Collision physics in the atomic and molecular universe

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Abstract. The wavelength range and high resolution of the space instruments \textit{Chandra, Newton, SOHO, Suzaku, Herschel, Spitzer}, and the upcoming ASTRO-H and James Webb Space Telescope have increased the need for laboratory collision-physics measurements to interpret astrophysical phenomena. A review will be given of charge exchange of highly-charged ions with neutral comet and planet atmospheres; and the formation of complex molecules in stellar regions. These space observations are linked to laboratory measurements of absolute charge-exchange cross sections; and molecular formation of species such as CO\textsubscript{2}, CH\textsubscript{3}OH, and CH\textsubscript{3}CH\textsubscript{2}OH involving fast H- and O-atom collisions with abundant interstellar molecules adsorbed on dust-grain analogues.

1. Introduction

Soft X-Rays and EUV photons result from the charge exchange (\textit{CEX}) of highly-charged ions in the solar wind (SW) with the neutral gas surrounding planets and bodies in the solar system \cite{1, 2}. The resulting X-ray spectra have allowed one to understand in more detail the interactions of the SW with planetary exospheres, comets, the heliosphere, and the terrestrial magnetosheath. In order to predict and map the observed X-ray emissions one requires SW composition, the neutral atmosphere composition, and knowledge of single and multiple \textit{CEX} cross sections. As an example, the pattern of the X-ray intensities observed around comets is centered sunward of the comet nucleus and remotely provides information on both the location of the cometary bow shock \cite{3} and on the location of the “cometopause” boundary. Studies are now being undertaken to use X-ray observations to study the SW flow around the Earth’s magnetosphere, including finding the locations of the shock, the magnetopause, and the magnetic cusps \cite{4, 5}. Such observations can be a useful tool for understanding the solar-terrestrial interaction. Examples of SW-induced X-rays are shown for the Chandra X-ray image of Comet 8P/Tuttle \cite{6} (figure 1a); and for simulated X-ray images of Venus arising from fluorescent scattering of solar X-rays, and X-rays from SW-\textit{CEX} observed at solar minimum \cite{7} (figure 1b).

Absolute single and multiple \textit{CEX} cross sections with resulting X-ray spectra are required input to and remove considerable uncertainty in planet and comet simulations. Results of theoretical calculations highlight the underlying physics, especially the contribution of multiple transfers and autoionizations in the \textit{CEX} process. Laboratory high-resolution X-ray spectra corroborate the space
Figure 1a. Chandra X-ray image of Comet 8P/Tuttle in the photon energy range 300-1000 eV (41-12.4 Å) [6]

Figure 1b. Simulated X-ray images of Venus arising from fluorescent scattering of solar X-rays (left panel), and from SW-CEX (right panel) observed at solar minimum. The Sun is to the right [7].

phenomena, and provide the $n\ell$ distribution of the emitting levels. There is also an excitement to generating laboratory X-ray spectra resembling spectra observed tens of million miles distant, in a very different setting of a comet or planet!

A second phenomenon receiving attention is the formation of complex molecular species in dusty protostellar and circumstellar regions. Results of the HIFI instrument aboard the Herschel Space Observatory have revealed a rich spectrum (shown in figure 2) of water and organic species in the Orion Nebula [8]. The presence of molecules such as H$_2$O, HCN, SO$_2$, H$_2$CO and CH$_3$OH await detailed simulations involving not only gas-phase collisions, but gas-grain interactions where grain surface type, area, and temperature have a major catalytic role.

Another surprising result from the Herschel Space Observatory is the observation of pulsed extremely high-velocity water jets (velocities of 50 km s$^{-1}$ relative to the source) at protostar L1448-MM in the Perseus Constellation [9]. Water is the fundamental building block of life on Earth, and is assumed to be an important marker for the possibility of life elsewhere in the Universe. Water is the dominant form of oxygen, and is third in abundance in the Universe to H and He. The chemical

Figure 2. Spectrum of water and organics in the Orion Nebula taken by HIFI/Herschel in the frequency range 0.48-2.0 THz (625-150 μm) [8]
origins of water are not understood. Herschel’s “Water in Star-Forming Regions” program - comprising 80 sources of water in the Universe - is directed at understanding water’s linkages with molecule formation, energy balance, and coagulation processes that ultimately produce planets [10]. It is essential to understand chemical and physical processes that form and deplete the water in astrophysical objects. To this end, dust is everywhere an active participant, and molecular-formation routes, including those for formation of H$_2$O, must include the action of dust as a “three-dimensional surface” and catalyst.

2. Solar-wind charge exchange and x-ray emissions
Recent measurements at the Jet Propulsion Laboratory (JPL) have been carried out in CEX between the highly-charged ions (HCIs) Fe$^{(5-13)+}$ present in the SW, with CO, CO$_2$ [11] and H$_2$O [12]. All three species are abundant in a variety of astronomical objects such as comets, planetary exospheres, circumstellar envelopes, and the interstellar medium (ISM). The process can be written as

\[
\text{Fe}^{q+} + \text{A-B} \rightarrow \text{Fe}^{(q-j)+} + \text{A-B}^{(j+s)+} + \text{se}, \tag{1}
\]

where $j+s$ is the number of electrons transferred from the target A-B, $j$ is the number of electrons transferred to – or captured by – Fe$^{0+}$, and $s$ is the number of free electrons ($e$) produced in the collision. Cross sections for up to $j = 3$ electrons have been measured in CO and CO$_2$, and up to $j = 5$ in H$_2$O. Details of the experiments, including instrumentation, tests for metastable levels, gas-cell exit aperture sizing, beam currents, and error limits are found in the references above and in earlier work [13]. A schematic diagram of the CEX portion of the HCI beam line is given in figure 3.

The JPL measurements in each case were combined with results of calculations in the $n$-electron classical trajectory Monte Carlo ($n$CTMC) method. Shown in figure 4 are results of experiments and theory in CO for single $j = 1$ and double $j = 2$ exchange; and in figure 5 results in CO$_2$ for $j = 1$ and $j = 3$. CEX results for H$_2$O are given in figure 6 for $j = 1$ and $j = 3$ exchanges. For ease of viewing, the $j=1$ capture cross sections for CO, CO$_2$ and H$_2$O in figures 4-6 have been plotted with the same ordinate scaling. To within $\approx 15\%$ there is a similarity of slope in the increase of the experimental $\sigma_{q,q-1}$ with $q$, in good agreement with results of the $n$CTMC theory. The increase in capture cross section with $q$ can be understood in terms of an ion’s capture sphere or impact parameter that increases with $q$. The similarity in shape and magnitude of the $j=1$ cross sections is consistent with the molecular targets’ behaving as “spectators” to the collision: they supply an electron to the high-$n$ quantum states of the projectiles. In the case of double and triple transfers, the experimental and $n$CTMC results have a

![Figure 3. Schematic view of the beam line for measuring absolute CEX cross sections [13]. The legend is: HCI beam-collimating apertures (A), target gas cell (C), retarding field plates (R), suppressor electrode (S), ion Faraday cup (FC), capacitance manometer (CM), and an HPGe X-ray detector (interchangeable with a grazing-incidence spectrometer) for X-ray spectra measurements.](image)
smaller variation with \( q \), and a factor of 2-5 between them. The shaded errors shown for the \( n \)CTMC theory results are based on the case – for the upper limit – where all higher transfers autoionize to the \( j \)-transfer being calculated; and on the case – for the lower limit – where all higher transfers are stabilized, and none autoionize to the \( j \)-transfer under consideration \([11, 12]\).

3. Atom-dust collisions and complex molecule formation
Dust plays an indispensable role in the chemical evolution of protostellar regions from the catalytic production of molecular hydrogen, to the formation of organic species such as \( \text{H}_2\text{CO}, \text{CH}_3\text{CH}_2\text{OH}, \text{CN} \), and sulfur-bonded species critical to the origins of life. Organic species found in cometary bodies trace their appearance, in part, to the presolar nebula. The lack of experimental and theoretical data on dust-catalyzed chemistry is only recently being addressed through observations, simulations, and laboratory studies to understand the chemical evolution of the molecular cloud core, from star formation to the development of the circumstellar/protoplanetary disk \([14]\). In addition, accretion in a protostar leads to formation of a circumstellar disk that will partially dissipate and eventually evolve.
into a protoplanetary disk. This formation is accompanied by energetic processes such as infalls, outflows, shocks, and impact of surrounding dust by thermal and superthermal neutral atoms. These impacts can lead to new chemical reactions of the outflowing neutrals with abundant grain-adsorbed species such as H$_2$, O$_2$, H$_2$O, NH$_3$, and CH$_4$. As an example of an energetic environment, shown in figure 7 is a representation of the circumstellar envelope (CSE) for an AGB star. The important elements of the CSE are the outflow of thermal and superthermal H and O atoms interacting with molecular species adsorbed on the circumstellar dust grains. The composition of the grain surface will vary with temperature region, so that higher freezing point species are condensed in the intermediate regions of the CSE, and all species (including H$_2$ and O$_2$) are frozen in the outer, colder CSE.

In order to simulate the effects of thermal and superthermal ground-state H($^2$S) and O($^3$P) atoms on dust grains, an atomic-beam source was used capable of generating these ground-state species at any selected energy between 0.1 and 50 eV, and colliding them with molecules adsorbed on dust-grain simulants. A schematic diagram of the apparatus is given in figure 8, and details discussed in Refs. [15-19]. Briefly, the fast atoms are produced first by molecular dissociative attachment to form their negative ion, the ion accelerated to the desired final energy, and the electron laser-detached to generate the corresponding neutral atom. Since only the visible lines of the Ar-ion laser are used, the photodetachment results in only ground-state species H($^2$S) or O($^3$P) from detachment of the respective H$^-$($^1$S) and O$^-$($^2$P) ions.

**Figure 6.** Results of the nCTMC calculation and radiative/Auger cascade processing for CEX in Fe$^{5-13+}$ collisions with H$_2$O (△) compared with experimental data (■) [12]. Shown are the single CEX results (left panel) and triple CEX results (right panel), with error bars representing the maximum estimated uncertainty from the cascade model.

**Figure 7.** Schematic view of characteristic regions of the circumstellar envelope (CSE) of an AGB star. Shown are distances $R_*$ from the central star and approximate temperatures in each region. The indicated reactions to be studied include H$_2$O formation by reduction of O$_2$ and oxidation of H$_2$; as well as depletion of H$_2$O by solar and ISM electrons, photons and ions.
Given in the following is a summary of recent results for molecular formation on dust-grain simulants, and a means for studying the important processes of water formation by oxidation and reduction reactions on grains. An initial measurement was undertaken to account for the high abundance of CO$_2$ detected in, for example, quiescent dark clouds such as Elias 16 where photochemistry has a minimal role [20]. The reaction O($^3$P) + CO(s) → CO$_2$(s) was studied at O-atom energies of 2, 5, 10, and 14 eV [17]. Results of these measurements at 5 eV are shown in figure 9. After exposure of the CO-covered surface to the O-atom beam, TPD-MS was carried out, releasing the surface-species and detecting them through their characteristic mass spectra. Shown in figure 9a is the production of CO$_2$ from the reaction O($^3$P, 5 eV) + CO(s) → CO$_2$(s). Measurements were also carried out at 2, 10, and 14 eV. Background checks were run, and tests carried out with laser “on” and laser “off” to confirm that the CO$_2$ was a product of the O-atom beam. These results are shown in figure 9b. Enhancement of CO$_2$ production is seen at mass 44 u at all O-beam energies. Shown in figure 9b (insert) is the relative production yield Y. This yield is defined as the ratio of mass signal with laser “on” to signal with laser “off,” relative to the same ratio for $^{12}$C. And hence a ratio Y = 1 for any mass indicates that the presence of fast O-atoms (i.e., laser detachment) did not enhance that mass. This yield is a maximum at O-atom energies of ≈ 10 eV. There are at present no calculations of the energy dependence for this process.

In a second series of measurements, the effects were studied of superthermal H($^2$S) atoms incident on a CO-layered surface [18]. A larger number of atomic and molecular masses was encountered in this case, and the deconvolution to convert the mass spectrum to species identification was carried out using a novel application of the Metropolis random-walk procedure. Here, a trial set α of masses was used, where α = {H$_2$O, CO, N$_2$, CO$_2$, O$_2$, H$_2$CO, CH$_4$, HCOOH, CH$_3$OH, CH$_3$CH$_2$OH}. The vector formed by the fragmentation pattern of each mass, weighted by an unknown abundance, is “walked” onto the experimental mass-fragmentation vector by variation of the abundances. To test convergence, the goodness-of-fit is evaluated with addition of other chemical species. Typical results of the calculations with the experimental TPD spectrum for masses 29 u and 30 u are given in figure 10a. The monitored masses was the set i = {12, 14, 16, 17, 18, 28, 29, 30, 31, 32, 44, 69}. From the
identifications and enhancements, the new chemical species produced in this collision were H$_2$CO (formaldehyde) and CO$_2$. The relative production yields $Y$ are shown in figure 11b. Heuristic chemical reactions to account for the production of these species are given in Ref. [18]. The molecule H$_2$CO is
commonly observed in many astronomical regions.

In a third series of measurements the effects of superthermal O(3P, 9 eV) atoms impinging on a CH₄-adsorbed surface was studied [19]. The purpose here was to detect the formation of CH₃OH via a simple chemical insertion of the O-atom into the CH₄ molecule. Results of the TPD spectrum are given in figure 11a. In fact, four new species were formed: CO₂, CH₃OH, HCOOH (formic acid), and CH₃CH₂OH (ethanol). The formation of CO₂ very likely proceeds through interaction of the O-beam with trace amounts of the CO — used as the O feed gas — coated upon the target surface. Clear production of CH₃OH is seen in figure 11b. This reaction very likely proceeds through the insertion O(3P, 9eV) + CH₄→ CH₃OH. Possible reaction paths are given in Ref. [19] for formation of HCOOH (via oxidation of CH₃OH) and CH₃CH₂OH (via insertion of a CH₂• radical into CH₃OH).

Figure 11a. Species-resolved signals |\vec{R}^α| for the reaction products CO₂, HCOOH, CH₃CH₂OH, and CH₃OH as obtained from one of four separately-measured TPD spectra in the reaction O(3P, 9 eV)+CH₄. Results from the four experiments were integrated and averaged to provide the net signals. The random-walk method was used to project the total measured TPD signal into the individual species contributions |\vec{R}^α|.

Finally, it is important to consider the chemical framework of the formation and depletion of the vast amounts of water in the Universe [9]. Given the prevalence of dust, thermal and superthermal atoms, and an abundance of grain-adsorbed molecules in protostellar and circumstellar regions, it is natural to consider the formation of water (with measurement of the absolute reaction yield) through simple channels of oxidation of grain-adsorbed H₂ by the reaction O(3P) + H₂→ H₂O; as well as the reduction of grain-adsorbed O₂ by the net reaction 4H•(S) + O₂→ 2H₂O. Modest amounts of atom energy (less than about 5 eV) would be required for the initial bond-breaking steps.

4. Future outlook
The solar wind CEX process operates at almost all the solar-system planets, moons, and comets. Planetary bodies. The SW consists of a rich array of HClis. The composition of planetary exospheres, comets, and moons includes a broad range of species such as He, Ar, H₂, N₂, CO, H₂O, and CO₂. The emitted CEX emissions can be used to detect comets; while comets and exospheres can be used to
probe the SW composition and velocity [2]. There are no CEX cross sections available for many of the HCIs, and it would be interesting to carry out measurements of O, Mg, Si, and Fe ions with the abundant neutrals such as He, H$_2$, H$_2$O and CO$_2$. There should also be X-ray spectra accompanying the cross-section measurements, in order to simulate in the laboratory the X-ray emissions detected in the space observations [21].

Use of ground-state superthermal atoms to study processes that occur in astrophysical objects opens reaction channels that have heretofore not been studied. Measurements of exit channels and absolute yields, especially in the case of water formation, are critical to understanding the importance of this reaction scenario. Given the fact that species such as CO, H$_2$O, NH$_3$, CH$_4$, and CH$_3$OH ─ together with dust ─ are relatively abundant in space, one can consider the extent to which the thermal and superthermal atoms can produce molecules larger than ethanol. There is the expectation that formation of the building blocks of life may be proceeding in some part through this route. To be complete, other paths that may form and deplete water, such as ionization and dissociation by electrons, photons, and ions must be studied, and their yields measured.

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References
[1] Cravens T E 2002, Science 296 1042
[2] Bhardwaj A et al 2007, Planet. Space Sci. 55 1135
[3] Dennerl K et al 2003, Proc. SPIE 4851 277
[4] Robertson I P and Cravens T E 2003, Geophys. Res. Lett. 30 1439; Robertson I P, Collier M R, Cravens T E and Fok M C 2006, J. Geophys. Res. 111 A12105
[5] Cravens T E, Robertson P I and Snowden S L 2001, J. Geophys. Res. 106 24,883
[6] Christian D J et al 2010, Ap. J. SS 187 447
[7] Dennerl K 2008, Planet. Space Sci. 56 1414
[8] Bergin E, courtesy of the ESA, HEXOS, and the HIFI Consortium (©2010); Decin L et al. 2010, A&A 516 A69
[9] Kristensen L E and van Dishoeck E F 2011, Astron. Nachr./AN 332 475
[10] van Dishoeck E F et al 2011, Pub. Astron. Soc. Pac. 138 123
[11] Simcic J, Schultz D R, Mawhorter R J, Chutjian A, Čadež I, Greenwood J B, Lisse C M and Smith S J 2010, Phys. Rev. A 81 062715
[12] Simcic J, Schultz D R, Greenwood J B, Mawhorter R J, McKoy B V, Smith S J, Winstead C and Chutjian A 2010, Ap. J. 722 435
[13] Čadež I, Greenwood J B, Lozano J A, Mawhorter R J, Smith S J, Niimura M and Chutjian A 2003, J. Phys. B 36 3303
[14] Garrod R T, Widicus Weaver S L, and Herbst E 2008, Ap. J. 682 283
[15] Chutjian A and Orient O J 1996, “Fast Beam Sources,” in Atomic, Molecular and Optical Physics: Atoms and Molecules (Experimental Methods in the Physical Sciences, Vol. 29B) (ed. F. B. Dunning and R. G. Hulet, Academic Press, San Diego).
[16] Madzunkov S, MacAskill J A and Chutjian A, unpublished results.
[17] Madzunkov S, Shortt B J, MacAskill J A, Darrach M R and Chutjian A 2006, Phys. Rev. A 73 020901(R)
[18] Madzunkov S, MacAskill J A, Chutjian A, Ehrenfreund P, Darrach M R, Vidali G and Shortt B J 2009, Ap. J. 697 801
[19] Madzunkov S, MacAskill J A and Chutjian A 2010, Ap. J. 712 194 (2010). Note that the product in Reaction (4) should be H$_2$(s) and not H$_2$O(s).
[20] Whittet D C B et al 1998, Ap. J. 498 L159
[21] Miller K A et al 2011, Ap. J. 742 130