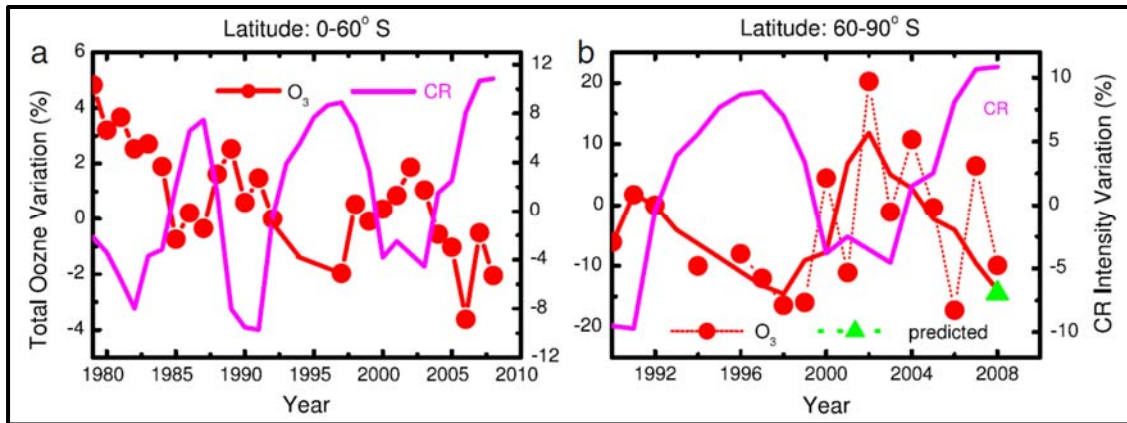
If the CRE mechanism is to be a significant contributor to ozone depletion, there should be an observed correlation between atmospheric cosmic ray intensity and ozone levels.[54, 59] Lu and Sanche show evidence for a latitudinal correlation between cosmic ray intensity and ozone content indicating that cosmic rays are strongly present at latitudes with high total ozone (Figure 5a). Hence, a potential source for ozone processing, cosmic rays, is present where there are significant levels of ozone which can be subsequently processed. In addition, they show that, as a function of altitude, ozone loss is maximum near an altitude of 15 km where cosmic ray ionization rate is largest (Figure 5b). Finally, they cite UARS satellite data which tracks CFC concentrations as a function of latitude and time. These measurements indicate CFC concentrations are larger during the polar fall compared to early polar spring both in the Arctic and Antarctic lower stratosphere (16 – 20 km).[54] Lu and Sanche conclude that the diminished CFC concentration by early spring is likely due to cosmic-ray-initiated dissociation of CFCs within PSCs (which are found predominately at lower stratospheric altitudes) during the wintertime when cosmic ray flux is at a maximum and solar radiation is absent.[54]



**Figure 5:**

Figure from [59]. a) Overlay of cosmic ray intensity (violet curve) as a function of latitude with monthly mean ozone levels. Black curve shows ozone levels for pre-ozone hole period (October 1979 in Antarctica and March 1979 for Arctic) and red-dotted curve shows ozone levels for the ozone hole period (October 1998 in Antarctica and March 1998 for Arctic) b) Plot of the cosmic ray ionization rate with ozone loss as a function of altitude. The ozone loss represents springtime ozone depletion over Syowa, Antarctica and was calculated by subtracting the ozone distribution curve for pre-ozone hole period (1968 - 1980) from the ozone-hole period (1991 - 1997).[54]

Cosmic ray flux has an 11-year cycle which is inversely correlated with the solar cycle.[64] At times of high solar activity, cosmic ray particle interactions with solar magnetic fields and material ejected from the sun reduce the number of cosmic rays reaching Earth's atmosphere. In 2001, Lu and Sanche demonstrated an inverse correlation of mean ozone content averaged over latitude with cosmic ray intensity variations which extended just over one 11-year cycle from 1979 - 1992.[54] This data was more recently extended to 2008 with a continued observed inverse correlation (Figure 6).[65]



**Figure 6:**

Figure from [59]. a) Plot of the relative changes in cosmic ray intensity with monthly average zonal mean total ozone for southern hemisphere latitudes 0 – 60°. b) Plot of the relative changes in cosmic ray intensity with monthly average zonal mean total ozone for southern hemisphere latitudes 60 – 90°.

The spatial and temporal links between cosmic ray flux and ozone depletion are suggestive of a significant CRE mechanism at work, and Lu contends that understanding cyclical patterns of ozone loss within the CRE mechanism allows for future predictions of ozone depletion in a way that the photochemical mechanism alone does not.[11] The green triangle in Figure 6b represents Lu's predicted value for O<sub>3</sub> variation for October 2008, [65] which is in reasonable agreement with the subsequently measured value.[59]

### *Questions*

While suggesting the CRE mechanism plays a very significant role in ozone depletion, Lu and others do not contend that cosmic rays are the only mechanism for CFC dissociation leading to ozone loss.[54, 59, 61, 65, 66] However, while agreeing with the experimental work investigating electron-induced CFC reactions and that such reactions can take place in the stratosphere, others question whether the CRE mechanism plays a significant role in ozone depletion.[67-70] Among points of contention are: 1) interpretation of CFC distribution from

UARS satellite data, 2) efficiency of CFC adsorption to PSC ice particles, 3) origin of the 11-year ozone cycle, and 4) the correlation between cosmic ray intensity and mean total column ozone.

Lu and Sanche conclude, based on UARS satellite data, that CFCs are mainly processed at the poles during the winter polar months consistent with a cosmic ray electron driven mechanism for CFC dissociation. Harris et. al. contend that CFCs are dissociated by solar UV photons predominately at low latitudes and mid to high stratospheric altitudes and hence such CFC processing is not limited to winter months.[67] They explain that the resulting observed CFC latitude differences (low polar CFC concentration by early spring compared to late fall) are due to the flow of lower latitude air to the pole each winter.[67] Patra et. al. are not as strong in their opposition to Lu and Sanche's interpretation contending Lu and Sanche's proposed mechanism could provide a viable explanation while also deferring to stratospheric air circulation processes as an explanation.[68]

Harris et. al. indicate there are unanswered questions regarding the efficiency by which CFCs in the atmosphere adsorb to PSC ice particles. Experiments show that CFCs adsorbed on H<sub>2</sub>O ice particles are efficient with a removal rate of  $4.3 \times 10^{-5} \text{ s}^{-1}$  for CF<sub>2</sub>Cl<sub>2</sub>. [54] This, as Harris et. al. point out, does not give the rate for CFC removal from the atmosphere as not all CFC molecules will adsorb to PSCs. A better understanding of the fraction of CFCs which adsorb to PSCs in the atmosphere will lead to a better understanding of the CRE mechanism's significance for ozone depletion.

Muller et al. suggest that the 11-year ozone cycle is not linked to variations in atmospheric cosmic ray flux variations, but rather directly to the solar-cycle, and that the cycle is reflected in upper stratosphere ozone variations at mid-latitudes where PSCs are not present.[70]

However, they indicate that detection of the solar-cycle effects on ozone depletion has been obscured by volcanic events and near-biennial oscillations in tropical stratospheric winds. Given that solar variations were detected in mid-latitude regions, Muller et al. conclude that it is unlikely that these mid-latitude variations were caused by polar processes.[70]

A final point of contention is the strength of the correlation between cosmic ray intensity and ozone depletion found by Lu.[65] Alvarez-Madrigal and Muller et. al. calculate the correlation coefficient  $r$  to be  $-0.52$ , which they interpret as a relatively weak correlation.[70, 71] Alvarez indicates, based on this correlation coefficient, that the CRE mechanism could explain 27% of the total ozone variations observed.[71] Lu's reply to this concern includes the following two explanations: 1) the low correlation coefficient is only indicative of a low linear correlation between ozone cosmic ray intensity and ozone depletion and 2) the CRE mechanism is not the sole mechanism for ozone depletion.[66] Subsequently, Lu updated an initially linear model relating total ozone in the spring Antarctic hole to cosmic ray intensity with a quadratic relationship with cosmic ray intensity:[59]

$$[O_3]_i = [O_3]_0[1 - k \times I_i \times I_{i-1} \times EESC_i]$$

In this model,  $[O_3]_i$  is the Antarctic steady-state total ozone in spring  $i$ .  $[O_3]_0$  represents the total ozone when halogen concentrations (EESC) are zero.  $I_i$  represents the cosmic ray intensity for spring  $i$ .  $k$  is a constant which takes into account the amount of PCSs available. While the numerical agreement is less than perfect, Lu claims that using this model the CRE mechanism alone well-fits the total ozone data trends from the 1950s to 2008, suggesting that the CRE mechanism is the dominant mechanism for ozone depletion.[59]

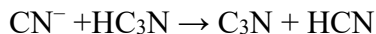
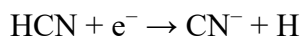


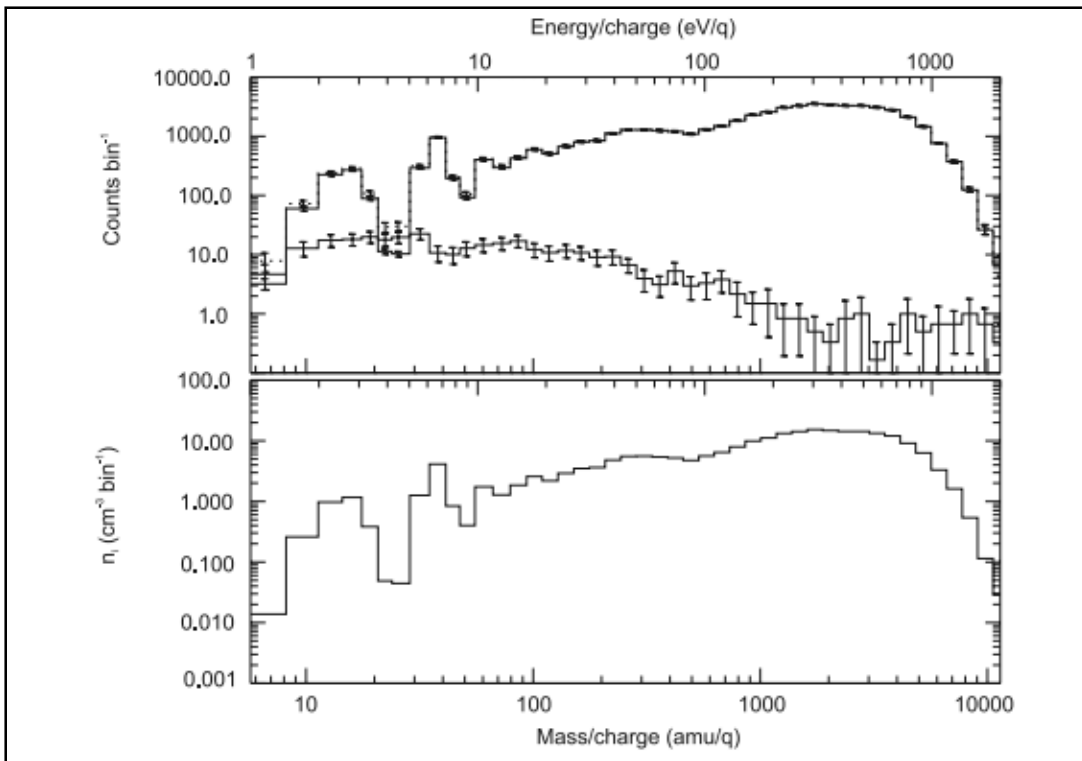
Despite unresolved questions regarding the exact relative importance of the CRE mechanism to the photochemical mechanism for ozone depletion, experimental work to date provides a strong case for the important role of low-energy electrons in ozone processing.

### **8.0 Low-Energy Electron-Induced Chemistry in Titan's Upper Atmosphere**

Titan has a permanent atmosphere, primarily composed of dinitrogen (97%) and methane (2%), with a surface pressure of ~ 1.5 atmospheres. Titan is the only satellite in the Solar system with an extensive atmosphere. It is close enough to Saturn for its atmosphere to be affected by the planet's external magnetospheric behavior.[72] Based on measurements from the Cassini probe, solar photons and the resulting photoelectrons are thought to dominate the overall behavior of Titan's upper atmosphere, but the observed nighttime atmospheric behavior is ascribed to small contributions from magnetospheric electrons.[73] Photoionization results in the production of copious amounts of low-energy secondary electrons which are thought to contribute to the dissociation of N<sub>2</sub> and CH<sub>4</sub> in Titan's atmosphere.[73]

Dissociative electron attachment to HCN has been identified as the first step in the production of heavy ( $m/z \sim 10,000$ ) negative ions (Figure 7) thought to play an important role in Titan's haze.[15]





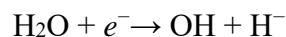
**Figure 7:**

Heavy negative ions in Titan's upper atmosphere as detected by the Cassini Plasma Spectrometer (CAPS).[74]

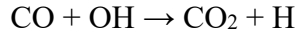
## **9.0 Could Dissociative Electron Attachment Explain the Relative Absence of Organics on**

### **Mars?**

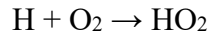
While the detection of perchlorates in the Martian soil may offer an alternate explanation,[75] the relative absence of organics on Mars has been attributed to dissociative electron attachment to water vapor in the Martian atmosphere, leading to the production of H<sub>2</sub>O<sub>2</sub> which may scavenge Martian organic material.[16] The first step involves production of OH radicals by low-energy electrons:



In the next step, the OH radicals are postulated to react with CO in the Martian atmosphere to produce H atoms:



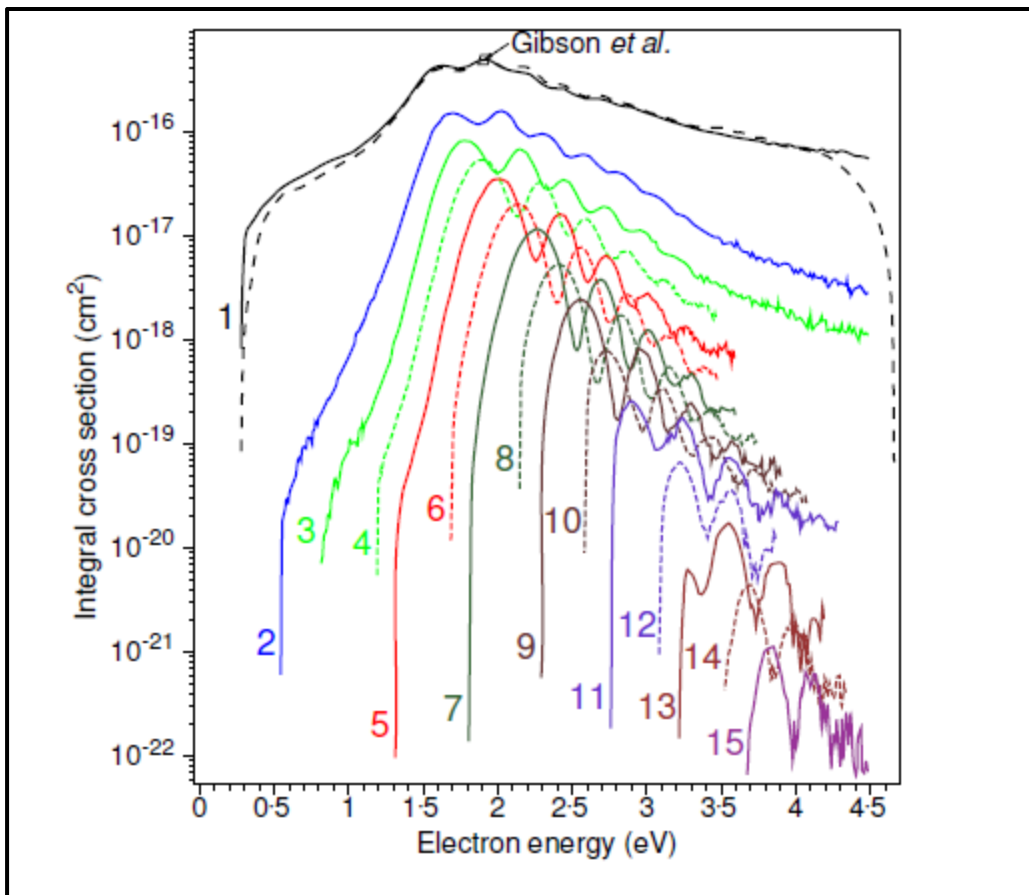
The H atoms are thought to increase the production of H<sub>2</sub>O<sub>2</sub> via the following mechanism:



In the presence of large electric fields, the above mechanism was shown to increase the column density of H<sub>2</sub>O<sub>2</sub> by a factor of over 200 compared to the abundance of H<sub>2</sub>O<sub>2</sub> produced by photochemistry alone.[16] Low-energy electrons responsible for this mechanism are thought to be produced by the large-scale electrostatic fields generated during Martian dust devils and storms. The enhanced production of H<sub>2</sub>O<sub>2</sub>, mediated by low-energy electrons, is postulated to have implications for life and habitability on Mars.[16]

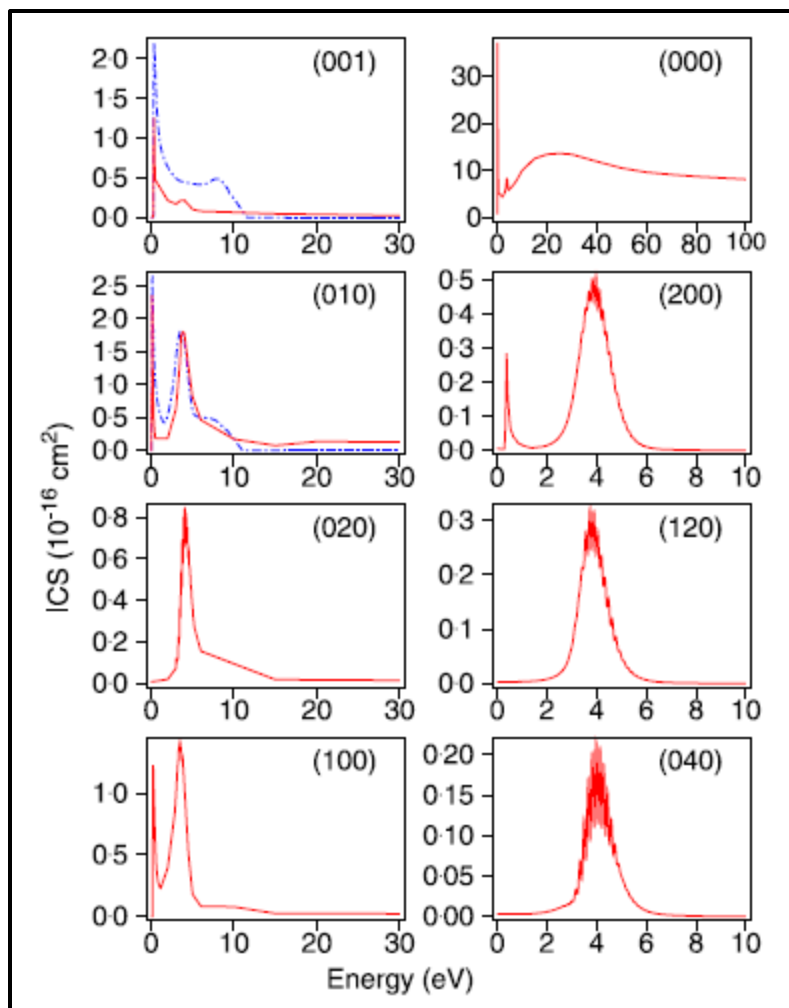
#### **10.0 Role of Low-energy Electrons in Energy Transfer Processes in the Atmospheres of Mars and Venus**

An important energy transfer process in the atmospheres of Mars and Venus involves low-energy electron impact vibrational excitation of CO and CO<sub>2</sub>, followed by radiative decay involving IR radiation.[76-78] In addition to incorporating integral cross sections for electron impact vibrational excitations of CO (Figure 8) and CO<sub>2</sub> (Figure 9), this conclusion was based on measurements of electron temperature and densities of electrons, CO, and CO<sub>2</sub>.



**Figure 8**

Incident electron energy dependence of the integral cross sections for electron-impact vibrational excitation of CO from the ground vibrational state to various numbered excited vibrational states.[77]



**Figure 9**

Incident electron energy dependence of the integral cross sections for electron-impact vibrational excitation of CO<sub>2</sub> for elastic collisions (000) and seven vibrational modes.[78]

## **Conclusions**

Low-energy (< 20 eV) electron-induced mechanisms play a pivotal role in high-energy radiation-induced processes, which are central to both terrestrial and extraterrestrial atmospheric changes. However, the relative importance of low-energy electrons in specific atmospheric processes is difficult to quantify. Nevertheless, low-energy electrons likely contribute to the (1) production of the three most important atmospheric negative ions ( $\text{CO}_3^-$ ,  $\text{NO}^-$  and  $\text{NO}_3^-$ ), (2) synthesis of heavy ( $m/z \sim 10,000$ ) negative ions in Titan's upper atmosphere, and (3) energy transfer processes in the atmospheres of Mars and Venus atmospheres. Current studies are exploring whether low-energy electrons contribute to (1) "relativistic runaway electron avalanche" which may trigger lightning flashes, (2) chlorofluorocarbon dissociation which may exacerbate the ozone hole, (3) aerosol nucleation which may enhance global warming, and (4) vibrational excitation of NO which may contribute to auroral emissions.

## **Acknowledgements**

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