

SHORT COMMUNICATION.

Ionization and Fragmentation of a Global Warming Gas by EUV and X-Ray Photons

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DOI:

Abstract

An experimental investigation of the processes leading to the fragmentation of the singly ionized 1,1,1,2-tetrafluoroethane (HFC-134a, CH_2FCF_3) by EUV and soft X-rays is presented. HFC-134a is taken into consideration as the most convenient replacement for CFC-12 in refrigeration applications due to the fact that it has null ozone depletion factor. Dissociation of the singly ionized HFC-134a molecule was induced by valence, direct and indirect C 1s core photoionization or photoexcitation and the ionic fragments were detected in coincidence (PEPICO mode) with the ejected electrons without energy analysis. The singly ionized parent ion CF_4CH_2^+ can be detected even at photon energies above the C 1s threshold.

Keywords: Fragmentation; HFC-134a; PEPICO; Photoionization; Synchrotron Radiation;

1. Introduction

The predominant source of heat to the Earth is energy from the Sun. Solar energy is transmitted by radiation and transformed into heat at the Earth's surface. Solar extreme ultraviolet (EUV) radiation is one of the major sources of energy load into Earth's and other planetary atmospheres in the solar system. The Earth also emits radiation back to space in order to counterbalance this absorption of energy. Part of the Earth's radiation is captured by greenhouse molecules and radiated back to the surface, culminating in the warming of our planet, the so-called greenhouse effect. Naturally existing greenhouse gases such as CO₂, CH₄, and N₂O are fundamental for keeping the surface temperature beyond the frosty point [1, 2,3].

There is, at the present date, much burden that anthropogenic growth in greenhouse gases could provoke significant warming of our planet. The naturally existing greenhouse molecules show huge boost during the past century as a result of anthropogenic actions.

Other greenhouse substances manufactured by the industry, such as HFC-134a, have also increased in the atmosphere during the last decades. It is well known that the Earth's mean surface temperature has been growing during the past hundred years by 0.6 K [1,2,3]. Conforming to the main stream climate models, this warmth rise is due to the emissions of greenhouse gases. The models also forecast an additional 1-5 K rise in the temperature during the next hundred years if greenhouse gases emissions remain increasing.

Measurements of temperature in Europe exist from about three centuries ago, and can provide a dependable thermometer going back one hundred and fifty thousand years [3]. The warming noticed over the past century is, in fact, the maintenance of a longer-term beginning in about XVII century C.E., long ahead anthropogenic emissions of greenhouse gases turned into significant. This longer-term tendency is thought to be due to natural variations in solar activity [3]. Returning further in time it can be observed that the Earth's surface temperature has passed through substantial natural fluctuations during the past ten thousands years, with temperatures eventually higher than now. Swings in solar activity may be the cause for this effect. Stretching the record back to one hundred and fifty thousand years demonstrates that the sequence of glacial and interglacial climates were guided by periodic swings in the Earth's orbit and inclination in relation to the Sun [3]. Taking into account the temperature record alone, it is not possible to ascribe the temperature rise over the past one hundred years as anything more than an ordinary fluctuation. Yet, as far as the researches are concerned, current climate models predict that the warming is in fact ascribed to increases in greenhouse gases [3].

Established on its chemical and physical properties, HFC-134a (see Fig. 1) is seen as the most convenient substitute for CFC-12 in refrigeration and air conditioning machines [1,2,3]. The effect of a substance on the environment is typified in terms of depletion of the ozone layer and augmentation of the greenhouse effect. The greenhouse effect is calculated in Global- Warming Potential (GWP). It was developed to allow comparisons of the global warming impacts of different substances. GWP measures the amount of energy the emissions of 1 ton of a substance absorbs over a given period of time, usually one hundred years, in comparison to the emissions of 1 ton of carbon dioxide, which has a GWP equal to one by definition. The destruction of the ozone layer is calculated in terms of the Ozone Depletion Potential (ODP), normalized to the effect of CCl₃F. HFC-134a has a GWP equals to 1430 and an insignificant ODP [1,2,3].

The HFC-134a has a long atmospheric lifetime, being the most plentiful hydrofluorocarbon in the atmosphere. Its average concentration is around five times the concentration of other HFCs [1,2,3].

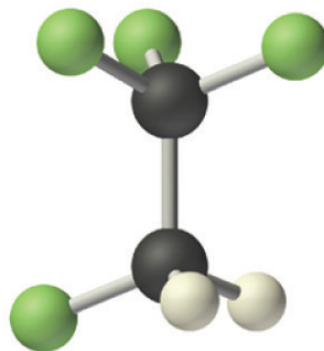
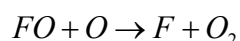
HFC-134a, CH₂FCF₃

Figure 1: The HFC-134a molecule (source: <https://chem.libretexts.org/>, downloaded on August, 8, 2019)

The use of HFC-134a is a relatively new issue, without expressive production before the 90's. However, after 1990, the amount produced grew significantly. Nonetheless, the emission of HFC-134a is not directly associated to its production, i.e., releases take place while the gas is used or after on its disposal.

HFC-134a contains, like several other hydrofluorocarbons, a CF₃ group. It has been recognized [2] that CF₃ groups do not bring about serious ozone harm. Despite of having insignificant ODP, the atmospheric degradation of HFC-134a can give rise to the liberation of fluorine atoms. The reaction of fluorine atoms with ozone is faster than the reciprocal reaction of chlorine atoms [2]. In addition, the reaction of FO with O is also fast, in order that the catalytic cycle:



In which the net result is



which can take place very rapidly. Additional cycles including fluorine atoms also exist. Notwithstanding, the reactions of fluorine atoms with methane and water vapor to form HF can also take place fastly and can compete with the reactions involving fluorine and ozone [1,2,3]. Hence, any cycle including fluorine atoms and that depletes ozone cannot have a large chain length, on account of fluorine atoms are efficiently removed to form HF.

Photons in the EUV and x-ray range are important sources of energy that can dissociate, excite, and ionize the neutral gases in the upper atmosphere. In this paper we present photoionization and photofragmentation data in valence and C 1s edge of HFC-134a molecule using synchrotron radiation and coincidence techniques.

2. Material and Methods

The experiment has been described in detail previously [4]. Briefly, in our experiment, we make use of coincident detection, in which two or more particles are observed and the interdependencies of their properties can thus be determined. Here, we apply photoelectron-

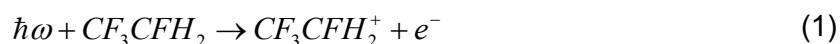
photoion coincidence (often referred to as PEPICO) spectroscopy. In this PEPICO experiment, we used a Wiley-McLaren-type ion time-of-flight (TOF) spectrometer. The experiment was performed at the TGM beamline at the Laboratório Nacional de Luz Síncrotron (LNLS), Campinas, Brazil, using monochromatized EUV (12 eV-100 eV) and soft X-ray (100 eV- 320 eV) radiation.

Photoelectrons and photofragments were swept from the interaction region by an intense static electric field (750 V/cm) which drove the electrons straight into a microchannel (MCP) detector without energy analysis, and the photoions into the TOF for the mass-to-charge ratio analysis. The measurements have been executed with the TOF drift tube parallel to the axis of polarization of the synchrotron light.

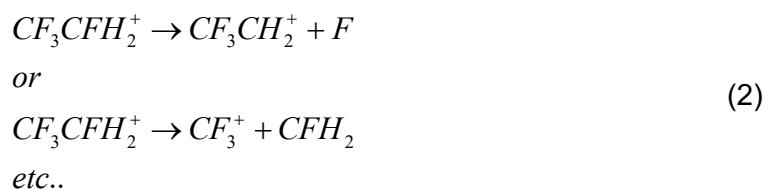
3. Results and Discussion

In this section, we take a closer look at the experimental results for the ionization of the HFC-134a molecule (first ionization potential is 10.12 eV) and interest ourselves with (i) Fragments branching ratios dependence of the photon energies in the region where the ionization of an electron from a valence orbital is possible; (ii) Fragments branching ratios dependence of the photon energies in the region where the ionization of an electron from an inner orbital, C 1s in the present case, is energetically allowed; and (iii) the overall dependence of fragments branching ratios on the photon energy of the branching ratios of the fragments from ionization threshold in the EUV region to the x-ray region to the X ray regions. Low energy photons (<10 eV) usually give rise to molecular dissociation (non-ionizing radiation). On the other hand, higher energies give rise to ionization (ionizing radiation) and fragmentation. The accurate distribution of these different processes depends on the respective cross sections and the atmospheric gases.

Photoionization of a neutral gas present in Earth's atmosphere gives rise to electron-ion pair. This is the main source of ionization in the ionosphere. When the energy of an ionizing photon exceeds the ionization potential of a molecule, the excess of energy goes either into electron kinetic energy or excitation of the resulting ion. The electrons pick up most of the excess of energy because the ions are heavier than the photoelectrons, and, due to momentum conservation, the ions recoil with low kinetic energy after the photoionization. Figure 2 presents a mass spectrum of HFC-134a taken at 100 eV photon energy. At this photon energy, ionization takes places directly and can be represented as:



The molecular parent ion may break apart into smaller fragments such as:



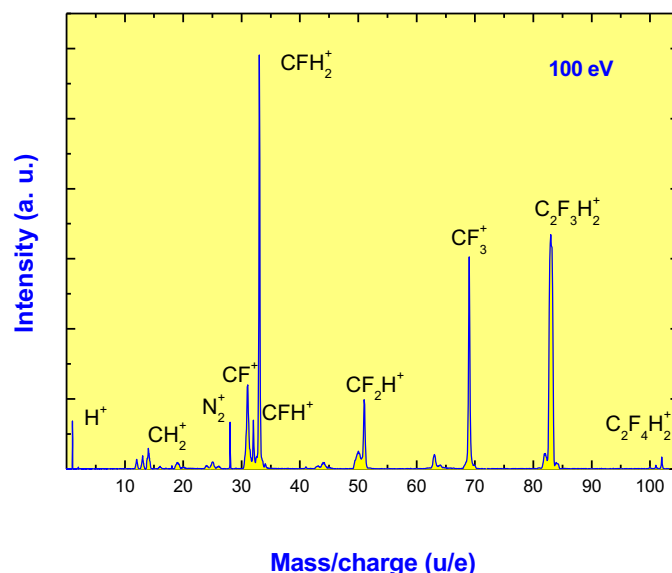


Fig. 2: Mass spectrum of HFC-134a at 100 eV photon energy. We can observe the presence of some background gases such as H_2O , N_2 and O_2 .

Figure 3 presents the branching ratios for the formation of the parent $\text{CF}_3\text{CFH}_2^+$ ion as function of the photon energy. For photon energies below 40 eV, we observe some experimental artifacts, due to the presence of high-order harmonic contaminations. It can be seen that, as the photon energy increases, so does the probability of fragmentation, so that the relative yield of $\text{CF}_3\text{CFH}_2^+$ decreases with the photon energy. Around 300 eV, just above $\text{C}1\text{s} \rightarrow \sigma^*$ excitations, the yield of $\text{CF}_3\text{CFH}_2^+$ is null, within the experimental uncertainties ($\sim 10\%$). Above the C 1s ionization threshold, we can observe a small contribution to the singly ionized parent molecule again.

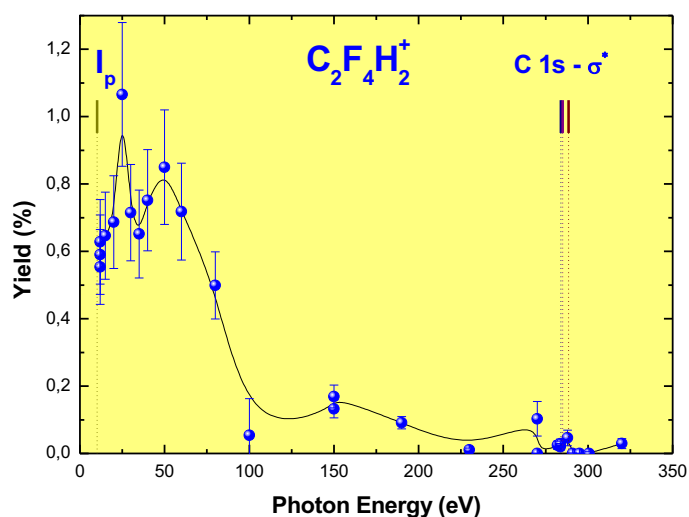


Figure 3 : Ion yield of the singly ionization $C_2F_4H_2^+$ molecule as a function of the photon energy (eV). The vertical bars indicate the first ionization potential (10.12 eV) and the $C\ 1s \rightarrow \sigma^*$ transitions.

Figure 4 shows the relative contributions of selected fragments of the $C_2F_4CFH_2$ molecule at 40 eV (valence) and 320 eV ($C\ 1s$ continuum). We can observe a drastic change in the relative distributions. For instance, at 40 eV the $C_2F_3H_2^+$ fragment, corresponding to a loss of a neutral F atom is the dominant ion in the mass spectrum (~36 %), followed by the CFH_2^+ (~31 %), and CF_3^+ .

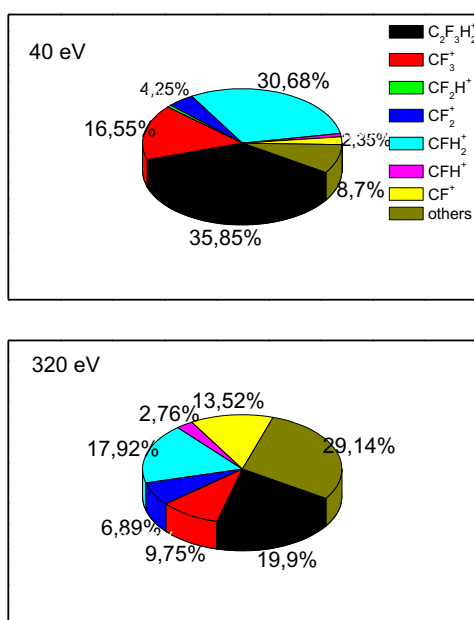


Figure 4 : Relative contributions of specific fragments of the HFC-134a at 40 eV and 320 eV.

4. Conclusions

We have presented experimental results for the ionization and fragmentation of HFC-134a, most plentiful hydrofluorocarbons in the Earth's atmosphere, and seen as the most convenient substitute for CFC-12, by EUV and X-rays photons using the PEPICO technique and synchrotron radiation. It is demonstrated that, as the photon energy increases, so does the probability of fragmentation, so that the relative yield of $CF_3CFH_2^+$ decreases with the photon energy. Around 300 eV, just above $C\ 1s \rightarrow \sigma^*$ excitations, the yield of $CF_3CFH_2^+$ is null, within the experimental uncertainties (~10 %). Above the $C\ 1s$ ionization threshold, we can observe a small contribution to the singly ionized parent molecule again.

Acknowledgments

One of us (ACFS) acknowledges CNPq, FAPERJ, FINEP and CAPES (Programa Abdias Nascimento) and the LNLS staff for their support.

References and Notes

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