Interactions of electron with atoms, molecules, ions

Ionization



Collisions of electrons with atoms

Classical or quantum approach?

Electron:

 $1eV \rightarrow v=5.9x10^{7} \text{ cm s}^{-1} \\ \tau \sim a_{0}/v \sim 10^{-8}/5.9x10^{7} = 2x10^{-16} \text{ s} \\ \lambda \sim 2A = 2x10^{-8} \text{ cm de Broglie}$

Ar+: 1eV →

v=2x10⁵cm s⁻¹ $\tau \sim a_0/v \sim 10^{-8}/2x10^5 \sim 6x10^{-14}s$ $\lambda \sim 9x10^{-11}$ cm de Broglie

Illustration of a variety of applications wherein cross-section data involving atomic & molecular physical processes are important.







At low energies

Threshold Photoelectron Source for Ultra-Low-Energy Electron Collision Experiments

Where have developed a new experimental technique for measuring the total cross section of ultra-low energy electron collisions with atoms and molecules utilizing synchrotron radiation. The present technique employs a combination of the penetrating field technique and the threshold photoionization of rare gas atoms using synchrotron radiation as an electron source in order to produce a high resolution electron beam at very low energy. The total cross sections for electron scattering from Kr in the energy range from 14 meV to 20 eV are obtained with the new technique. In addition, resonant structures in the total cross sections due to Kr⁻ (4p⁵5s² P_{3/2}) and Kr⁻ (4p⁵5s² P_{1/2}) Feshbach resonances are also observed for the first time.

low energies - 2010

Channel electron multiplier (CEM)



Figure 1

Schematic view of the experimental set-up. The system consists of an electron scattering apparatus with a photoionization cell, a photoion collector, and photon flux monitor of the monochromatized SR.

Cold Collision Experiments

- photoelectron source induced by SR -

Ar + hv \rightarrow Ar⁺ + e $\Delta E \leq 10 \text{ meV}$ $E_0 \leq 30 \text{meV}$



Total cross section of Xe in low energy region (preliminary data)



Xe, Kr, O₂

Threshold Photoelectron Source for Ultra-Low-Energy Electron Collision Experiments

Where have developed a new experimental technique for measuring the total cross section of ultra-low energy electron collisions with atoms and molecules utilizing synchrotron radiation. The present technique employs a combination of the penetrating field technique and the threshold photoionization of rare gas atoms using synchrotron radiation as an electron source in order to produce a high resolution electron beam at very low energy. The total cross sections for electron scattering from Kr in the energy range from 14 meV to 20 eV are obtained with the new technique. In addition, resonant structures in the total cross sections due to Kr⁻ ($4p^55s^2 P_{3r2}$) and Kr⁻ ($4p^55s^2 P_{1r2}$) Feshbach resonances are also observed for the first time.





Figure 2

Total cross sections for electron scattering from krypton. The vertical arrow at around 10 eV shows the position of the structure due to $Kr^{-}(4p^{5}5s^{2}P_{32})$ Feshbach resonance.

Details of Ramsauer effect







Frequencies of elastic collisions

 $\delta I=-NQI_p \, \delta x$ $I_P=I_0 \exp(-QNx)$ $I_0(v)$ **X**. $\mathbf{I}_{\mathbf{D}}$)(v)







"vc/p,10 gc-1, mop-1---α H₂ Хе 25 Kr Ar 4 15 He 5 Ne · 8 12 16 20 24`28 32 36 8 12 16 20 24 28 32 36 4 4



 $a_0 = 0.53 \times 10^{-8} \text{ cm} \sim 0.5 \text{ A}$ Radius of the first Bohr orbit of H atom



Collision Frequencies

Very low energies

Very low collision energies

TOPICAL REVIEW

Electron-molecule collisions at very low electron energies

F B Dunning

Department of Physics and the Rice Quantum Institute, Rice University, PO Box 1892, Houston, TX 77251, USA

J. Phys. B: At. Mol. Opt. Phys. 28 (1995) 1645-1672. Printed in the UK



Electron attachment at very low electron energies



Kvantová mechanika Jednorozměrný rozptyl



Kvantová mechanika I J. Klíma B. Velický MFF 1992

Jednorozměrný rozptyl

Vlnová funkce má tvar superposice Brogoliových vln

$$k = \sqrt{2mE/h^2}$$

$$\psi_k(x,t) = (Ae^{ikx} + Be^{-ikx})e^{iE_kt/h} \quad x \le -a$$

$$\psi_k(x,t) = (Fe^{ikx} + Ge^{-ikx})e^{iE_kt/h} \quad x > a$$

$$-a$$

$$+a$$

$$V_0$$

$$\psi_k(x,t) = (Ce^{ik'x} + De^{-ik'x})e^{iE_kt/h} \quad |x| \le a$$

$$k' = \sqrt{2m(E+V_0)/h^2}$$

a) dopadající částice → A
b) odražená částice → B
c) procházející částice → F≠0,G=0



Parametry jsou E, V₀, a

Tok dopadajících částic

$$j_{in} = \frac{hk}{m} |A|^2$$

Tok odražených částic

Tok prošlých částic

$$j_{rf} = \frac{hk}{m} \left| B \right|^2$$

 $j_{tr} = \frac{hk}{m} |F|^2$

Hladkost řešení v bodech ±a Urči konstanty B, C, D, G, Hodnota A je vstupní parametr

$$C = \frac{F}{2}(1 + \frac{k}{k'})e^{i(k-k')a}$$
$$D = \frac{F}{2}(1 - \frac{k}{k'})e^{i(k+k')a}$$
$$A = function(F)$$



Koeficient průchodu T, koeficient odrazu R

$$\frac{1}{T} = \left|\frac{A}{F}\right|^2 = 1 + \frac{V_0^2}{4E(E+V)}\sin^2(2k'a)$$







Excitation energies

Energy levels H



Energy levels H



<u>13.6eV x 8065,5 cm⁻¹ \rightarrow 109000 cm⁻¹ \rightarrow (91nm)</u>

Energy levels He

Grotrian diagram He Ionization energy He



vacuum ultraviolet



Molecules

Time scale of interaction with electron





- What happens to the molecule when an electron goes by?
 - 70 eV electron => 5 x 10⁶ m/s
 - Molecule = 10 A = 1 nm
 - Transit time = $2 \ge 10^{-16} = 2 \ge 10^{-16}$
 - Molecular vibrations > 10⁻¹² s
 - Electronic time scale $\sim 10^{\text{--}16}~\text{s}$
 - Frank-Condon principle: nuclei remain frozen in position



Interaction with molecules

Typical potential curves of diatomic molecules and H₂



FIG. 13.1. Potential energy curves for electronic states of H_2 and H_2^+ lying within 20 eV of the ground state.

Franck-Condon Principle



FIG. 21. Illustrative diatomic molecule and molecule-ion potential energy curves. The actual energy difference between curves a and b, c, and d is much greater than represented.





Franck-Condon Factors

$$P \sim < \psi_{\text{initial.}} \psi_{\text{final}} >^2$$

Photoelectron spectrum H2

Franck-Condon Factors











Cross sections for vibrational excitation, dissociation, ionization... H_2







FIG. 13.37. Cross-sections assumed by Engelhardt and Phelps in their analysis of swarm data in H₂ and D₂ for electrons of characteristic energy greater than 1 eV. Q_d momentum-transfer cross-section, Q_i , ionization cross-section, Q_{diss} dissociation cross-section, Q_{ph} photon excitation cross-section, Q_v vibrational excitation cross-section (— H₂, — — D₂).

Details of interaction of electron with H_2 (1990)



Cross Sections and Related Data for Electron Collisions with Hydrogen Molecules and Molecular Ions^{a)}

H. Tawara, Y. Itikawa,^{b)} H. Nishimura,^{c)} and M. Yoshino^{d)}

National Institute for Fusion Science.⁶⁾ Nagoya 464-01, Japan

(Received July 5, 1989; revised manuscript received November 1, 1989)

Data are compiled and evaluated for collision processes of excitation, dissociation, ionization, attachment, and recombination of hydrogen molecules and molecular ions (H_2^+, H_3^+) by electron impact as well as for properties of their collision products.

Key words: electron impact; hydrogen molecule; hydrogen molecular ion; scattering; elastic integral; vibrational excitation; rotational excitation; dissociation; ionization; photon emission; cross section.





FIG. 16. Cross sections of the production for total ion, molecular hydrogen ions, protons and double protons. Those of proton production from H and H(2s) are also shown for comparison (see Ref. 125). Note that the short curves, for proton production at lower energies, correspond to the processes via ²Σ_g (near-zero energy protons) and ³Σ_u (repulsive state), respectively.

10

J. Phys. Chem. Ref. Data, Vol. 19, No. 3, 1990

Dissociative ionization

$H_2 + e \rightarrow H^+ + H + e$







FIG. 11.30. Momentum-transfer cross-section for electrons in N_2 . —— derived by Engelhardt, Phelps, and Risk from analysis of swarm data. — · — · — · — derived by Pack and Phelps from analysis of their drift velocity observations. — — derived from drift velocity observations of Crompton and Sutton. · · · · total cross-section measured by Ramsauer method.



FIG. 11.31. Cross-sections for rotational and vibrational excitation of nitrogen. Q_4^6 is the cross-section for the rotational excitation $J = 4 \rightarrow J = 6$. $\Sigma_v Q_v$ is the sum of the cross-sections for vibrational excitation consistent with the swarm data.

Rotational excitation N₂





Figure 2-2-1. Vibrational-rotational levels (quantum numbers v and J) of a few diatomic molecules. The (v = 1, J = 0) level of H₂ lies 0.54 eV above the ground state (v = 0, J = 0). Rotational level spacings for H₂ are uniquely large, about 15J meV, where J is the quantum number for the upper level. For the ortho species of H₂ $(o-H_2)$, the nuclear spins are parallel; for the para version $(p-H_2)$, the nuclear spins are antiparallel. [From Shimamura (1984).]

Vibr. excitation of N_2 fine structure





Fig. 10.32. Fine structure observed by Golden and Nakano in the transmission of electrons through N_2 . The points are obtained from a number of plots of the transmitted current. Because of electron optical effects no significance attaches to the relative magnitudes of peaks and troughs.

of a theory such as that outlined above. Haas suggested that we must regard the collisions as taking place in two stages—the incident electron is first captured to form a negative ion N_2^- that is energetically unstable but has a lifetime greater than a vibrational period. It eventually breaks up, becoming a neutral molecule that may be in an excited vibrational state—in other words, the process is regarded as a resonance one of the same type as that found in elastic scattering of electrons by helium and other atoms and molecules (see Chap. 9).



FIGURE 1. Potential energy curves for N1 and N1*.*
Next → IONIZATION

Time scale of ionization





	Physical Measurement Laboratory	National Institute	of Standards and Technology	
Electron-Impact Ionization Cross Sections				
	Introduction and References	Table of Atoms	Table of Molecules	

http://physics.nist.gov/cgi-bin/Ionization/ion_data.

Table of Ionization Cross Sections at Specific Energies (tab-delimited ASCII)

Atomic Orbital Constants for BEB Calculation of the Direct Cross Section **Total Ionization Cross Section**

Ionization cross section

Ionization

Simple Ar + e⁻(ε_0) \rightarrow Ar⁺ + e₁⁻(ε_1) + e₂⁻(ε_2)

Complicated

 $N_{2}(v,j) + e^{-}(\varepsilon_{0}) \xrightarrow{} N_{2}^{+}(v,j) + e_{1}^{-}(\varepsilon_{1}) + e_{2}^{-}(\varepsilon_{2})$ $\xrightarrow{} N^{+}(\varepsilon_{KIN}) + N(\varepsilon_{KIN}) + e_{1}^{-}(\varepsilon_{3}) + e_{2}^{-}(\varepsilon_{4})$

 $NH_3 + e^{-}(\varepsilon_0) \rightarrow \dots$ to many channels

lonization energies



$$Ar + e^{-}(\varepsilon_0) \rightarrow Ar^{+} + e_1^{-}(\varepsilon_1) + e_2^{-}(\varepsilon_2)$$



Ionization energies





Ionization Energy

• First ionization energy (IE₁)

The minimum amount of energy required to remove the most loosely bound electron from an isolated gaseous atom to form a 1+ ion.

 $atom_{(g)} + energy \rightarrow ion^{+}_{(g)} + e^{-}$

Element/Compound	Ionization Potential (Volts or eV)	
Не	24.6	
Ar	15.8	
H ₂	15.4	
N ₂	15.6	
0 ₂	12.1	
CO2	13.8	
со	14.1	
с	11.3	
Si	8.2	
Fe	7.9	
Ni	7.6	
Na	5.1	
к	4.3	
Cs	3.9	

Electron affinity

 $A + e^{-}(\varepsilon_0) \rightarrow A^{-}$

Electron Affinity

- · Electron affinity is the amount of energy absorbed when an electron is added to an isolated gaseous atom to form an ion with a -1 charge.
- Electron affinity is a measure of an atom's ability to form negative ions.

 $atom(g) + e^- + EA \rightarrow ion^-(g)$



Ionization energies

Electron affinity





 $A + e^{-}(\varepsilon_0) \rightarrow A^+ + 2e$

 $A + e^{-}(\varepsilon_0) \rightarrow A^{-}$

Ionization of molecules

Potential Energy Surface Description of the Ionization of Dihydrogen



Ionization of molecules

Potential Energy Surface Description of the Ionization of Dihydrogen



Ionization energies of molecules



Ionization energies of molecules



Photoelectron spectrum H2



$$\mathbf{P} \sim < \Psi_{\text{initial.}} \Psi_{\text{final}} >^{2}$$



CO



Ionization cross section He and N₂







BEB W. Hwang, Y.-K. Kim and M.E. Rudd, J. Chem. Phys. **104**, 2956 (1996).

Electron impact



New J. Phys. **11** (2009) 063047 doi:10.1088/1367-2630/11/6/063047 **Cross sections for the interactions of 1 eV– 100 MeV electrons in liquid water and application to Monte-Carlo simulation of HZE radiation tracks**

Ianik Plante^{1,2} and Francis A Cucinotta¹

Ionization cross section He and N₂







BEB W. Hwang, Y.-K. Kim and M.E. Rudd, J. Chem. Phys. **104**, 2956 (1996).



New J. Phys. **11** (2009) 063047 doi:10.1088/1367-2630/11/6/063047 **Cross sections for the interactions of 1 eV– 100 MeV electrons in liquid water and application to Monte-Carlo simulation of HZE radiation tracks**

Ianik Plante^{1,2} and Francis A Cucinotta¹

2.3. Electron impact ionization



Why?

- The cross section for the impact ionization is by orders of magnitudes higher than the cross section for the photo ionization.
- The cross section depends on the mass of the colliding particle. Since the energy transfer of a heavy particle is lower, a proton needs for an identical ionization probability an ionization energy three orders of magnitudes higher than an electron



ELGURE 4

Ionization cross sections as functions of energy for ionizing collisions with fast electrons, protons, and photons. (From Winter, H., in Experimental Methods in Heavy Ion Physics, Springer-Verlag,

Ionization by electron impact



Thomson's formula









Calculated ionization cross section of the ${}^{3}P_{0}$ state in Ne using the DM formalism. The full curves refer to the contributions from the various subshells and have been labeled appropriately. The sum of the various subshell contributions has been labeled by the symbol6. Also shown is the Born calculation of Ton-That and Flannery (broken curve, see text for details). The experimental data points (diamonds) are those of Johnston *et al*. Two typical error bars (combined systematic and statistical uncertainty) are shown for the experimental data.

Ionization if $\Delta \epsilon > I$ Formula of Rutherford for coulomb force $d\sigma = e^4 d\Theta/4\epsilon^2 \sin^4(\phi/2)....\sigma_i = \pi e^4/I \cdot (\epsilon - I)/\epsilon^3$

 $\sigma_{i} = 4\pi a_{0}^{2} (I_{H} / \epsilon)^{2} \cdot (\epsilon - I) / I$ $\Rightarrow \sigma_{i} = 4\pi a_{0}^{2} (I_{H} / \epsilon)^{2} \cdot (\epsilon / I - 1) = f_{function}(\epsilon / I)$ $\sigma_{i} = \sum \sigma_{in} \quad \text{sum of the various subshell contributions}$

Near the threshold \rightarrow linear approximation





Ionization cross section – idea of experiment



Electron impact ion source – ion source of mass spectrometer



Electron impact ionization



Figure 3. Cross Section of an Electron Impact Source

. . . .







Open Design

Gas-Tight Design

Ionization cross section N₂

BEB W. Hwang, Y.-K. Kim and M.E. Rudd, J. Chem. Phys. **104**, 2956 (1996).

e⁻ on N₂ 3.0 σ_i (10⁻¹⁶ cm²) 0.7 0.7 0.0 100 1000 10 T (eV)

Ionization cross section -acetylene C₂H₂ Product channels

Pragmatic approach





FIG. 6. Ionization efficiency curves for several ions from acetylene (493).

Ionization cross section data from http://webbook.nist.gov



How to recognize spectra ???

Ionization - EII of CH₄

Determination of ionization energies (IEs) for EII of CH₄ for the following reactions:

\rightarrow CH ⁺ ₄ + 2e	(1)
\rightarrow CH ⁺ ₃ + H + 2e	(2 <i>a</i>)
\rightarrow CH ⁺ ₃ + H ⁻ + e	(2 <i>b</i>)
\rightarrow CH ⁺ ₂ + H ₂ + 2e	(3)
\rightarrow CH ⁺ + H +H ₂ + 2e	(4 <i>a</i>)
\rightarrow CH ⁺ + H ⁻ + H ₂ + e	(4 <i>b</i>)
\rightarrow C++2H ₂ +2e.	(5)



Electron energy (eV)

Figure A.1. Ion yield curve for CH_4^+ , CH_3^+ and CH_2^+/CH_4 obtained through digitalization of the data from [3]. Full curves present fits through these data. Arrows indicate the estimated IEs derived by the fitting procedure.



Figure 5. Ion yield curve for CH_2^+ , CH^+ and C^+/CH_4 as measured at 293 K. Full curves present fits through the experimental data. Arrows indicate the IEs derived by the fitting procedure. Note that for the case of CH^+ only IE₂ and IE₃ have been derived from the present data; IE₁ has been calculated from the known EA of H (see text).

σw(E, p) =	0	for $E < IE_1(Ar)$
	$A_1(E - \mathrm{IE1})^{d1}$	for $E > IE_1$ and $E < IE_2$
	$A_1(E - \text{IE1})^{d1} + A_2(E - \text{IE2})^{d2}$	for $E > IE_2$

Multiple ionization

Multiple ionization of helium and krypton by electron impact close to threshold: appearance energies and Wannier exponents



Figure 1. Ion signal as a function of electron energy for the formation of He^+ ions (top) and He^{2+} ions (bottom) in the near-threshold region. The measured data are shown as open circles, the fits are shown as solid curves. The AEs, which are indicated, are the AEs for the individual data sets shown and may differ from the AE values listed in table 1 which were obtained from a comprehensive analysis of many individual data sets.

Table 1. AE values in eV for the formation of He^+ and He^{2+} ions in comparison with other measured or calculated AE values.

	Spectroscopic value [1]	Redhead [45]	This work
He ⁺	24.59	_	24.6 ± 0.15
He ²⁺	79.00	77.58	79.05 ± 0.3

J. Phys. B: At. Mol. Opt. Phys. 35 (2002) 4685–4694

Ionization of He



Ionization of the excited state

Ionization of singly charged He







Multiple ionization

Multiple ionization of helium and krypton by electron impact close to threshold: appearance energies and Wannier exponents



Figure 2. Ion signal as a function of electron energy for the formation of Kr^{n+} ions (n = 1-6) in the near-threshold region. The measured data are shown as open circles, the fits are shown as solid curves. The AEs, which are indicated, are the AEs for the individual data sets shown and may differ from the AE values listed in table 2 which were obtained from a comprehensive analysis of many individual data sets.

Multiple ionization





High efficiency Grid ion source



- Open design
- Two filaments (W)
- Low degassing rate
 - mimimum amount of material
 - Pt-Ir wires for formation chamber
 - Molybdenum filament
 holders
- Easy to degas via electron bombardment
- Filaments on positive potential



Ion optics Mass filter

Rod system

Filament

Entance

onfice

Cathode

Grid

Flight paths of electrons



Flight paths of electrons 3D



Flight paths of positive ions



Flight paths of ions 3D





Cross Beam ion Source, calculations



Flight paths of ions


Cross Beam ion Source



Cross Beam ion source with magnets

- Two filaments
- Easy to degas
- Good ion focussing
- Bakeable to 300°C



Mass spectrometer



16 mm rod system for highest resolution, stability and transmission (e.g. He/D₂ separation)

8 mm rod system for High-End RGA and analytical applications

6 mm rod system for common RGA

90° off axis arrangement

efficient suppression of

- photons
- fast neutral particles
- stray ions





- Ion Detection
 - Discrete Dynode SEM
 - Bakeable to 400°C
 - for analog amplification and for pulse counting

IONS

Low noise (< 0.1 cps)



QMA



90° off axis arrangement

efficient suppression of

- photons
- fast neutral particles
- stray ions





Mass spectrum



W.K. Huber, N. Müller, and G.Rettinghaus, Vacuum, 41, 2103 (1990)

Typical UHV spectrum

Ionization of clusters



 $\sigma_{\text{average total}} = Z. \sigma_{\text{effective}}$



Ionization of C60 Fulleren



1000

1000

calculation.

Distribution of carbon clusters produced under various experimental conditions.

- a) Low helium density over graphite target at time of laser vaporization.
- b) High helium density over graphite target at time of laser vaporization.
- c) Same as b), but with addition of "integration cup" to increase time between vaporization and cluster analysis.

Electron-Impact Induced Fragmentation of Fullerene Ions

The measurements were performed employing the electron-ion crossed-beam setup. A commercially available powder of fullerenes was evaporated with an electrically heated oven. The neutral vapor was introduced into a 10 GHz Electron Cyclotron Resonance Ion Source (ECRIS). The extracted ion beam was collimated to $2x2 \text{ mm}^2$ after mass to charge analysis and crossed with an intense electron beam. The energy of the electrons can be varied between 10 and 1000 eV. After the electron-ion interaction the fragment ions C_{58}^{q+} were separated from the incident ion beam of C_{60}^{q+} by a 90⁰ magnet and detected by a single-particle detector. The flight time between the interaction of the C_{60}^{q+} ions and the analysis of the product ions is in the order of 10 μ s. The current of the parent ion beam was measured simultaneously in a Faraday cup.

Binding energy value of about 11 eV

$$e^- + C_{60}^+ \rightarrow C_{58}^+ + C_2^- + e^-$$

$$e^{-} + C_{60}^{2+} \rightarrow C_{58}^{2+} + C_2^{-} + e^{-}$$

$$e^{-} + C_{60}^{3+} \rightarrow C_{58}^{3+} + C_2 + e^{-}$$

IONIZATION



FRAGMENTATION



Absolute cross sections s for the electron-impact induced C₂ fragmentation of C₆₀ $^{q+}$ ions.

Electron-Impact Induced Ionization of Fullerene Ions

calculation.

IONIZATION



A semi-empirical concept for the calculation of electron-impaction cross-sections of neutral and ionized fullerenes



International Journal of Mass Spectrometry 223-224 (2003) 1-8



Fig. 3. Cross-section for the formation of C_{60}^{2+} ions following electron-impact single ionization of C_{60}^{2+} . The experimental data (\bigcirc) are from Ref. [23], the solid line represents the present

Cross sections for vibrational excitation, dissociation, ionization... H_2



Figure 3. Optical excitation function for VUV photons measured with channeltron and MgF₂ window (1120-1300 Å); pressure 4×10^{-7} bar; collection time 7 h; 4.9 meV/channel. Energy positions of known resonances are indicated. The dissociation energy for H(2p)+H(1s) is marked by an arrow.

FIG. 13.37. Cross-sections assumed by Engelhardt and Phelps in their analysis of swarm data in H_2 and D_2 for electrons of characteristic energy greater than 1 eV. Q_d momentum-transfer cross-section, Q_i , ionization cross-section, Q_{diss} dissociation cross-section, Q_{ph} photon excitation cross-section, Q_v vibrational excitation cross-section (----- H_2 , $---- D_2$).

Cross sections for ionization... H_2



FIG. 13.19. Variation of the ionization cross-section of H₂ near the threshold as observed by Marmet and Kerwin.

photon excitation cross-section, $Q_{\rm y}$ vibrational excitation cross-section (---- ${\rm H}_2$, ——— D₂).

Koniec rospravky

Ionization cross section

Ionization, excitation

Complicated

$N_{2}(\mathbf{v},\mathbf{j}) + \mathbf{e}^{-}(\varepsilon_{0}) \longrightarrow N_{2}^{+}(\mathbf{v},\mathbf{j}) + \mathbf{e}_{1}^{-}(\varepsilon_{1}) + \mathbf{e}_{2}^{-}(\varepsilon_{2})$ $\longrightarrow N^{+}(\varepsilon_{\mathrm{KIN}}) + \mathbf{N}(\varepsilon_{\mathrm{KIN}}) + \mathbf{e}_{1}^{-}(\varepsilon_{3}) + \mathbf{e}_{2}^{-}(\varepsilon_{4})$

$NH_3 + e^{-}(\varepsilon_0) \rightarrow \dots$ to several product - channels



Figure 8. Rate constants for Rydberg destruction and free-ion production in Rydberg atom collisions with SF₆. The data are plotted as a function of $n^* = n - \delta$ when δ is the quantum defect. O, K(np) destruction (Zheng *et al* 1990); \blacktriangle , K(nd) free-ion production (Zollars *et al* 1986); \blacksquare , Ne(ns) free-ion production (Harth *et al* 1989);, ..., calculated values $l=2, l=l_{max}=n-1$ (Klar *et al* 1994a).

 $\mathbf{K}(n\mathbf{p}) + \mathbf{H}_{2}\mathbf{S}(J, \tau) \rightarrow \mathbf{K}^{+} + \mathbf{H}_{2}\mathbf{S}(J', \tau') + \mathbf{e}^{-}.$

Photoionization from Ar metastable



Figure 4. Schematic diagram of the laser-induced photoionization apparatus used for attachment studies (Klar et al 1994b).

Franck-Condon principle - FOTOIONIZATION

MO diagram for the three highest occupied MOs in CO accessible by HeI radiation. PES of CO obtained by HeI radiation and potential energy curves for the neutral molecule and the three ionized states.



Total collision cross sections Na, K, Cs...





FIG. 1.6. Schematic diagram of the arrangement of apparatus developed by Simpson for observing fine structure in the variation with energy of the transmission of electrons through gases.



Very low collision energies

TOPICAL REVIEW

Electron-molecule collisions at very low electron energies

F B Dunning

Department of Physics and the Rice Quantum Institute, Rice University, PO Box 1892, Houston, TX 77251, USA

J. Phys. B: At. Mol. Opt. Phys. 28 (1995) 1645-1672. Printed in the UK



Figure 1. Schematic diagram of the vuv photoionization apparatus used for attachment studies (Chutjian and Alajajian 1985a, b).

$$\operatorname{Kr}({}^{1}S_{0}) + \hbar\omega \rightarrow \operatorname{Kr}^{+}({}^{2}P_{1/2}) + e^{-}(\varepsilon)$$

 $e^{-} + SF_{6} \rightarrow SF_{6}^{-*}$ $e^{-} + CCl_{4} \rightarrow CCl_{4}^{-*} \rightarrow CCl_{3} + Cl^{-}$

Electron attachment at very low electron energies



Figure 2. Cross section for electron attachment to SF_6 . \blacksquare , $\bar{\sigma}_e$ -K(*np*); ---, $\sigma_e(v)$ -K(*np*) (Ling *et al* 1992). O, $\bar{\sigma}_e$ -Rb(*ns*) (Zollars *et al* 1985); ----, free electrons (Klar *et al* 1992a, b); ---, free electrons (Chutjian and Alajajian 1985); \triangle , free electrons (Pai *et al* 1979, Chutjian and Alajajian 1985a); ----, theory (Klots 1976).

Partial cross section for excitation



Fig. 4. Cross-section set for NO (1986).



Figure 3. Cross sections for electron attachment to CCl₄. \bullet , $\bar{\sigma}_e$ -K(*np*); -, $\sigma_e(\nu)$ -K(*np*) (Frey *et al* 1994b); O, $\bar{\sigma}_e$ -K(*np*) (Ling *et al* 1992); —, free electrons (Hotop 1994); ---, free electrons (Orient *et al* 1989); Δ , free electrons (Christodoulides and Christophorou (1971); ---, theory (Klots 1976).



Fig. 6. Electron collision cross-section set for NH_3 (1986).

 $NH_3 + e$

 $e^{-} + SF_{6} \rightarrow SF_{6}^{-*}$ $e^{-} + CCl_{4} \rightarrow CCl_{4}^{-*} \rightarrow CCl_{3} + Cl^{-}$

Rate coefficients of elementary processes

$$A + B \xrightarrow{k} C + D$$

$$A + B \xrightarrow{k} products$$

$$\frac{d[A]}{dt} = -k[A][B]$$

- Electron atomic ion rec.
- Electron ion recomb.
- Ion ion recombination
- Ion molecule reactions
- Attachment

• Penning ionization

reactants	products
$Ar^+ + e^-$	Ar + hv
$O_2^+ + e^-$	O + O
Ar ⁺ + Cl ⁻	Ar + Cl
$H_{2}^{+}+H_{2}^{-}>$	$H_3^+ + H$
$\text{CCl}_4 + \text{e}^-$	Cl ⁻ +CCl ₃
$He^* + Ar$	$Ar^+ + e^- + He$

~300 K

 $\sim 10^{-11} \text{cm}^3 \text{s}^{-1}$

2x10-7cm3s-1

2x10-8cm3s-1

2x10⁻⁹cm³s⁻¹

~10⁻⁷cm³s⁻¹

7x10-11cm3s-1

rate coefficient

Kinetics of elementary process

$$H_2^+ + Ar \implies ArH^+ + H$$

$$d(n_{H2^+})/dt = -k n_{H2^+} n_{Ar}$$

$$n_{H2^+} << n_{Ar}$$
 $n_{H2^+} = (n_{H2^+})_0 \exp(-kn_{Ar}t)$





Electron attachment at very low electron energies



Figure 2. Cross section for electron attachment to SF_{4} . \blacksquare , $\bar{\sigma}_{e}$ -K(*np*); ---, $\sigma_{e}(v)$ -K(*np*) (Ling *et al* 1992). O, $\bar{\sigma}_{e}$ -Rb(*ns*) (Zollars *et al* 1985); ----, free electrons (Klar *et al* 1992a, b); ---, free electrons (Chutjian and Alajajian 1985); \triangle , free electrons (Pai *et al* 1979, Chutjian and Alajajian 1985a); ----, theory (Klots 1976).

Collisions of electrons with atoms – Ramsauer's method



Photo cathode

Mono energetic electrons

Lenard 1903 Akesson 1916 Ramsauer 1921

ATENUATION METHOD



Collisions of electrons with atoms – Ramsauer's method



FIG. 1.1. Ramsauer's apparatus for measurement of collision cross-sections.

Lenard 1903 Akesson 1916 Ramsauer 1921



Collisions of electrons with atoms – Rams

S₅ S₅ B B C

FIG. 1.1. Ramsauer's apparatus for measurement of collision cross-sections.

Lenard 1903 Akesson 1916 Ramsauer 1921





Channel electron multiplier (CEM)

Total collision cross section – e/atoms



A, Kr, and Xe.

 $a_0=0.53 \times 10^{-8} cm \sim 0.5 A$ Radius of the first Bohr orbit of H atom



FIG. 1.11. Total collision cross-sections of atomic hydrogen.
observed by Brackmann, Fite, and Neynaber; —— observed by Neynaber, Marino, Rothe, and Trujillo.



Understanding plasma

Collisions Classification of collisions

elastic inelastic

 \rightarrow

 \rightarrow

The concept of collision cross-section $\delta I = -NQI_p \delta x$ $I_P = I_0 \exp(-QNx)$

Hypothetical gas of rigid spheres of cross section Q

Slow decrease of interaction potential - Small deviation → problem with concept of integral cross section

Electronic and ionic impact phenomena Volume 1 – Collisions of electrons with atoms H.S.W. Massey and E.H.S.Burhop, Oxford, Clarendon Press, 1969 Kinetics of elementary process

$$e + Ar \implies Ar^+ + 2e$$





k(T

Collisions of electrons with atoms (atomic beams)



FIG. 1.2. Schematic diagram of the arrangement of apparatus used by Fite, Brackmann, and Neynaber for observation of elastic scattering of electrons by atomic hydrogen.

Position (angle), mass and energy sensitive detectors

Threshold Photoelectron Source for Ultra-Low-Energy Electron Collision Experiments

Where have developed a new experimental technique for measuring the total cross section of ultra-low energy electron collisions with atoms and molecules utilizing synchrotron radiation. The present technique employs a combination of the penetrating field technique and the threshold photoionization of rare gas atoms using synchrotron radiation as an electron source in order to produce a high resolution electron beam at very low energy. The total cross sections for electron scattering from Kr in the energy range from 14 meV to 20 eV are obtained with the new technique. In addition, resonant structures in the total cross sections due to Kr⁻ (4p⁵5s² P_{3/2}) and Kr⁻ (4p⁵5s² P_{1/2}) Feshbach resonances are also observed for the first time.

low energies - 2010

Channel electron multiplier (CEM)



Figure 1

Schematic view of the experimental set-up. The system consists of an electron scattering apparatus with a photoionization cell, a photoion collector, and photon flux monitor of the monochromatized SR.