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AWARD NAGW-4118

"Electron Collisions with Free Radicals"

Principal Investigator: Kurt H. Becker, Physics Department, CCNY

Final Report for the Period July 1, 1994 - December 31, 1997 (includes a 6-months unfunded extension period)

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In the first phase of the project, we measured absolute partial ionization and dissociative ionization cross sections for the SO_2 molecule and the SO free radical. The work on SO_2 was motivated by the scarce and controversial ionization cross section data base for this molecule (discrepancies of up to a factor of 4 for some partial cross section). In addition, experimentally determined total single SO_2 ionization cross sections disagreed with theoretical predictions. We employed two different experimental techniques, the fast-beam method and in collaboration with a group in Germany a high-resolution mass spectrometric method to measure absolute partial ionization and dissociative ionization cross sections for SO_2. The results are as follows:

(1) Parent ionization is the dominant ionization channel with a maximum cross section of about 2.4×10^{-20} m^2 at 80 eV and the cross section is dominated by direct ionization processes. The cross section shapes provides no evidence of the presence of any indirect ionization processes.

(2) The formation of the SO^+ fragment ion has also an appreciable cross section with a maximum value of 1.7×10^{-20} m^2 at 80 eV. The SO^+ ion is formed with little excess kinetic energy.

(3) Other fragment ions (O^+, S^+, and O_2^+) are formed with significantly smaller cross sections. Maximum values range from $0.2 - 0.5 \times 10^{-20}$ m^2.

(4) The high resolution mass spectrometer allowed us to identify to different ions contributiing to what other investigators had identified as the same charge-to-mass ratio (m/z = 32), viz. S^+ (m/z = 31.97207) and O_2^+ (m/z = 31.98983). We also measured individual cross section for the formation of these 2 ions with maximum values of 0.4×10^{-20} m^2 (S^+) and 0.25×10^{-20} m^2 (O_2^+). Our work provided the first evidence for the formation of the O_2^+ ion from the dissociative ionization of SO_2. Excess energies for the formation of these ions are near-thermal.

(5) The total SO_2 ionization cross section was measured to be about 5×10^{-20} m^2 at the maximum (90 eV) which agreed reasonably well with a semi-empirical calculation carried out by us and with another recent calculation using a Binary Encounter Bethe (BEB) approach. The energy dependence of the cross section indicates that direct ionization processes dominate.

The unique capabilities of the fast-beam technique were also used to investigate the ionization and dissociative ionization of the SO free radical. The SO results are summarized below:

(1) The ionization is dominated by the formation of the SO^+ parent ion through direct ionization mechanisms with a maximum cross section of 3.25×10^{-20} m^2 at 70 eV
(2) The S^+ fragment ion is also formed with an appreciable cross section of 1.35×10^{-20} m^2 at 60 eV, whereas the maximum cross section for the formation of the O^+ fragment ion is only 0.45 x 10^{-20} m^2 at 70 eV. Both ions are formed with excess kinetic energies of up to 2 eV per fragment.
(3) The total SO single ionization cross section of 5×10^{-20} m^2 at 60 eV is in excellent agreement with the result of a calculation using the modified additiviy rule.

Subsequently, the focus of the research shifted to the ionization/dissociative ionization of the CH_x (x=1-3) free radicals (and the CH_4 molecule, which served s a benchmark for the reliability of our results for the free radicals). Hydrogen-containing targets present a formidable challenge to our experimental technique because the various ionic product differ by only 1 amu which makes it difficult (i) to mass separate the primary ion beam extracted from the discharge source prior to charge neutralization and (ii) to separate the various product ions from a given target in the hemispherical analyzer. We devoted several months to establish and verify the optimum operating conditions of our apparatus for the work with the CH_x species as a test case for other hydrogen-containing targets of relevance to planetary atmospheres. This was done through a combination of ion trajectory modeling calculations and in-situ experimental studies. One of the major consequences of this work was the realization that it is usually more convenient to work with the deuterated rather than the protonated species. Since ionization cross sections are insensitive to isotope effects, data obtained for the deuterated species (e.g. CD_x) are equally applicable to the protonated species (CH_x). The CD_x results obtained can be summarized as follows:
(1) For all four targets, CD_4, CD_3, CD_2, and CD, the parent ionization cross section had roughly the same value of 1.65×10^{-20} m^2 at 70 eV.
(2) For all four targets, parent ionization was the dominant process.
(3) For all four targets, dissociative ionization channel was dominated by one channel, viz. the removal of one D atom, $CD_x + e^- \rightarrow CD_{x-1}^+ + D + 2\,e^-$.
(4) The major dssociative ionization channel gets progressively weaker (compared to the parent ionization channel) as one goes from CD_4 to CD.
(5) The ionization of vibrationally excited CD_4 molecules (up to 2 eV of vibrational excitation) results in an enhanced ionization cross section, but the enhancement is limited to the near-threshold region below about 25 eV.

During the final phase of the project, we investigated the ionization of the SiH_x (x=1-3) radicals and carried out some preliminary studies regarding the ionization of the NH_2 and NH free radicals. The following observations for the ionization of the SiD_x radicals are noteworthy (again we worked with the deuterated rather than the protonated target species):

(1) the parent ionization cross section has the same value for all three targets, SiD_3, SiD_2, and SiD with a value of 3.7×10^{-16} cm^2 at 70 eV.

(2) the parent ionization dominates over dissociative ionization channels

(3) there is only a single dissociative ionization channel with an appreciable ionization cross sections for all three targets, viz. the one in which one D atom is removed from the parent radical

(4) the cross section for this dominant dissociative ionization channel is the same for all three targets and has a value of 1.2×10^{-16} cm^2 at 70 eV

(5) all fragment ions are formed with little, if any excess kinetic energy

In related aspects of the research we worked on the further development and application of a semi-empirical additivity rule for the calculation of total single ionization cross sections. In almost all cases where we compared experimentally determined cross sections to calculated cross sections we found reasonably good, or at least satisfactory agreement between calculated and experimentally determined cross sections.

During the final part of the 3-year funding period we also developed new instrumentation, a temperature-stabilized filter for optical measurements in the vacuum ultraviolet region (around the wavelength of the Ar resonance lines at 104.8 and 106.7 nm) and we began implementation of a technique that will allow us to determine the kinetic energy distribution of fragment ions. Preliminary data have already been obtained for the dissociative ionization of propoane. Other hydrocarbons will be studied in the future.

Publications from the NASA support research in refereed journals and refereed Invited Papers:

1. "Electron Impact Ionization of the SO Radical", J. Chem. Phys. 102, 770-3 (1995), with V. Tarnovsky, A. Levin and H. Deutsch
2. "Electron Impact Ionization of the SO_2 Molecule", J. Chem. Phys. 103, 211-18 (1995), with V. Tarnovsky, A. Levin, R. Basner, M. Schmidt and H. Deutsch
3. "Electron-Impact Ionization of CD_x (x=1-4)", J. Phys. B 29, 139-52 (1996), with V. Tarnovsky, A. Levin, and H. Deutsch
5. "Electron Impact Ionization of the SiD_x (x=1-3) Free Radicals",, J. Chem. Phys. 105, 6315-21 (1996), with V. Tarnovsky and H. Deutsch
6. "Fundamental Electron Collision Processes Relevant to Low-Temperature Plasmas", in "Phenomena in Ionized Gases - Invited Papers of the XXII. Conference on Phenomena in Ionized Gases (ICPIG)", edited by K. Becker, W.E. Carr, and E.E. Kunhardt, American Institute of Physics Press: New York (1996), p. 75-90 (Invited Paper)
7. "Electron-Impact Ionization of Molecules of Interest to Plasmas", in " Atomic Processes in Plasmas - Invited Papers of the X. APS Topical Conference on Atomic Processes in Plasmas", edited by W. Goldstein, American Institute of Physics Press: New York (1996), in press, with V. Tarnovsky (Invited Paper)
8. "Electron-Impact Ionization of CD_x and SiD_x (x=1-3) Free Radicals", Proc. X. SASP, Engelberg, Switzerland (1996), edited by M. Quack and J.P. Maier, VDF-Verlag: Zürich (1996), p. 264-67, with V. Tarnovsky, A. Levin and, H. Deutsch (Invited Paper)
9. "Electron Impact Ionization Cross Sections Relevant to Threshold Ionization Mass Spectroscopy in CH_4 Plasmas", Proc. National Symposium on Plasma Science, Indian Institue of Technology (IIT), Kanpur (1995), edited by P. Ghosh, Prentice-Hall of India, New Delhi, India, p. 9-13, with V. Tarnovsky (Invited Paper)

In addition, there are 2 papers accepted for publication and in press and 10 contributed conference contributions were presented acknowledging research support from NASA .