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Monte Carlo model for electron degradation in methane gas

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ABSTRACT

We present a Monte Carlo model for degradation of 1–10,000 eV electrons in an atmosphere of methane. The electron impact cross sections for CH_4 are compiled and analytical representations of these cross sections are used as input to the model."Yield spectra", which provides information about the number of inelastic events that have taken place in each energy bin, is used to calculate the yield (or population) of various inelastic processes. The numerical yield spectra, obtained from the Monte Carlo simulations, is represented analytically, thus generating the Analytical Yield Spectra (AYS). AYS is employed to obtain the mean energy per ion pair and efficiencies of various inelastic processes. Mean energy per ion pair for neutral CH_4 is found to be 26 (27.8) eV at 10 (0.1) keV. Efficiency calculation showed that ionization is the dominant process at energies >50 eV, for which more than 50% of the incident electron energy is used. Above 25 eV, dissociation has an efficiency of ~27%. Below 10 eV, vibrational excitation dominates. Contribution of emission is around 1.2% at 10 keV. Efficiency of attachment process is ~0.1% at 8 eV and efficiency falls down to negligibly small values at energies greater than 15 eV. The efficiencies can be used to calculate volume production rate in planetary atmospheres by folding with electron production rate and integrating over energy.

1. Introduction

Electron collision with molecule can result in various processes, like ionization, dissociation, and excitation of the target molecule, which can produce new species that can be more reactive as well as physically and chemically different from their parent molecule. Secondary electron released during ionization can also initiate further reactions. By-products of all these processes can initiate further reactions which are of great interest in the field of radiation chemistry, environmental chemistry, planetary aeronomy processes, like aurora and dayglow, and also in astrophysical and biological systems (Mason, 2003; Campbell and Brunger, 2009). To understand such phenomena, a thorough knowledge of electron degradation when it collides with atoms or molecules is required.

Methane is the simplest hydrocarbon present in the solar system (Mueller-Wodarg et al., 2008). It causes infrared absorption in the atmosphere of Jupiter and Saturn and is an important atmospheric constituent in the planets Uranus and Neptune (Broadfoot et al., 1979). In Titan, photochemistry is governed by ionization and dissociation products of nitrogen and methane (Lavvas et al., 2011). Collision of solar photons or photoelectrons with methane molecules causes the neutral dissociation or ionization of the molecule which in turn leads to the generation of simple hydrocarbon radicals and ions. The subsequent reactions caused by these radicals and ions, either with themselves or with methane and other background gases, cause the production of higher order hydrocarbons, be it alkanes, alkenes or alkynes (Banaszkiewicz et al., 2000; Strobel, 2004) and leading to polymerization which may produce UV-dark haze in auroral region of Jupiter (Singhal et al., 1992) and very heavy ionic species in Titan's atmosphere (Coates et al., 2007; Wahlund et al., 2009). Hydrogen cyanide, an important precursor for the formation of amino acids and proteins, is formed from those reactions for which methane acts as a precursor (Romanzin et al., 2005). Fifth flyby of Titan by Cassini–Huygens mission found regions of low radar reflectivity which are interpreted as lakes, with methane as a major constituent (Cordiar et al., 2009).

The aim of this study is to present a Monte Carlo model which describes the degradation of electrons with energy in the range 1 eV–10 keV in a CH_4 atmosphere. Gan and Cravens (1992) used solution of Boltzmann equations for studying degradation of electrons in CH_4 and they calculated energy transfer rates for elastic and various inelastic processes assuming a Maxwellian electron distribution. The Monte Carlo method is a stochastic method, which has been widely used for studying the problem of electron energy degradation in gases relevant for planetary atmospheres (Cicerone and Bowhill, 1971;

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Ashihara, 1978; Green et al., 1977; Singhal et al., 1980; Singhal and Green, 1981; Singhal and Bhardwaj, 1991; Bhardwaj and Singhal, 1993; Bhardwaj and Michael, 1999a; Bhardwaj and Micheal, 1999b; Michael and Bhardwaj, 2000; Shematovich et al., 2008; Bhardwaj and Jain, 2009). In this method, history of collisions of particles is simulated, and conclusions are drawn from the statistics of those histories. Even though time consuming, at some levels it is found to be the most realistic simulation possible for studying electron energy deposition (Solomon, 2001). The energy loss process of electrons is actually discrete in nature and this nature is exactly captured in the Monte Carlo model. The method makes use of probabilistic decision making techniques, and accuracy of the result largely depends on the number of simulations carried out. The study involves two steps: compilation of cross sections for all e-CH_4 collision processes and development of an energy apportionment method to determine how electron energy is distributed in various loss channels.

2. Cross sections

2.1. Total and differential elastic

Total elastic scattering cross section for methane have been measured by Boesten and Tanaka (1991), Bundschu et al. (1997), Iga et al. (1999), and Kanik et al. (1993). All these measurements are in good agreement with each other. Measurements of Boesten and Tanaka (1991) in the energy range 1.5–100 eV was fitted using analytical formula by Shirai et al. (2002). At energies above 100 eV, data of Kanik et al. (1993) has been used for fitting. This analytically fitted form of elastic cross section is used in the current study and is shown in Fig. 1.

The direction in which the electron is scattered after collision with a CH_4 molecule is determined using differential elastic cross sections (DCS). DCS for e-CH_4 collision has been measured by many workers. Values of DCS used in the present work are given in Table 1. In the low energy range of 3–15 eV, DCS measurements of Mapstone and Newell (1992) are used. However, DCS value at 5 and 10 eV is taken from Cho et al. (2008). Cross sections for energies between 20 and 100 eV also are taken from Cho et al. (2008). From 200 to 500 eV, measurements of Iga et al. (1999) and at 700 eV measurements of Sakae et al. (1989) are used. Since DCS measurements are not available for CH_4 for energies greater than 700 eV, linearly extrapolated values of cross sections are used.

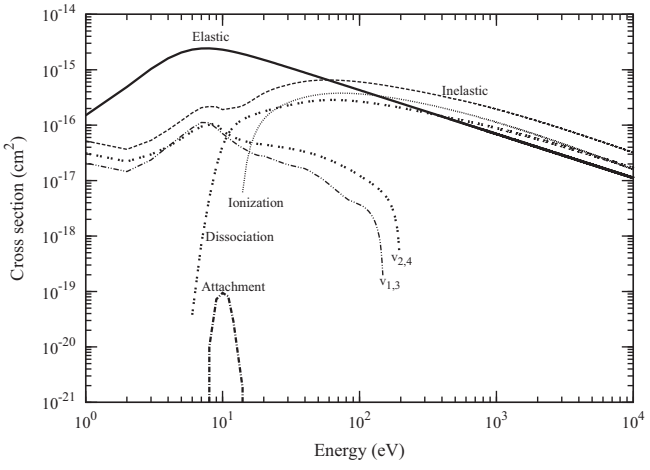

Fig. 1. Cross sections for elastic and inelastic processes for e-CH_4 collisions. $\nu_{1,3}$ and $\nu_{2,4}$ are the cross sections for stretching and bending vibration modes, respectively.

2.2. Attachment

Dissociative electron attachment process of CH_4 results in the production of H^- and CH_2^- ions. Cross section for this process was measured by Sharp and Dowell (1967) and Rawat et al. (2007). Former cross sections were analytically fitted by Shirai et al. (2002), which are used in the present work and is shown in Fig. 1.

2.3. Vibrational excitation

Methane molecule is found to have four normal modes of vibration: ν_1 with threshold energy 0.362 eV, ν_2 with 0.190 eV, ν_3 with 0.374 eV and ν_4 with 0.162 eV. But it is difficult to resolve these modes experimentally as they have very close transition energies. Hence, experimental data are available for the combined cross section for symmetric ν_1 and antisymmetric ν_3 stretching vibrations ($\nu_{1,3}$), and symmetric ν_2 and antisymmetric ν_4 bending vibrations ($\nu_{2,4}$) of CH_4.

Shyn (1991) measured vibrational excitation cross sections for methane at 5.0, 7.5, 10.0 and 15 eV. Tawara (1992) measured cross sections in the energy range 0.16–100 eV. DCS values in the 0.6–5.4 eV range, measured by Bundschu et al. (1997), were integrated to obtain the integral cross section. Vibrational excitation cross sections used in the current study are taken from Davies et al. (1988) in which cross section values are given for a larger energy range; 0.450–100 eV for $\nu_{1,3}$ mode, and 0.162–150 eV for $\nu_{2,4}$ mode. The values of Davies et al. (1988) and Tawara (1992) agree well at energies 10–100 eV. However, at energies less than 10 eV there is a difference between two cross sections to a maximum of 50% at few energies. Good agreement is found when cross sections of Davies et al. (1988) are compared with that of Bundschu et al. (1997). Measurements of Shyn (1991) are found to be lower than the values of Davies et al. (1988) by ~50%. Vibrational cross section used in our study is shown in Fig. 1.

2.4. Ionization

Ionization and dissociative ionization of CH_4 results in the production of ions CH_4^+, CH_3^+, CH_2^+, CH^+, C^+, H_2^+ and H^+. Cross sections for these ionization processes have been measured by many authors, e.g., Tian and Vidal (1997), Chatham et al. (1984), Adamczyk et al. (1966) and Straub et al. (1997). Straub et al. (1997) have measured the cross sections in the energy range 15–1000 eV and it is found to be the most reliable among various available measurements (Liu and Shemansky, 2006). These measurements were later revised due to instrumental recalibration and was published in Lindsay and Mangan (2003) (here after referred to as Straub's revised measurements). Liu and Shemansky (2006) derived the oscillator strength and excitation functions for various ionization channels of CH_4 and calculated the cross section values. These cross sections are in good agreement with Straub's revised measurements. However cross sections reported by Liu and Shemansky (2006) exclude the contribution by pair production (e.g. (CH_2^+, H^+), (C^+, H^+)). Erwin and Kunc (2008) using scaling law developed analytical expressions for calculating cross sections for various ionization channels of methane, which are valid at all non-relativistic energies. These expressions allow calculation of the electron impact ionization cross sections in an easier, and more direct way than the functions derived by Liu and Shemansky (2006). Good agreement is found between these theoretical ionization cross sections when compared with Straub's revised measurements and measurements of Tian and Vidal (1997). Maximum deviation (~20%) is found for H^+ production.

For the present work, we have taken the cross sections for CH_4^+ and CH_3^+ production from Liu and Shemansky (2006). For CH_2^+ production, the cross section for positive ion pair formation (CH_2^+, H^+), measured by Lindsay et al. (2001), has been added with the