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Charge Transfer in Collisions of Ions with atoms and molecules

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Bibliography

- The Physics of Multiply and Highly Charged Ions.
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- Volume 1. Sources, Applications and Fundamental Processes
- Volume 2 Interactions with Matter

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1. Introduction.

Charge changing collisions between multiply charged ions and atoms are of practical importance in many high temperature laboratory and astrophysical plasmas. Why is this so?

Even if complete local thermodynamic equilibrium (LTE) is rarely attained in most laboratory or astrophysical plasmas, the ion velocity distribution ions is near Maxwellian with

$$v_i \approx v_e \sqrt{m_e / m_i}$$

The cross sections for ion-atom and electron atom collisions being of the same order of magnitude, ion-atom rate constants are smaller than the electron-atom rate constants by a factor of 50-200. So why is ion-atom charge exchange important?

The reason is that that the fractional ion abundance is rarely in LTE. LTE requires collision processes to be dominant in the plasma. But while this is usually true for two-body elastic, inelastic and ionizing collisions, it is not always the case for ion-recombination processes.

Purely collisional electron-ion recombination in a collision is a three-body process, which is efficient only at high electron densities. At lower electron densities, radiative recombination is often the dominating process.

This has little consequence for the fractional ion abundance for H or He but it can have a dramatic effect on the fractional abundances of the higher charge states of minor complex species (such as C, N, O,...), whose spectral lines are often used for spectroscopic diagnostics of the plasma. So we need to understand the microscopic processes of ionization and recombination. Furthermore, the presence of these ions leads to cooling processes, whose effect on the temperature of the plasma is appreciable.

But the main reason why multiply charged ions interacting with common neutral atoms such as hydrogen or helium is so important arises from the fact that these ions possess bound electron states at energies lower than the bound states of H or He. So even at thermal collision energies these ions can capture an electron from the target atom without any energy constraints. (This may be compared with electron collisions where only the energetic electrons of the tail of the Maxwellian distribution are capable of ionising the target atom.)

The process of charge exchange is therefore a major contributor to the electron-ion recombination process.

Some of the most striking manifestations of charge transfer reactions are to be found in several astrophysical objects, such as gaseous planetary nebulae ionized by the UV radiation of a bright star and Seyfert galaxies ionized by X-rays of an active galactic centre. Only by the inclusion of charge transfer reactions can the astrophysical models be made to reproduce the actual observations. The reaction rates for the critical reactions of $O2+/H$ and $N2+/H$ adjusted to fit the observations are found to be in excellent agreement with calculations and experiment.

Other such illustrations of the charge transfer process (in particular of its state selective nature) is revealed by the emission from comets of X-ray photons with energy of hundreds of eV . These photons are produced by excited states of highly charge ions in the solar wind (C, N, O, Ne, Mg, Si, Fe,...) populated by electron capture from the cold cometary gas. The process is similar to what happens in a tokamak when cold gas is injected into the divertor region.
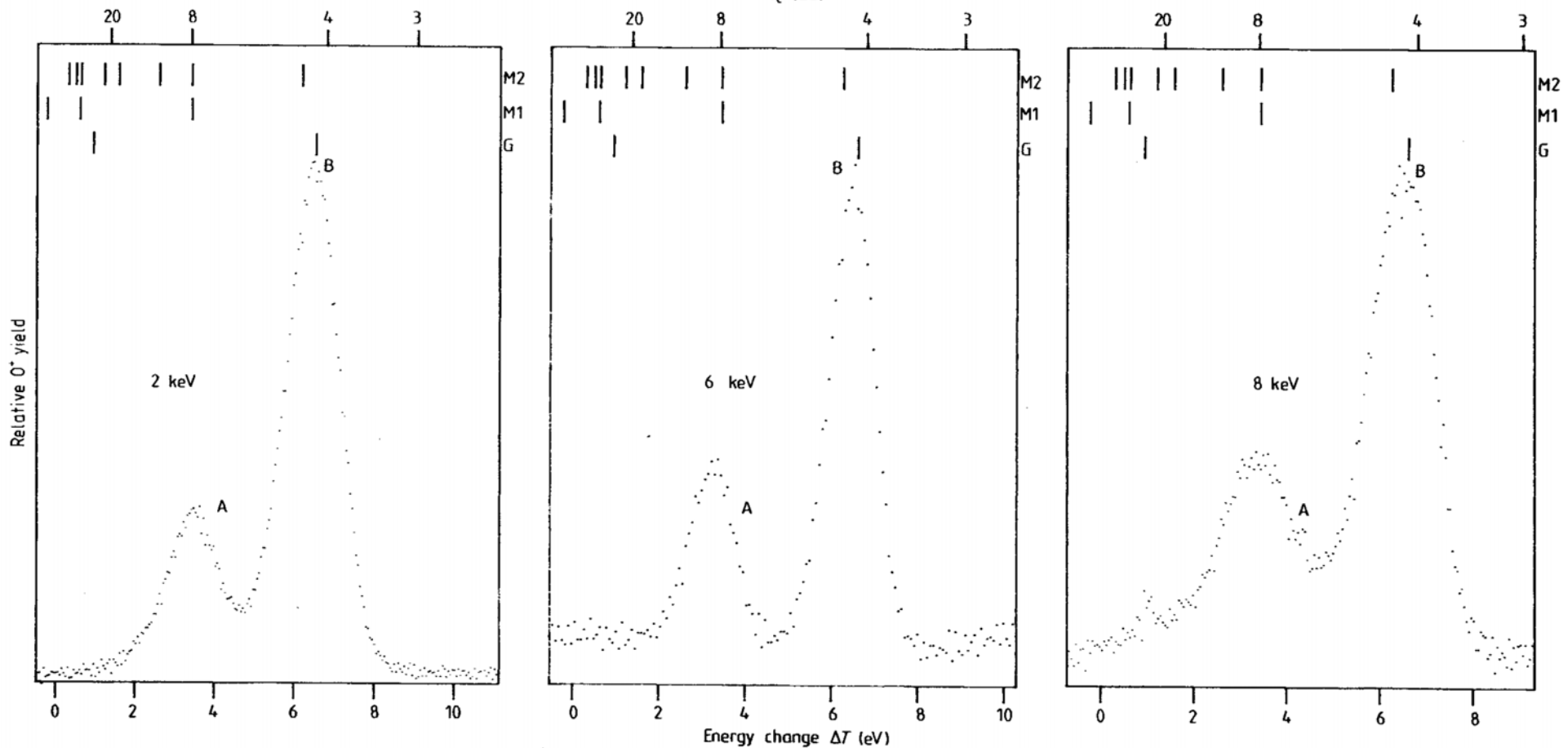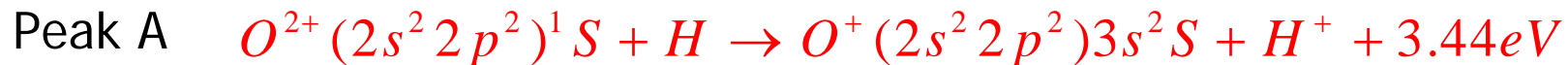
Figure 1. Energy change spectra for one-electron capture by O^{2+} ions in atomic hydrogen at energies of 2, 6 and 8 keV.

Energy gain spectrum in O2+/H collisions.

Peak A $\quad O^{2+}(2s^2 2p^2)^1 S + H \rightarrow O^+(2s^2 2p^2)3s^2 S + H^+ + 3.44 eV$

Peak B $\quad O^{2+}(2s^2 2p^2)^3 P + H \rightarrow O^+(2s2p^4)^4 P + H^+ + 6.64 eV$

Question. Why such selectivity?

Several questions are immediately raised.

Why do we only observe these specific electron capture channels?

Why are the cross sections for electron capture do so large, given the difficulty to transfer energy from a heavy particle (atom or ion) to a light particle (electron)?

The simplest explanation can be given in terms of a quasi-molecular description of the collision complex. At collision energies less than a few keV/amu, the ions have a velocity which is much smaller than the typical electron velocity of the electrons. (A proton of 25 keV has a velocity of an electron in a Bohr orbit). So we may think of the collision complex in terms of the adiabatic representation (Born-Oppenheimer approximation) used to describe bound states of stable molecules. In the collision, the electrons find themselves in a quantum state, whose energy adjusts adiabatically to the nuclear motion;

In a stable molecule, the electronic states are weakly coupled. But in a collision, the initial state of the collision partners may be correlated to an excited electronic state of the quasi-molecule. Sometimes excited adiabatic states of molecules are subject to crossings (or avoided crossings) of their potential energies. In the vicinity of these crossings, little energy needs to be transferred from the electrons to the nuclei. So an electronic transition leading to charge transfer is probable.
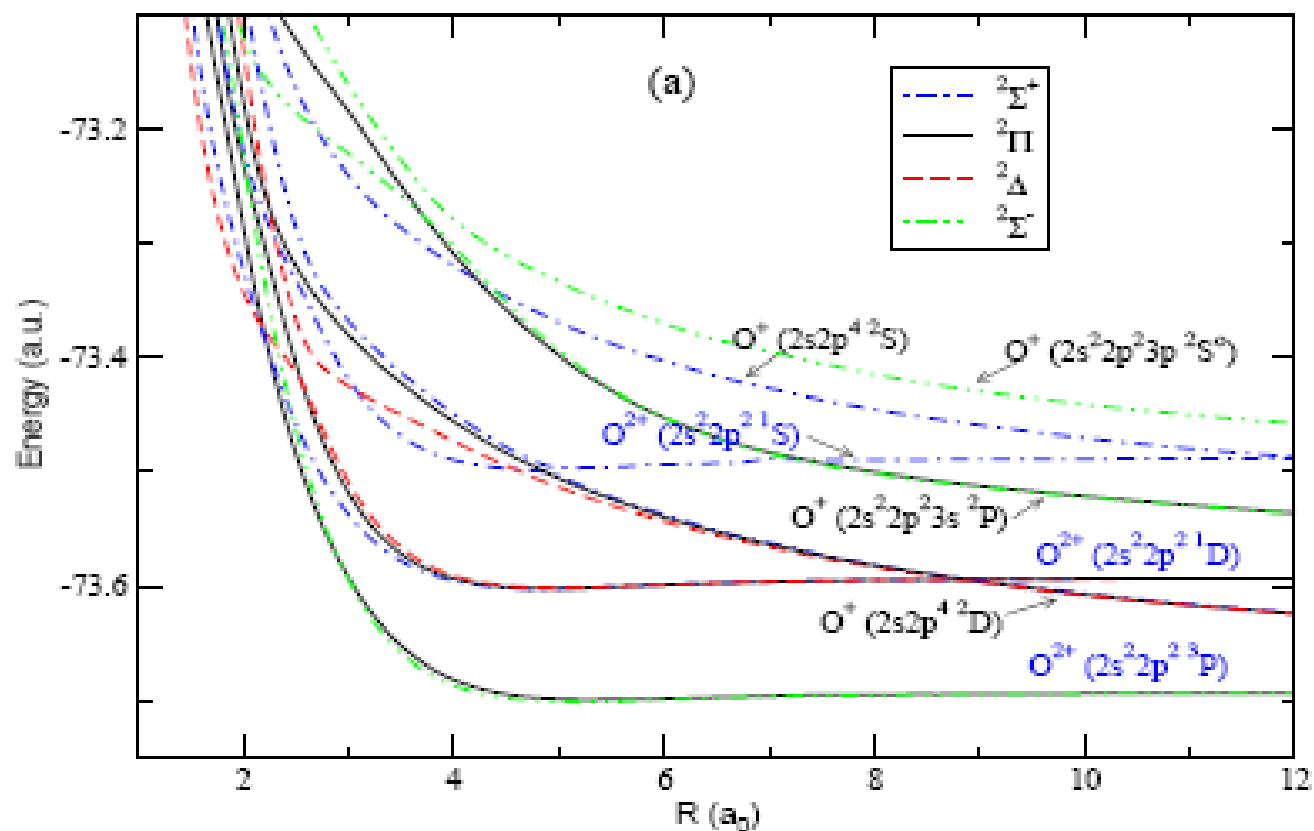
FIG. 1: Potential energy curves of the doublet states of the OH2+ quasi molecule. Indicated in the figure are the states of the O2+ and O+ ions to which the molecular states dissociate in the asymptotic limit.
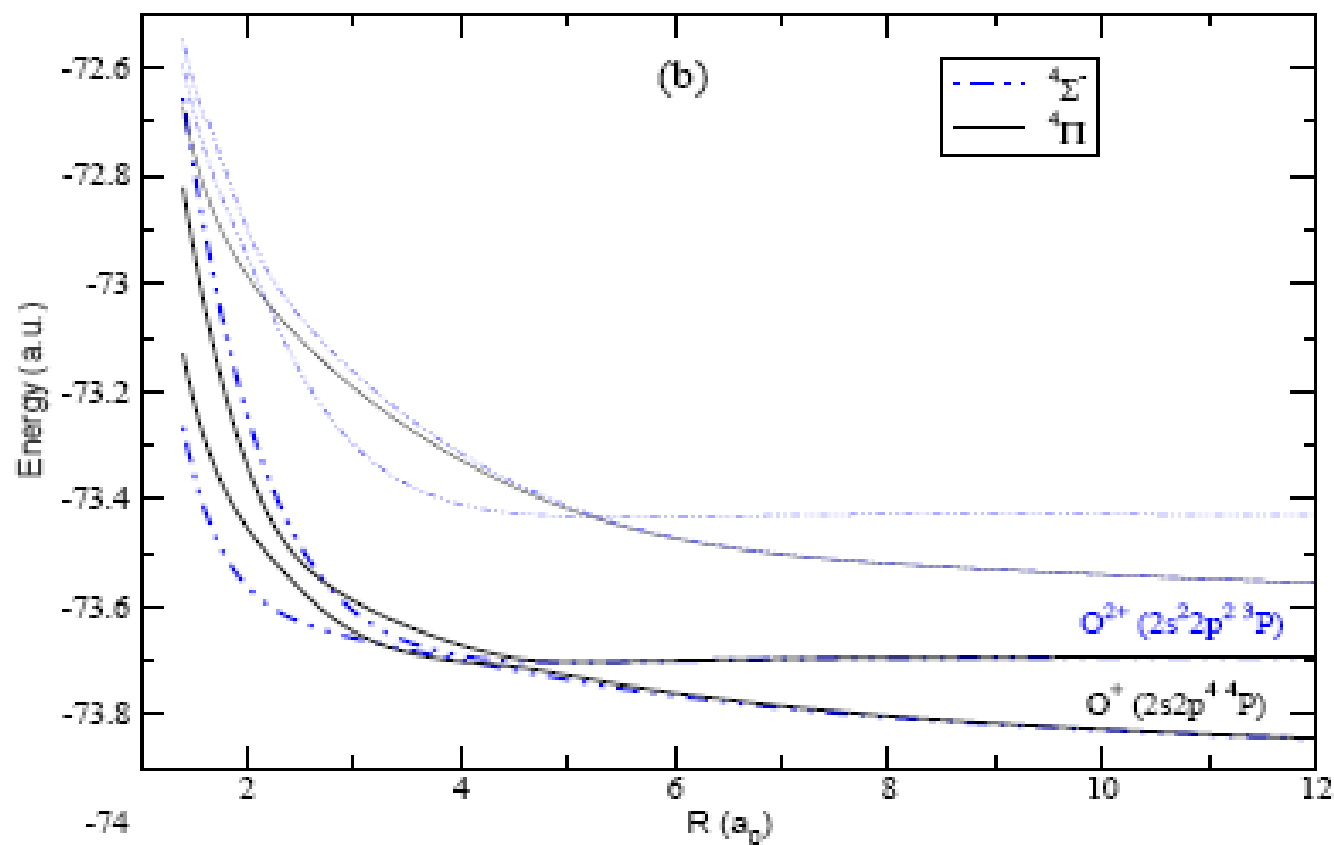
FIG. 1: Potential energy curves of the quartet states of the OH2+ quasi molecule. Indicated in the figure are the states of the O2+ and O+ ions to which the molecular states dissociate in the asymptotic limit.
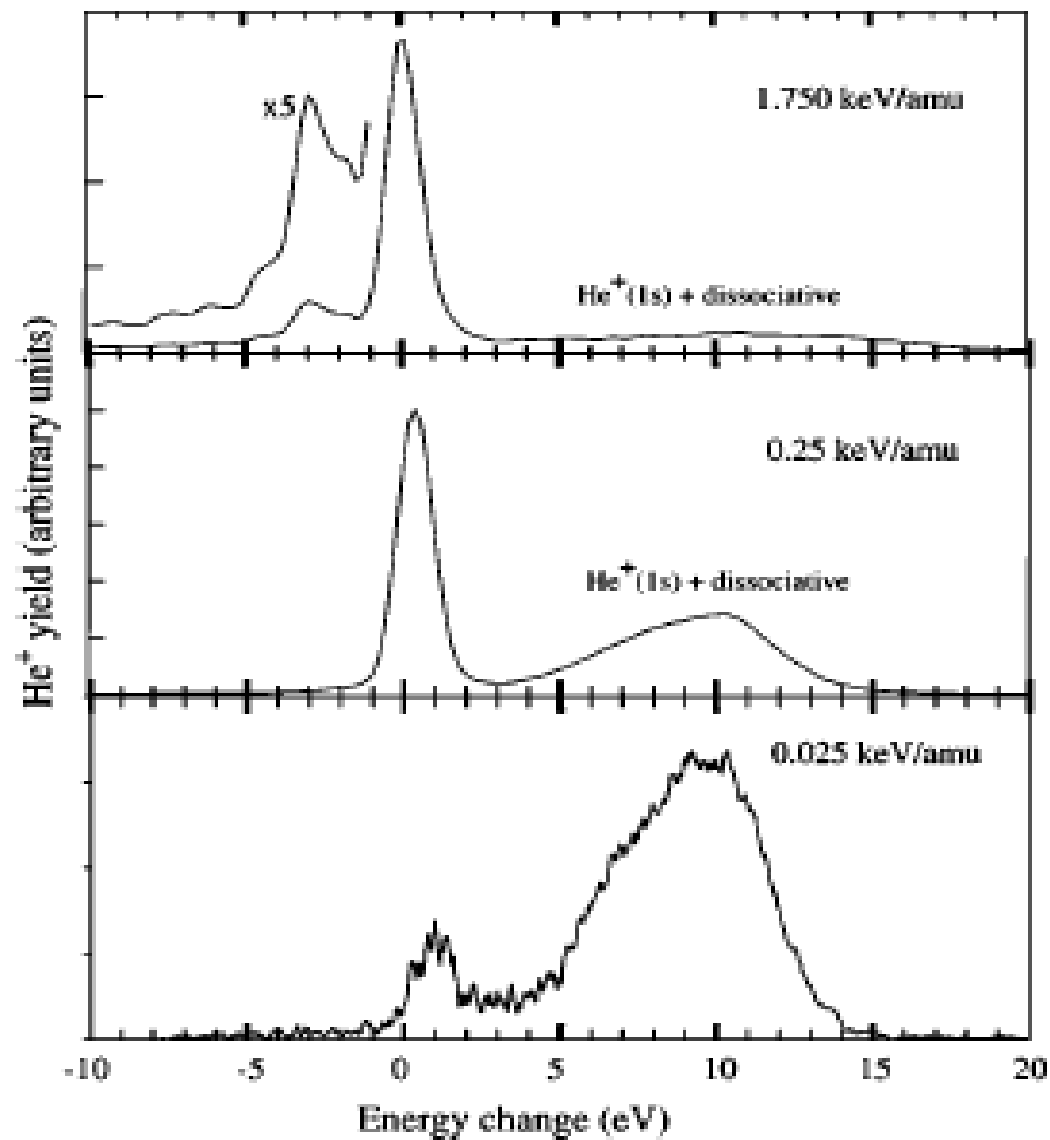
FIG. 1. Energy change spectra for one electron capture by He^{2+} ions in H_2O at three representative energies recorded by the QUB and WMU translational energy spectrometers (see text).
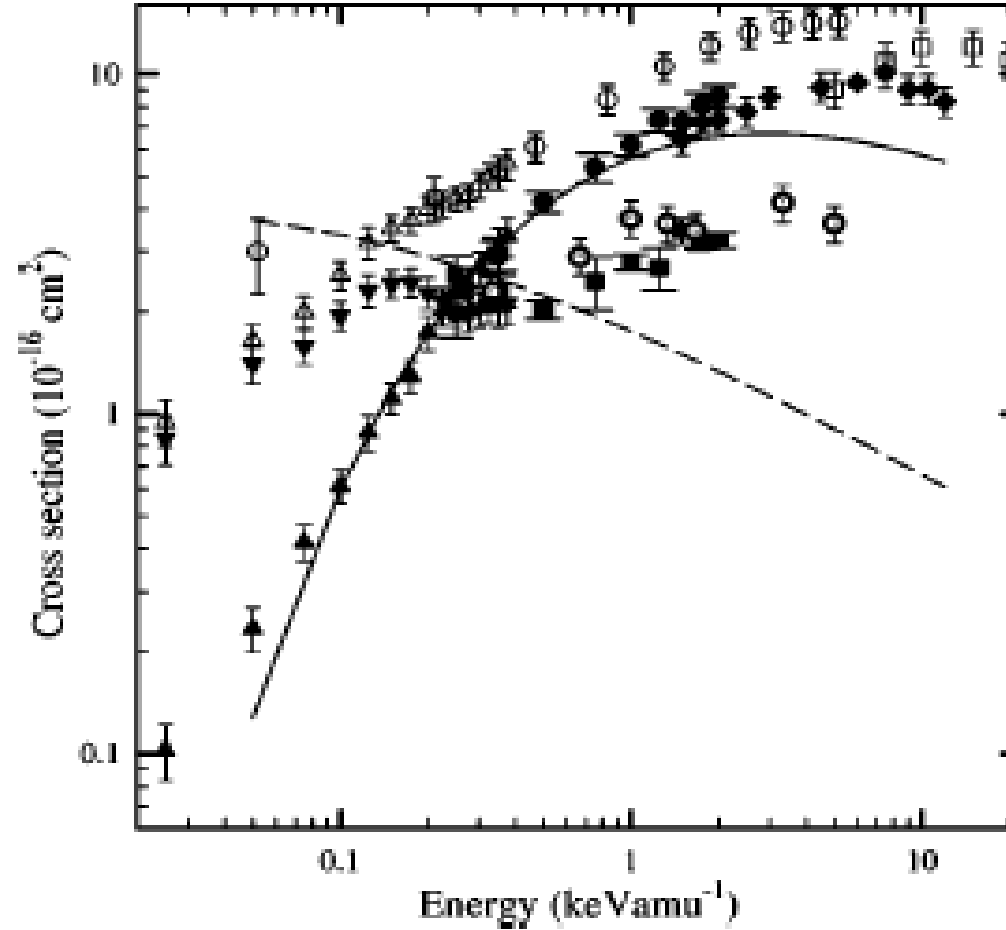
FIG. 5. Cross sections for one electron capture by He^{2+} ions in H_2O. Total cross sections: open squares, Rudd *et al.* [6]; open circles, Greenwood *et al.* [9]; open triangles, present work. Capture into He^+ ($n=2$) states: closed circles, QUB; closed triangles, WMU. He II ($2p$-$1s$): closed diamonds, KVI. Capture into He^+ ($n=1$) state: closed squares, QUB; inverted triangles, WMU. Transfer ionization: circles with cross hairs, HMI. Theory: solid line, He^+ ($n=2$) formation: dashed line. He^+ ($n=1$) formation.

FIRST X-RAY IMAGE OF A COMET
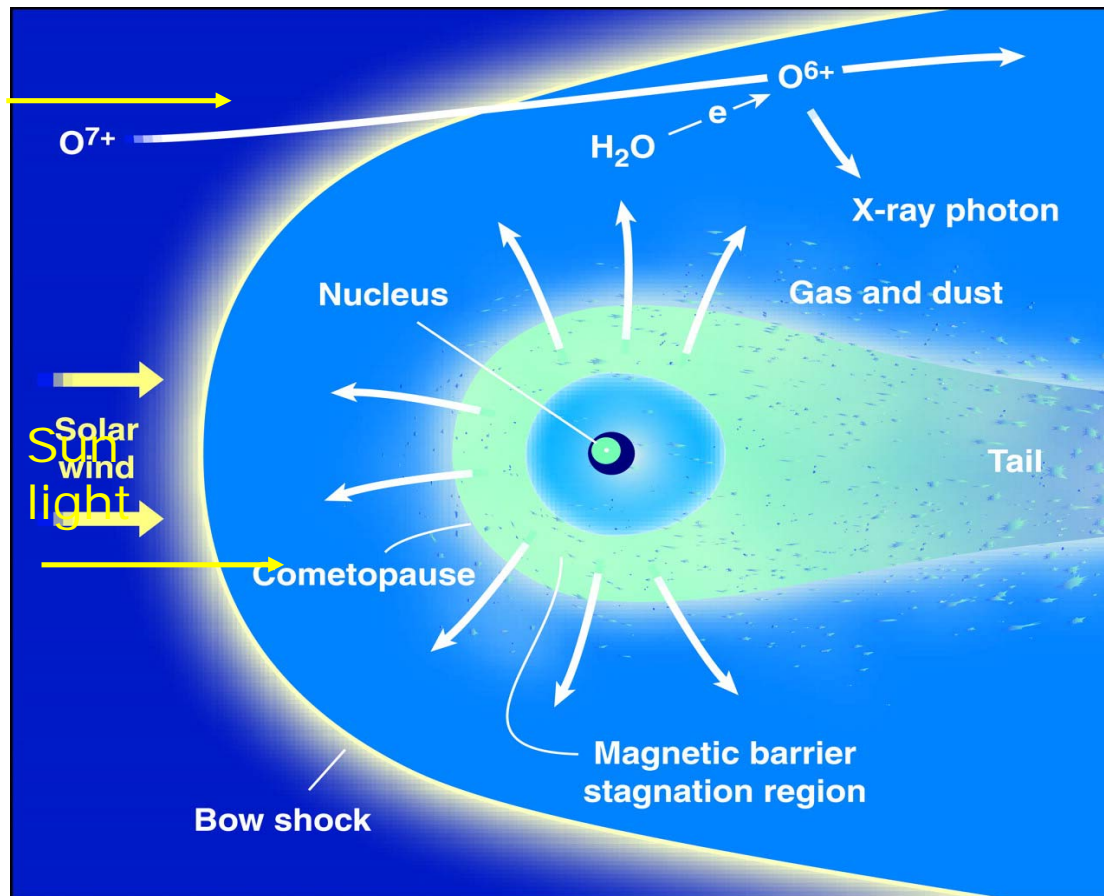
Comet Hyakutake · C/1996 B2   ROSAT HRI

March 27, 1996

sampled region

nucleus +

Sun

10 arcmin

55 000 km
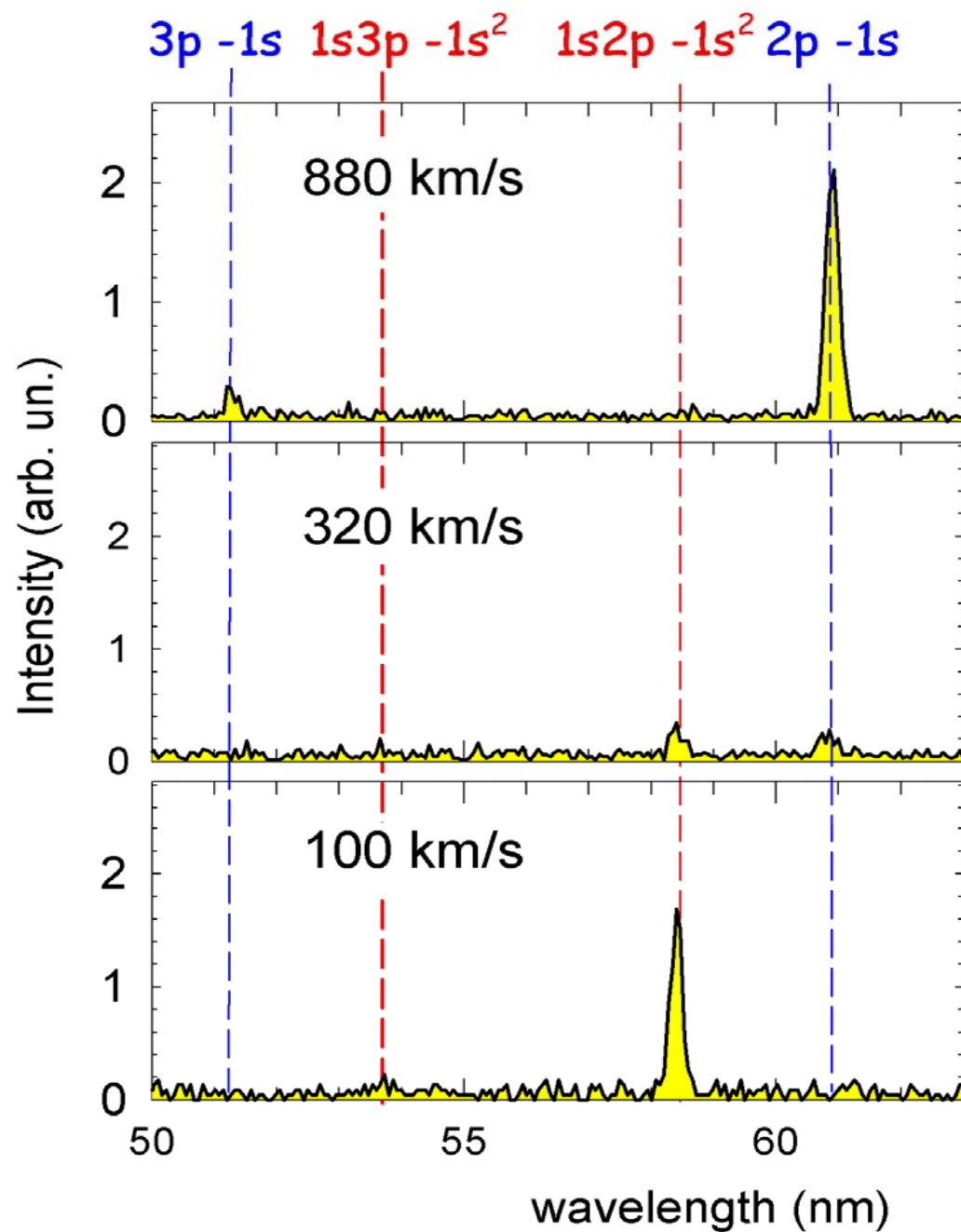
comet motion
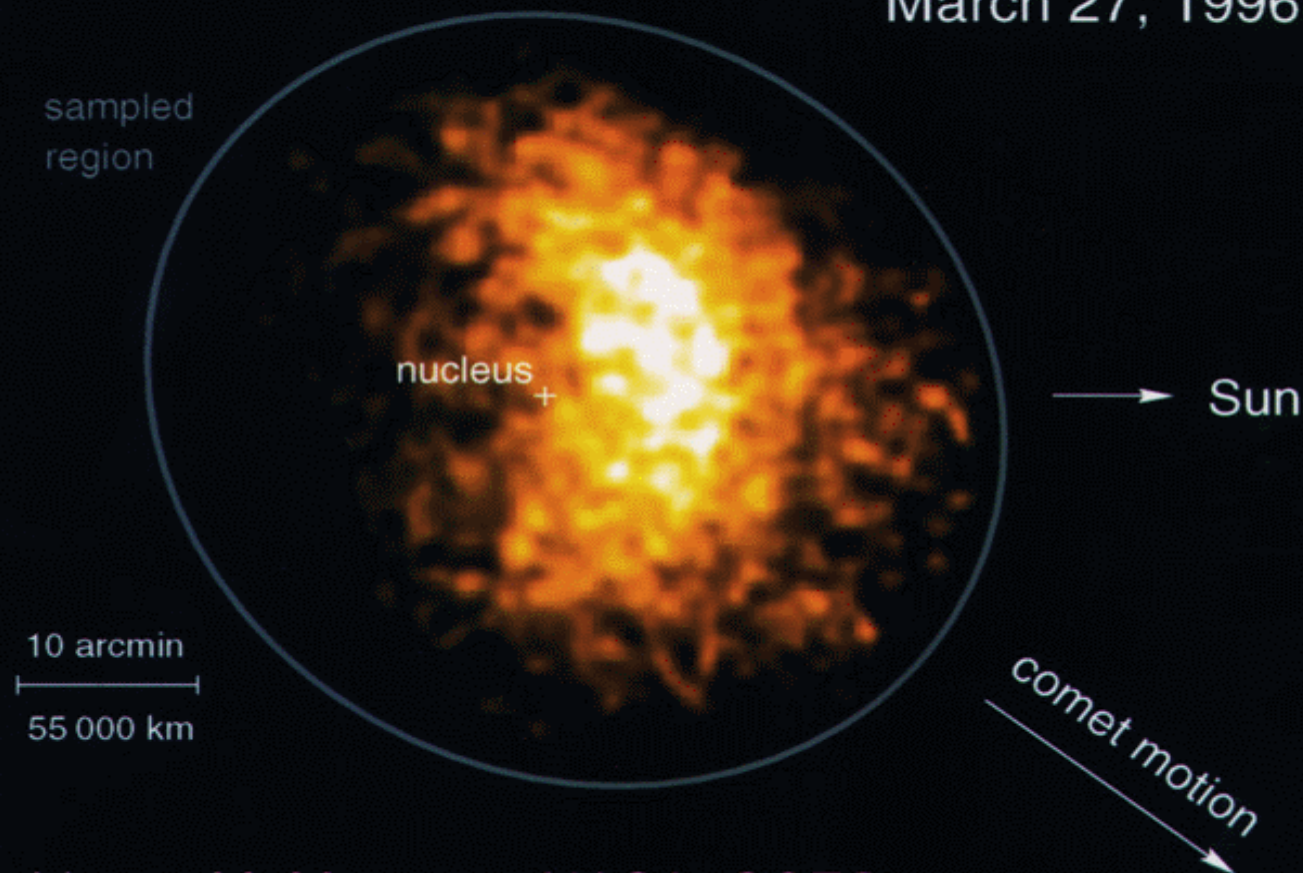
C. Lisse, M. Mumma, NASA GSFC

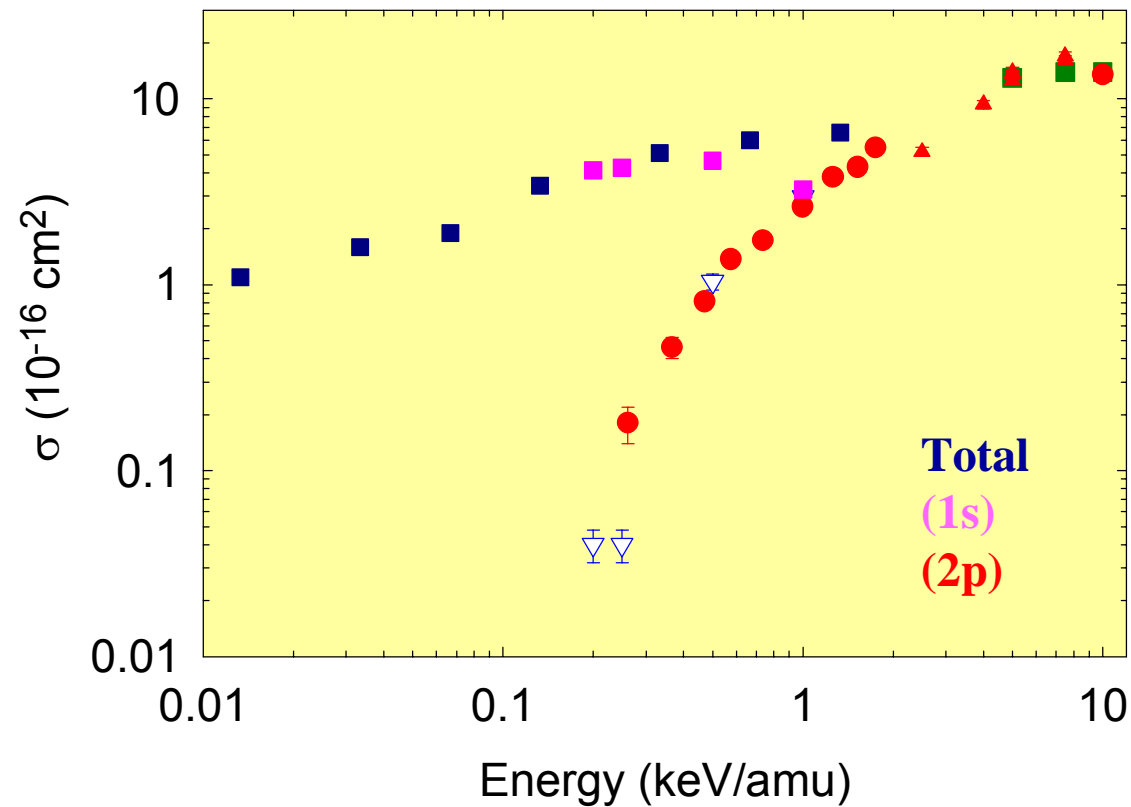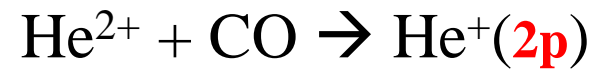K. Dennerl, J. Schmitt, J. Englhauser, MPE

Comets & the Sun

- Nucleus produces water
- at ca. 3000 kg/s (10^{29} mol/s)
- Ionized and/or dissociated
- Picked up by Solar Wind
- Dragged into tail

- 10^6 km Bowshock
- 10^5 km Cometopause
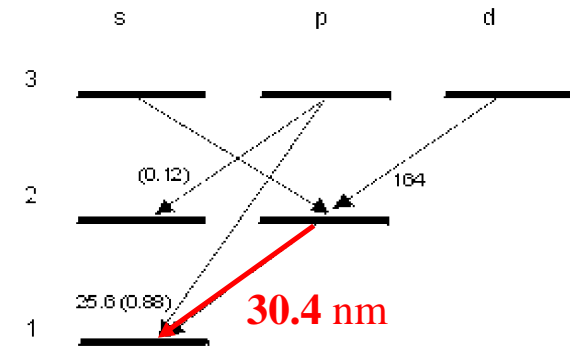- 10^3 km Contact surface
- 10 km Nucleus

Light emission spectra from He^{2+} + CO collisions at various collision velocities
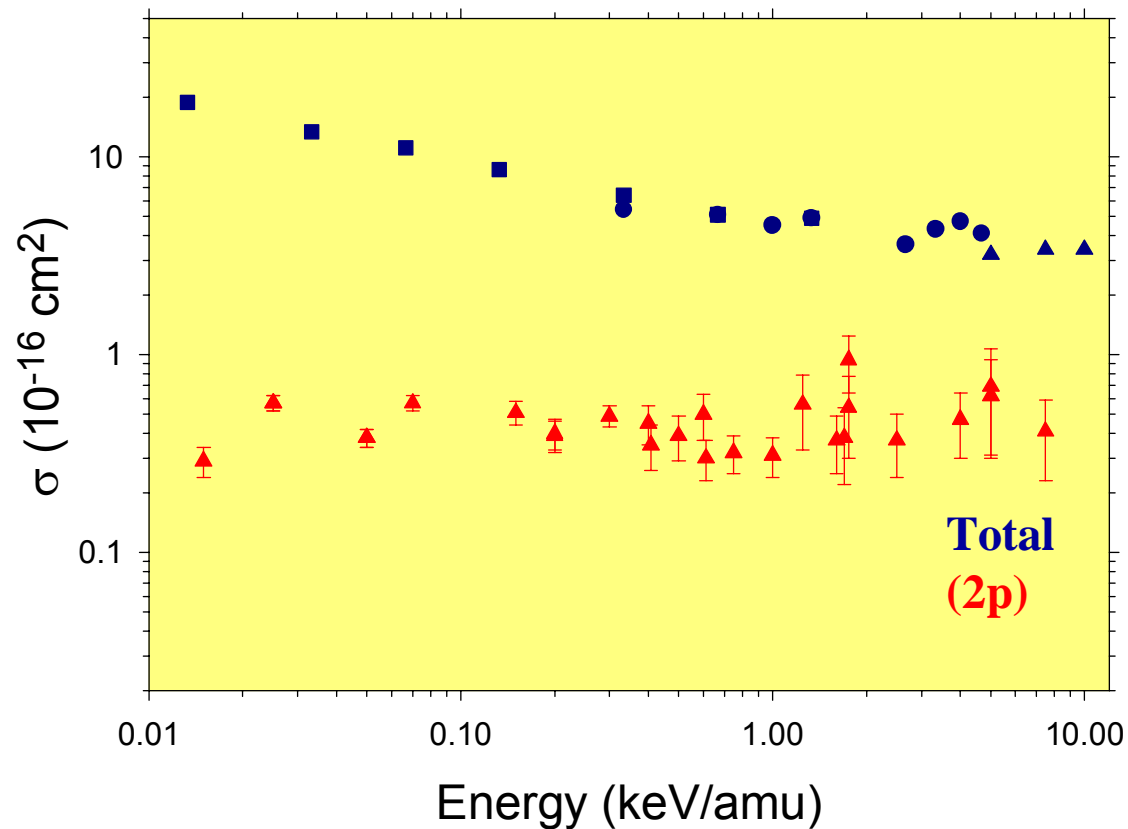
Single electron capture

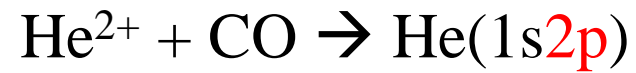$$He^{2+} + CO \rightarrow He^{+}(\textbf{2p})$$

He$^+$ emission

!! 30.4 nm !!

Double electron capture

$$He^{2+} + CO \rightarrow He(1s2p)$$

He emission
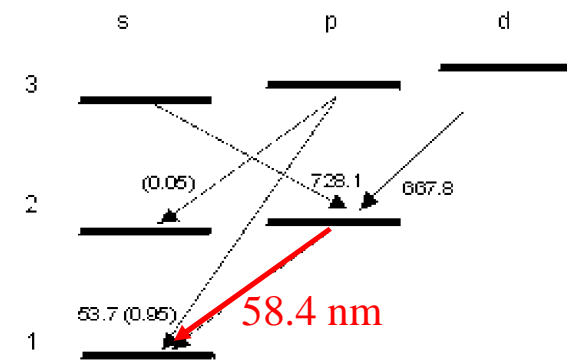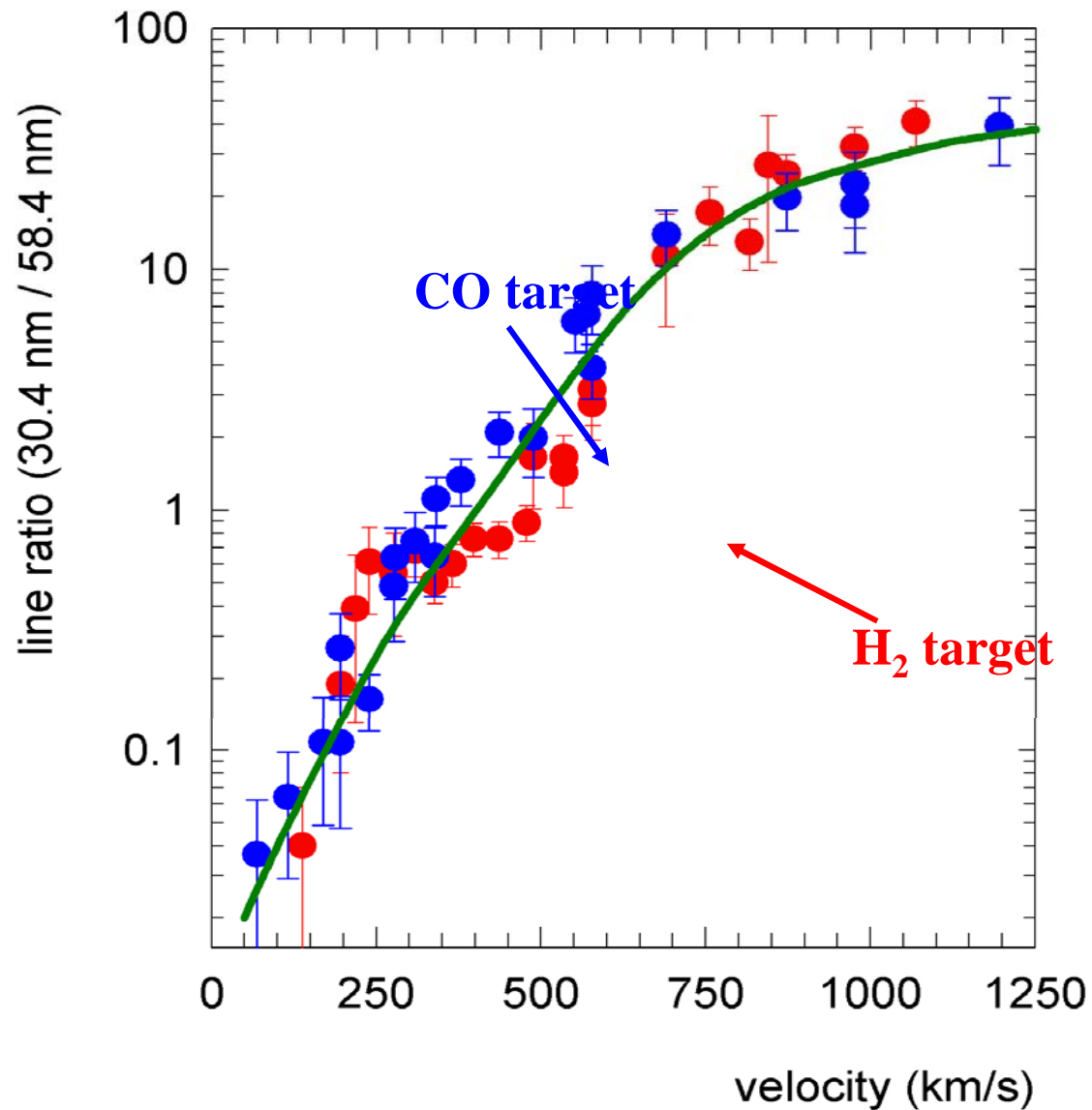
!! 58.4 nm !!

- Velocity dependent intensity ratio of 30.4/58.4 nm lines ($He^+_{(2p-1s)}/He_{(1s2p-1s^2)}$)

Since the recognition of the charge transfer process as an important contributor to the problem of plasma diagnostics, much activity has developed both at an experimental and theoretical level.

On the experimental side, there are several complementary techniques:
- photon emission spectroscopy ion (KVI Groningen)
- translation spectroscopy (Belfast, Orsay, …)
- merged beam (Oak Ridge National Laboratory)

But few existing experiments were designed to measure absolute cross sections.

Translation spectroscopy techniques are the most efficient for collision energies in the range of several hundred eV/amu.
Photon emission spectroscopy techniques cover a wide energy range, but the interpretation of the data is indirect.
Merged beams allow cross section measurement at very low energies.

Although we are still some way from a comprehensive and accurate data required for modelling the microscopic processes in a plasma, we now have fairly clear ideas of the dominant processes.

Electron-capture cross section at near-thermal collision energies for Si 4+/D

Marc Pieksma, M. Gargaud, R. McCarroll, and C. C. Havener

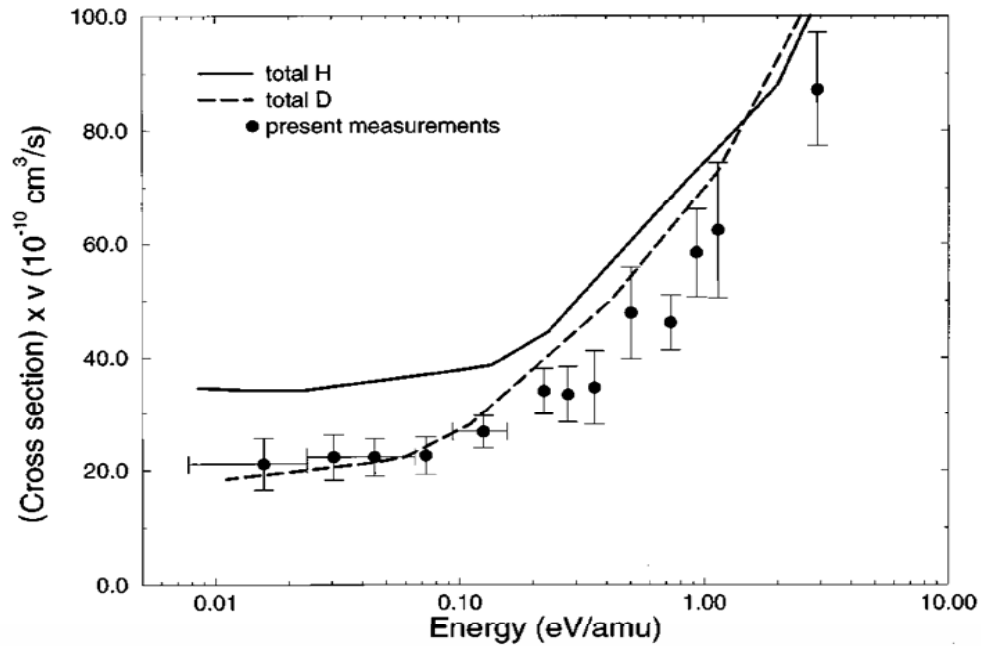FIG. 1. A simplified schematic drawing of the ion-atom merged-beams setup.

FIG. 3. The same data as in Fig. 2, but now showing the total electron-capture cross section times the collision velocity as a function of collision energy.
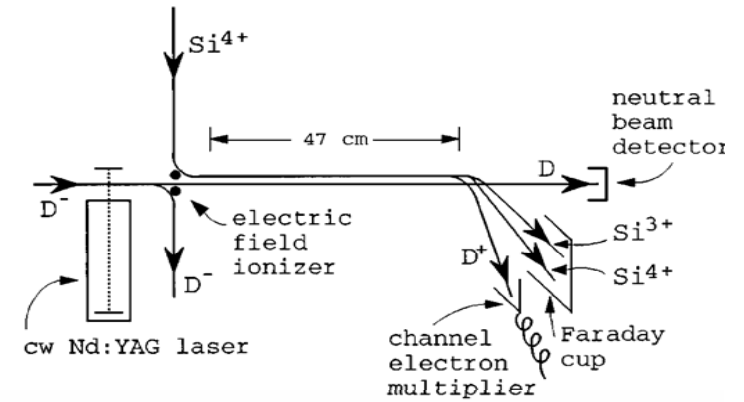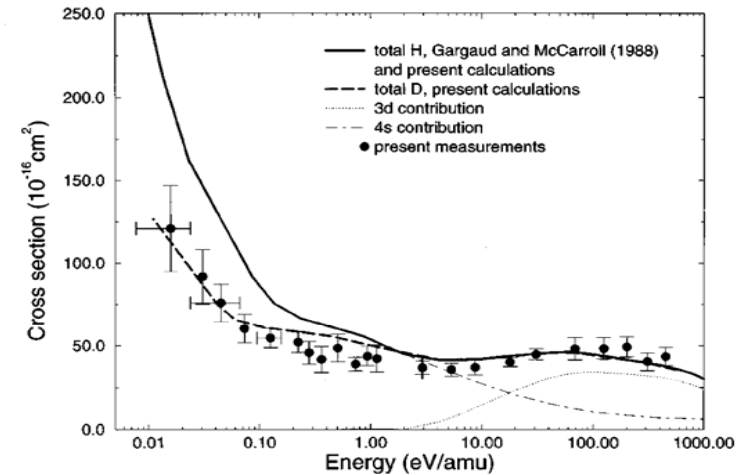

FIG. 2. A comparison of the dependence on the collision energy of the experimental and the theoretical total electron-capture cross sections of the $Si^{4+}+D$ system. Also included are theoretical calculations for $Si^{4+}+H$. See text for details.
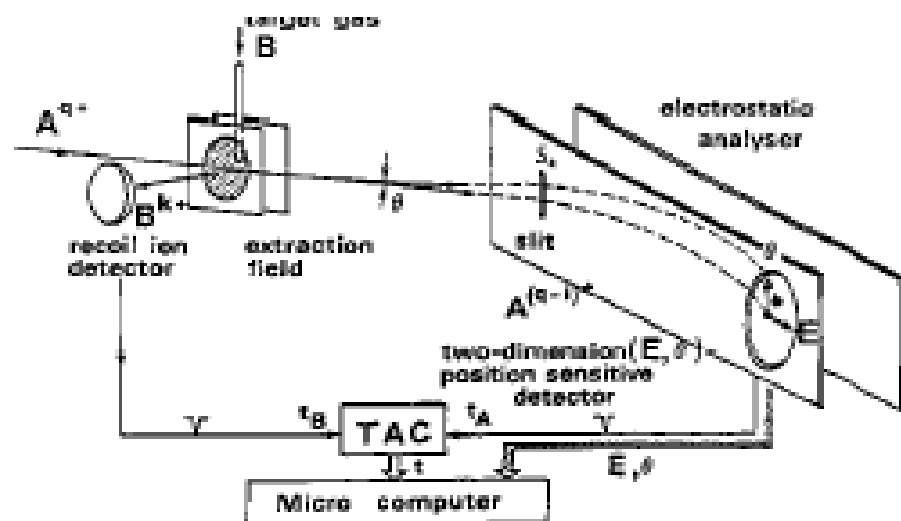
Figure 4. The coincident energy gain spectrometer used by the Orsay group.

M Barat & P. Roncin, J Phys B; At Mol Opt Phys **25**, 2205 (1992)

Figure 5. Coincident energy gain spectra for O^{8+}-He at 12 keV. (a) O^{7+} in coincidence with He^+: simple capture populates selectively the $O^{7+}(n=4)$ states. (b) O^{6+} in coincidence with He^{2+}: double captures populate the two autoionizing series $O^{6+}(3,3)$ and $O^{6+}(3,4)$. Notice that the spectra are symmetric around 0°.

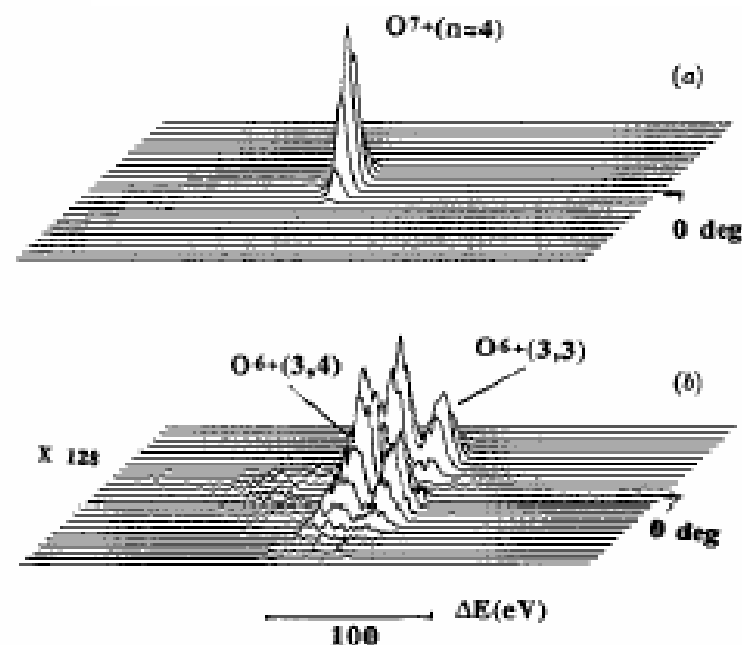On the theoretical side there has been a continuing effort for more than 30 years covering collision energies from thermal up to several 100 keV.

One of the main advantages of the theoretical calculations is their ability to provide absolute cross sections in the low energy range where experiment still has problems. So theory and experiment are complementary to each other.

In this review, I shall concentrate on theoretical models developed in the energy range from thermal energies up to a few keV/amu, which corresponds to the energy range required for most applications.

We shall start with the simple classical over-barrier model (OBM) originally designed for one-electron capture but later extended to multi-electron capture. This model was developed by experimentalists to provide a qualitative interpretation of their results, even though it fails to take into account many of the finer effects. But it has the advantage of being capable of being generalized easily to treat the case of multiple capture.

We shall the concentrate on the adiabatic model of the collision process, which although more difficult to apply than the OBM, gives a more satisfactory description of the state selective nature of the electron capture process.

The Over Barrier Model (OBM)

q+

(q-1)+   +

R   0   R   0   R   0
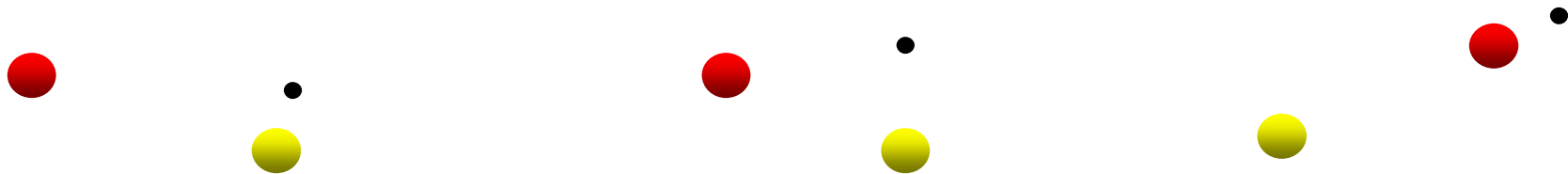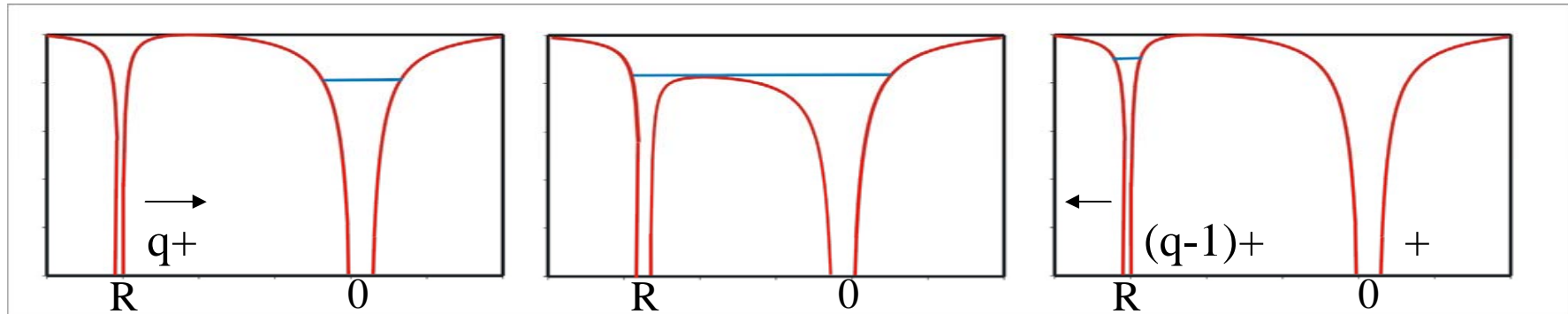
Section 2. The dynamics of ion-atom collisions in an adiabatic representation.

Ions and atoms are quantum particles and a fully quantum mechanical model is required to treat the dynamics of electron capture processes in a collision.

When the centre of mass (CM) energy is of the order of a few hundred eV/amu or greater, the de Broglie wave-length of the nuclear motion is much less than the Bohr radius . So while, a quantum description of the internal electronic motion of the collision system is always required, a semi-classical description of the nuclear motion is adequate.

On the other hand, when the CM energy is less than a few tens of eV/amu, electronic energy exchanged in the collision is comparable with the collision energy and a quantum mechanical description of the dynamics is required.

In the intermediate energy range between 50-500 eV/amu, the specific choice of method depends to a large extent on the aims of the calculation. The semi-classical approach is simpler, but its implementation is practical only when small angle scattering is dominant. But if we are concerned with large angle scattering processes, a quantum calculation is simpler tp apply even for energies as high as 1keV/amu.

We may observe that throughout the entire energy range for which quantum methods are either required or convenient to use, the relative collision velocity is much smaller than the velocity of the bound electrons. Even for energies of the order of 1keV/amu, the velocity is only 0.2 of that of an electron in a Bohr orbit.

Under these conditions, the collision system evolves in a nearly adiabatic manner. So, as in molecular spectroscopy, it is convenient to use the adiabatic electronic states as a basis for the representation of the system in collision. Of course, the influence of non-adiabatic effects is much greater than for the bound spectroscopic levels of stable molecules, but the underlying physical model is very similar.
.
In the adiabatic model, the Schrödinger equation is first solved assuming the nuclei to be clamped at some fixed internuclear distance R. In this way a series of adiabatic eigenfunctions may be generated, whose eigenenergies depend parametrically on R. Because of the axial symmetry of the interaction potential, the projection Λ_n of the electronic angular momentum on the internuclear axis is conserved. If the adiabatic energy curves are well separated from each other for all R, the system evolves adiabatically during a collision and energy exchange is unlikely to occur.

The crossing of adiabatic energy curves corresponding to states of the same symmetry is forbidden by the *von Neumann-Wigner* non-crossing rule, but well defined avoided crossings do exist. Non-adiabatic coupling may then become important and electronic transitions between different adiabatic states can take place. When the adiabatic energies of states with different symmetry cross or (which is often the case) become quasi degenerate, they are strongly coupled by non adiabatic Corioli's coupling.
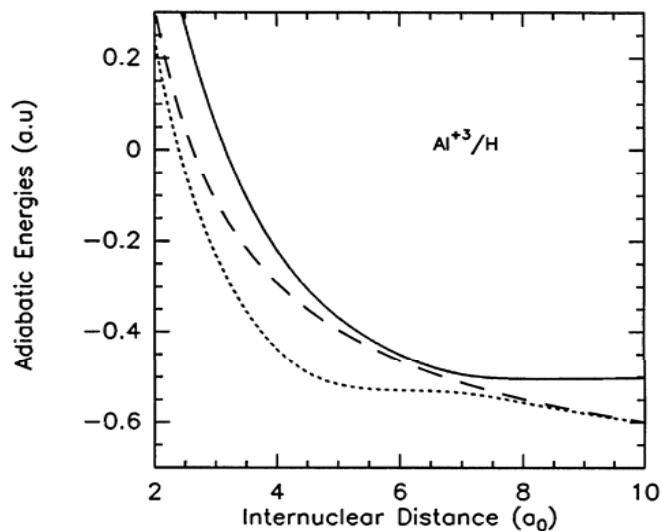

Figure 1. Adiabatic potential energies of the AlH3+ molecular ion. The full curve designates the the 2Σ state correlated to the [Al3+/H(Is)] entry channel. The dotted and dashed curves designate the 2Σ and 2Π states correlated to the [Al3+(3p)/H+] electron capture channels

Avoided crossings, tend to be well localized, and for most systems, only a small number of non-adiabatic transitions occur. So, even if there are accessible many non-adiabatic channels, only those with avoided crossings are activated in low energy collisions.

Avoided crossings are well localized, and for most systems, relatively few in number. So, even if there are accessible many non-adiabatic channels, only those subject to avoided crossings are activated in low energy collisions.

But, while an adiabatic representation of the system allows us to visualize the collision process there are some conceptual difficulties (even leaving aside the problem of determining the adiabatic eigen energies and eigen functions).

Electronic adiabatic states generated from the clamped nuclei approximation only match the correct asymptotic boundary conditions in an approximate way.
At very large internuclear distances, the kinetic energy of the bound electrons with respect to the CM of the nuclei exceeds the adiabatic interaction potential.

Besides, the adiabatic basis is defined with respect to a rotating reference frame so that account must be taken of Coriolis coupling between degenerate states with Λ_n in the dissociation limit.

The use of a finite adiabatic basis set to describe the collision is responsible for the existence of non-vanishing asymptotic couplings between certain reaction channels, which make it formally impossible to extract transition amplitudes.