Low temperature plasma

EPRP 5BBB 11 03 2025



Experiments at low temperature



Fig. 42. Proposed positive-ion chemistry for dense interstellar clouds [182].

Motion in fast oscillating field



Motion in fast oscillating field

$$\mathbf{r}(t) = \mathbf{r}(0) - \mathbf{a} \cos(\Omega t) \qquad \mathbf{r}(t) = \mathbf{R}_0(t) + \mathbf{R}_1(t)$$
$$\mathbf{a} = q \mathbf{E}_0 / m \Omega^2 \qquad \mathbf{R}_1(t) = -\mathbf{a}(t) \cos \Omega t$$
$$\mathbf{E}_0(\mathbf{R}_0 - \mathbf{a} \cos \Omega t) = \mathbf{E}_0(\mathbf{R}_0) - (\mathbf{a} \cdot \nabla) \mathbf{E}_0(\mathbf{R}_0) \cos \Omega t + \cdots$$

effective potential
$$V^*(\mathbf{R}_0) = q^2 E_0^2 / 4m\Omega^2$$

adiabaticity parameter $\eta = 2q |\nabla E_0|/m\Omega^2$

RF trap $m\ddot{\mathbf{r}} = q\mathbf{E}_{0}(\mathbf{r})\cos(\Omega t + \delta) + q\mathbf{E}_{s}(\mathbf{r})$



Volume 1 Theory and Ion Chemistry

$$\mathbf{r}(t) = \mathbf{r}(0) - \mathbf{a}\cos(\Omega t)$$

$$\mathbf{a} = q\mathbf{E}_0/m\Omega^2$$



Figure 1

Motion of a charged particle in an oscillatory electric field. If the field is homogeneous (left) the particle oscillates with an amplitude **a** given by Eqn. (3). In time average, it remains centered at r(t)/r(0) = 1. In the inhomogeneous field (right) the charged particle seems to be pushed away from the center by a force that is called "field gradient force." It is a general and important rule that charged particles are seeking regions of weaker fields.

2.2 Adiabatic Approximation

Inhomogeneous electric field

This observation can be derived in a more fundamental way by using an adiabatic approximation for solving Eqn. (1). For treating time-dependent problems adiabatic theories, in which fast and slow components are separated, are well established in theoretical physics and mathematics. Here, the rather simple calculation, which can be found elsewhere (1), is based on the idea that a solution of Eqn. (1) has the form of Eqn. (2), i.e., consists of an oscillatory part superimposed on a smooth drift term. The mathematical result leads to several important conclusions. One is that the field gradient force, acting on the particle as illustrated in the right-hand part of Fig. 1, can be derived from the time-independent mechanical potential V^* given by

$$V^* = q^2 E_0^2 / 4m\Omega^2 + q\Phi_{\rm s} \tag{4}$$

where Φ_s is the electrostatic potential. A derivation of the effective potential V^* , which is also called ponderomotive potential, pseudopotential, or quasipotential, can be found in Landau and Lifshitz (2).

RF Ion Trap

Confinement of charged particles in rf or AC fields



RF Ion Trap













Effective Potential:

$$V_{eff} = \frac{q^2 E_0^2}{4m\Omega^2} \qquad \eta = \frac{2q |\nabla E_0|}{m\Omega^2}$$

2n-Pole:

$$V_{eff} = \frac{n^2 q^2 V_0^2}{4m\Omega^2 r_0^2} \left(\frac{r}{r_0}\right)^{2n-2}$$
$$\eta = 2n(n-1) \frac{qV_0}{m\Omega^2 r_0^2} \left(\frac{r}{r_0}\right)^{n-2}$$

Effective potential







Trajectory in a 32-pole ($\eta_m \sim 0.55$).

22-pole ion trap



Figure 10.13: Three-dimensional numerical simulation of the trajectory of a singly charged ion (mass 3) in a 22-pole trap. RF parameters as above, static voltages at the end caps +0.1 V, kinetic energy of the ion $E_{kin} = 7.5 \text{ meV}$ (~ 90 K). For clarity, only part of the side plates are drawn and the upper rods and part of one of the side plates with the end electrode inside is cut away.





Figure 10.6: Isometric view of the 22-pole ion trap. The diameter and length of the 22 rods is 1 mm and 40 mm, respectively.





Figure 10.6: Isometric view of the 22-pole ion trap. The diameter and length of the 22 rods is 1 mm and 40 mm, respectively.

Figure 10.10: Two-dimensional numerical simulation of the trajectory of a singly charged ion (mass 3) in a 22-pole trap. RF parameters as above, kinetic energy of the ion $E_{\rm kin} = 7.5 \text{ meV}$ (~ 90 K).





Figure 10.12: Zoom into a region close to the electrodes. At the turning points the ion performs small wiggling motions under the influence of the radio frequency field.

TV 22-pole Ion Trap



cold head T > 5 K

Effective potential V* $V^* = q^2 E_0^2 / 4m\Omega^2$

Adiabaticity parameter η $\eta = 2 q |\nabla E_0| / m\Omega^2$

parameters: q, m, E₀, Ω , scaling: $m\Omega^2$ $\eta \sim E_{max}^{(n-2)/(2n-2)} = E_{max}^{9/20}$ d = 1 mm2 $r_0 = 10 \text{ mm}$

 $r_0 = (n-1) d/2$ 2n = 22



D. Gerlich Physica Scripta, T59 (1995) 256



Fig. 1. 22-Pole rf ion trap consisting of 22 rf electrodes for radial confinement (arranged at an inner diameter of 10 mm) and of two pairs of cap electrodes in the two axial directions. The trap is mounted on a cold head and surrounded with the thermal radiation shielding (not shown). The five vertical shaping lenses placed around the rf electrodes are set to the same potential as the DC potential of the trap.

Ion trap





Figure 3.3: The 22-pole ion trap forms the central element of the new ion trap setup. It is mounted on a helium cryostat and can be cooled to temperatures between 8 - 300 K. The base plate of a 50 K thermoshield can be seen, which reduces the heat input on the trap housing caused by blackbody radiation. The 22 rf electrodes are surrounded by five electrostatic ring electrodes, which can be used to shift the stored ions inside the trap. Cylindrical endcaps are used to confine the ions in axial direction.



RF trap – Multipole fields

2.4 Multipole Fields

In a real experimental device, the electric field $E_0(\mathbf{r})$ is determined by the boundary conditions imposed by suitable electrodes. For guiding and trapping ions a variety of electrode arrangements have been developed (1). The best-characterized examples are linear multipoles, which are used in many applications. Their ideal potential is given by

$$\Phi(r,\varphi) = \Phi_0 \hat{r}^n \cos n\varphi \tag{7}$$

where $\Phi_0 = U_0 - V_0 \cos\Omega t$ is the applied potential, 2ncorresponds to the number of poles, and $\hat{r} = r/r_0$ is a reduced radius. In general one operates a multipole "RF-only", i.e. $U_0 = 0$. From this potential one can derive the electric field

$$|E_0| = \frac{V_0}{r_0} n \hat{r}^{n-1} \tag{8}$$



$$\Phi(r,\varphi) = \Phi_0 \hat{r}^n \cos n\varphi$$
$$|E_0| = \frac{V_0}{r_0} n\hat{r}^{n-1}$$
$$V^* = q^2 E_0^2 / 4m\Omega^2 + q\Phi_s$$

$$V^* = \frac{1}{8} \frac{\left(qV_0\right)^2}{\varepsilon} \hat{r}^{2n-2} + qU_0 \hat{r}^n \cos n\varphi$$



RF trap



Figure 2

Trajectory of an ion illustrating the motion in the vicinity of two octopole rods (hatched semicircles). It can be seen that the trajectory can be composed of a smooth part $\mathbf{r}_0(t)$ and an oscillating part. The turning radius can be calculated from the effective potential indicating the adiabatic conservation of kinetic energy. If the ion moves towards a rod, the momentary energy is modulated between 0 and $3E_0$. This is shown in the right-hand part of the figure, which shows the exact ion kinetic energy as an ion approaches a rod directly (upper trajectory shown on the left).



Effective potential



RF trap



Figure 10.1: Electrostatic potentials for Quadrupole (n=2) and 22-pole (n=11) geometries.





Figure 10.2: Effective potentials for quadrupole, octopole and 22-pole geometries as a function of the distance from the symmetry axis

Photodetachment O- and OH-

CHAPTER 4. ABSOLUTE PHOTODETACHMENT CROSS SECTIONS STUDIED 26 IN A 22-POLE TRAP

- 4.1 Absolute photodetachment cross sections of O^- and OH^-
- 4.1.1 Photodetachment via 2D tomography



Figure 4.1: Schematic of the photodetachment tomography technique. Anions are stored in the 22-pole ion trap and are depleted via photodetachment induced by a laser beam propagating parallel to the symmetry axis of the trap. The position of the laser beam can be scanned over the trapping volume using a moveable lens, which is mounted on a 2D translation stage.



Figure 4.5: The energy levels of OH⁻ and OH for the first rotational states. The arrows indicate dipole allowed transitions from the first three rotational levels.

Histogram



Figure 4.2: Histogram of the measured photodetachment rate for O⁻ as a function of the transverse position of the laser light in the ion trap. Each bin represents an individual decay measurement at a given position. The graph reflects the ion density distribution in the 22-pole trap, as the ion column density is proportional to the detachment rate. The insets show two examples for individual loss rate measurements with laser light induced ion loss.

Molecules

Ion Distribution in 22-pole Ion Trap



O. Asvany, S. Schlemmer / International Journal of Mass Spectrometry 279 (2009) 147-155

Photodetachment cross section



Figure 4.6: Measured OH⁻ photodetachment cross sections at threshold. The datasets show measurements at two different trap temperatures. Different rotational branches open up with increasing photon energy. The single branches have been fitted with the relation $(\epsilon - EA)^{0.28}$ which represents a modified Wigner threshold law [76]. From the relative contribution of the branches we can derive an internal temperature of the molecule assuming a Boltzmann distributed population of the levels.



Figure 4.5: The energy levels of OH⁻ and OH for the first rotational states. The arrows indicate dipole allowed transitions from the first three rotational levels.



Molecules

Tomography of the trapping potential



Figure 4.10: a) Measured density distribution of trapped OH⁻ ions at 300 K buffer gas temperature with the rf amplitude set to 160 V. The sketched geometry shows the layout of the ion trap, viewed along its symmetry axis. It includes the copper housing, the 22 rf electrodes (end-on), a surrounding shaping electrode, and the end electrodes. b) Zoom into the measured ion density distribution, each pixel represents an individual decay rate measurement. c) One-dimensional cut through the density distribution along the horizontal axis. d) Effective potential derived from the density distribution by assuming a Boltzmanm distribution of the trapped ions at 300 K.

Ion density distribution



Figure 4.11: a) Ion density distribution at 170 K with an rf amplitude of 160 V. It shows a substructure of ten clearly distinct maxima. b) Cut through the effective potential, derived from the the density distribution. Overall, the potential is in accordance with the effective potential of an ideal 22-pole (solid line).

Ion temperature

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Internal state thermometry of cold trapped molecular anions

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Fig. 2 Laser-induced trap loss of OH^- above the J = 0 photodetachment threshold. All rotational states contribute to this decay channel. The inset shows a two-dimensional tomography scan, which represents the column density of the ions in the 22-pole trap (see methods).

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Fig. 3 Photodetachment cross section of OH^- at a trap temperature of 50 K for varying photon energy. The steps in the cross section are due to the opening of loss channels corresponding to the J = 2, 1and 0 rotational states of the anion.

Fig. 4 Rotational temperatures of OH^- anions determined from the ratio of the observed photodetachment transitions originating in J = 1 and J = 2 levels, respectively, for different temperatures of the helium buffer gas in the 22-pole trap.

Energy distribution



Figure 22. Numerically determined kinetic energy distributions calculated for H^+ under inclusion of collisions with room-temperature normal- H_2 . The details of the model are described in the text. The two left panels show results for an 8-pole and a 16-pole. For comparison, the right panel depicts thermal distributions at three temperatures. The scales have been chosen to stress the high-energy tail of the distributions. For an octopole, a weak potential distortions of only 20 mV has a dramatic effect.

No colisions

Trajectories of ions in 22-pole trap





+ m=20u × m=2u

Energy Distribution (no collisions)



O. Asvany, S. Schlemmer / International Journal of Mass Spectrometry 279 (2009) 147-155

With collisions





Effective potential 8-pole trap



Effective potential 8-pole trap



Figure 45. Perspective view of the major elements of a typical guided-ion-beam apparatus. Ions are created in a storage ion source, are mass and energy selected in a quadrupole and are injected into an octopole via a funnellike electrode. The scattering cell usually consists of a gas-containing cylinder surrounding the octopole. The ion beam is pulsed by opening the gate at the exit of the ion source and by pulsing the two halves of the middle element of the lens system.

22-Pole Low Temperature Ion Trap





Experiment



Fig. 2. (Color online) Experimental setup used in the present study. H^+ ions are produced in the ion storage source from hydrogen, selected by the quadrupole mass filter and injected to the 22-pole trap via the electrostatic quadrupole bender. The 22-pole trap is situated in the central chamber (22PT). Extracted ions are analyzed by the second quadrupole mass spectrometer and detected using Daly detector. The background pressure is lower than 10^{-7} Pa.

Radiative decay of ions in ion trap



Figure 32. Direct determination of radiative lifetimes of highly excited H_3^{+*} and D_3^{+*} ions using the method of laser induced dissociation. The radiative decay of H_3^+ is 2.73 times faster than for the deuterated ion in accordance with the mass dependence of an infrared transition, $\tau \sim m^{1.5} = 2.83$.



Figure 33. Measurement of the radiative decay of highly excited CH_2^{+*} ions by CO_2 laser induced dissociation. The different lifetimes may be taken as an indication for competition between infrared and electronic transitions. The dashed line below 200 μ s indicates symbolically the very short lifetime derived in section IV.B from the measured rate coefficient for radiative association of C⁺ with H₂. The microsecond range is outside the time window of the experiment due to the transport of the ions from the ion source to the ion trap.

Molecules



Molecules



22pole trap, reactions at 10 K

Variable temperature ion trap studies of CH₄⁺ + H₂, HD and D₂: negative temperature dependence and significant isotope effect

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 $CH_4^+ + H_2 \rightarrow CH_5^+ + H;$



Fig. 1. The H_3^+ and H_2D^+ ions are stored in a linear rf multipole trap, consisting of 22 stainless steel rods with diameter 1 mm. The indicated copper box is mounted onto a cold head that can reach 10 K. There is one input and one exit electrode for filling the trap with primary ions and for extracting the product ions for mass analysis and counting the ions using a Daly detector.




Measurement of the rate coefficient Decay curve



Figure 62. Measurement of the rate coefficient for the exothermic reaction $He^+ + O_2 \rightarrow O^+ + O + He$ by real-time registration of the O⁺ products using a multichannel scaler. In this experiment, the He⁺ ions are safely enclosed in the ring electrode trap, the only loss being due to reactions with O_2 . A fraction of the fast O⁺ products escapes over the properly adjusted dc barrier at the exit electrode. Their rate is directly proportional to the reactive decay rate kn_2 of the He⁺ ion cloud.

Para and ortho hydrogen



Fig. 9. Exponential decay of H_3^+ due to formation of clusters in ternary collisions with hydrogen ($[H_2] = 1.2 \times 10^{14} \text{ cm}^{-3}$). The formation of H_3^+ ions and larger clusters is about four times faster in collisions with p-H₂ than with n-H₂. The ternary rate coefficients are $k_3(n-H_2) = 1.4 \times 10^{-28} \text{ cm}^6$ /s and $k_3(p-H_2) = 5.8 \times 10^{-28} \text{ cm}^6$ /s.

Association and clusters





Fig. 11. Artists view of the possible H_{15}^+ geometric structure, the most abundant ion in the 10K equilibrium distribution.

Fig. 10. Time dependence of the mass composition of the ion trap content after initial injection of H_3^+ ($T_n = 10$ K, $[H_2] = 3.5 \times 10^{14}$ cm⁻³). Left panel: p-H₂, right panel n-H₂. The spectra are in relative units, normalized to the maximum. Note the difference in the storage times which are given in ms. The two lowest mass spectra are in both cases already very close to thermodynamic equilibrium. Their similarity is completely unexpected due to the rotational energy which can be provided by the n-H₂.

Deuteration is easy



Deuteration was not so easy



H-atom source



age 1 of 9	Physical Chemistry Chemical Physics CREATED USING THE RSC LaTEX PCCP ARTICLE TEMPLATE – SEE www.vsc.org/electronicfiles FOR DETAILS	View Article Online
ARTICLE TYPE	www.t	sc.org/XXXXX10F9XXXXXXXX

$$\begin{array}{l} \mathrm{OH^-} + \mathrm{D_2} \longrightarrow \mathrm{OD^-} + \mathrm{HD}, \\ \mathrm{OD^-} + \mathrm{H_2} \longrightarrow \mathrm{OH^-} + \mathrm{HD}, \end{array}$$

 $\Delta H = -17.2 \text{ meV}, (1)$ $\Delta H = 24.0 \text{ meV}.$ (2)

 $\rm H/D$ exchange in reactions of $\rm OH^-$ with $\rm D_2$ and of $\rm OD^-$ with $\rm H_2$ at low temperatures

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Using a cryogenic linear 22-pole rf ion trap, rate coefficients for H/D exchange reactions of OH⁻ with D₂ (1) and OD⁻ with H₂ (2) have been measured at temperatures between 11 K and 300 K with normal hydrogen. Below 60 K, we obtained $k_1 = 5.5 \times 10^{-10}$ cm³ s⁻¹ for the excergic reaction (1). Increasing the temperature above 60 K, the data decrease with a power law, $k_1(T) \sim T^{-2.7}$, reaching $\approx 1 \times 10^{-10}$ cm³ s⁻¹ at 200 K. This observation is tentatively explained with a decrease of the lifetime of the intermediate complex as well as with the assumption that scrambling of the three hydrogen atoms is restricted by the topology of the potential energy surface. The rate coefficient for the endoergic reaction (2) increases with temperature from 12 K up to 300 K, following the Arrhenius equation, $k_2 = 7.5 \times 10^{-11} \exp(-92 \text{ K/T})$ cm³ s⁻¹ over two orders of magnitude. The fitted activation energy, $E_{\text{A-Exp}} = 7.9$ meV, is in perfect accordance with the endothermicity of 24.0 meV, if one accounts for the thermal population of the rotational states of both reactants. The low mean activation energy in comparison with the enthalpy change in the reaction is mainly due to the rotational energy of 14.7 meV contributed by ortho-H₂(*J* = 1). Nonetheless, one should not ignore the reactivity of pure para-H₂ because, according to our model, it already reaches 43 % of that of ortho-H₂ at 100 K.



Energies

 $OH^- + D_2 \longrightarrow OD^- + HD$, $OD^- + H_2 \longrightarrow OH^- + HD$,

$$\Delta H = -17.2 \text{ meV}, (1)$$

 $\Delta H = 24.0 \text{ meV}.$ (2)



Fig. 1 Right panel: Stationary points of the potential energy surface for the reaction $OD^- + H_2 \longrightarrow OH^- + HD$. The energies are corrected for zero point energies, for details, see text. The arrows (with dashed lines) indicate the binding energies of the intermediate complexes $OD^- \cdot (H_2)$, $OH^- \cdot (HD)$ and $H^- \cdot (DOH)$. Left panel: Rotational energy levels ^{47,53} of OD^- and H_2 . The two arrows indicate the energies required for forming ground state products.

Energies of H₂ and D₂

1eV corresponds to ~ 11604K

E/in K

170.6

510.6

1009.5

1682.6

2494.9

84.71

255.29

510.6

835.5

1253.2

0

128.1

383.4

0

T

300K

0.128

0.657

0.117

0.092

0.004

0.001

0.179

0.202

0.383

0.115

0.098

0.015

250K

0.150

0.694

0.098

0.055

0.0016

0.0002

0.213

0.227

0.384

0.098

0.066

0.008

0

0

0

0

E/meV

0

14.7

44

87

145

215

0

7.3

22

44

72

108

0

11.04

33.05

j

0

1

2

3

4

5

0

1

2

3

4

5

0

1

2

H₂

 \mathbf{D}_2

HD



 H_2 and D_2 are taken from O. Wick dissertation HD is calculated using B_{e} from Herzberg and comparison with H_{2} from table

Energies of H₂ and D₂

E/meV

14.7

7.3

11.04

33.05

j

Η,

 \mathbf{D}_2

HD

1eV corresponds to ~ 11604K



HD is calculated using B_{e} from Herzberg and comparison with H_{2} from table

Decay curves

$OH^- + D_2 \longrightarrow OD^- + HD$,	$\Delta H = -$
$\mathrm{OD^-} + \mathrm{H_2} \longrightarrow \mathrm{OH^-} + \mathrm{HD},$	$\Delta H = 24$

17.2 meV, (1) 4.0 meV. (2)

respectively. The free parameters of the fit were the reaction rates $r_1 = k_1[D_2]$ and $r_2 = k_2[H_2]$ as well as the initial numbers of trapped ions.









Fig. 2 Normalized number of primary ions (OH⁻, closed symbols) and product ions (OD-, open symbols) as a function of storage time. Operating conditions were $T_{22PT} = 25,60,100$ K, the densities of D2, He, and H2 are listed in Table 1.

Fig. 3 Rate r_1 of the reaction (1) as a function of deuterium number density [D₂] at trap temperatures $T_{22PT} = 20, 125, 150$ K.

Exothermic reaction





Fig. 4 Measured temperature dependence of the rate coefficient k_1 for H/D exchange reaction (1). The calculated Langevin collisional rate coefficient is indicated as k_{1L} . The assumption that exclusively the rotational ground state of D₂ can react leads to the dash-dotted line (see text). Thermal FDT data of Viggiano and Morris⁴⁰, SIFT data of Grabowski *et al.*³⁹, and HPMS data of Mautner *et al.*⁴¹ are also included. The dashed line shows $k_1(T)$ calculated from equation (5) with the parameters given there.

$$\frac{k_{10}}{k_1} - 1 = \left(\frac{T}{T_0}\right)^m$$

Exothermic reaction





Fig. 4 Measured temperature dependence of the rate coefficient k_1 for H/D exchange reaction (1). The calculated Langevin collisional rate coefficient is indicated as k_{1L} . The assumption that exclusively the rotational ground state of D₂ can react leads to the dash-dotted line (see text). Thermal FDT data of Viggiano and Morris⁴⁰, SIFT data of Grabowski *et al.*³⁹, and HPMS data of Mautner *et al.*⁴¹ are also included. The dashed line shows $k_1(T)$ calculated from equation (5) with the parameters given there.



Fig. 5 Plot of $(k_{10}/k_1 - 1)$ versus *T* for the data shown in Fig. 4 emphasizing on the power law T^m . Data with a statistical error above 100% in this representation are not shown.

Endothermic reaction





Fig. 2 Normalized number of primary ions (OH⁻, closed symbols) and product ions (OD⁻, open symbols) as a function of storage time. Operating conditions were $T_{22PT} = 25,60,100$ K, the densities of D₂, He, and H₂ are listed in Table 1.



Fig. 6 Normalized number of primary ions (OD⁻, closed symbols) and product ions (OH⁻, open symbols) as a function of storage time. The trap was at $T_{22PT} = 12, 21, 78, 200$ K, the densities of D₂, He and H₂ in the trap are listed in Table 2.

Energies

$$\begin{array}{ll} \mathrm{OH^-} + \mathrm{D_2} \longrightarrow \mathrm{OD^-} + \mathrm{HD}, & \Delta H = -17.2 \ \mathrm{meV}, \ (1) \\ \mathrm{OD^-} + \mathrm{H_2} \longrightarrow \mathrm{OH^-} + \mathrm{HD}, & \Delta H = 24.0 \ \mathrm{meV}. \ \ (2) \end{array}$$



Fig. 1 Right panel: Stationary points of the potential energy surface for the reaction $OD^- + H_2 \longrightarrow OH^- + HD$. The energies are corrected for zero point energies, for details, see text. The arrows (with dashed lines) indicate the binding energies of the intermediate complexes $OD^- \cdot (H_2)$, $OH^- \cdot (HD)$ and $H^- \cdot (DOH)$. Left panel: Rotational energy levels ^{47,53} of OD^- and H_2 . The two arrows indicate the energies required for forming ground state products.

Temperature dependence

$$OH^- + D_2 \longrightarrow OD^- + HD,$$
 $\Delta H = -17.2 \text{ meV}, (1)$
 $OD^- + H_2 \longrightarrow OH^- + HD,$ $\Delta H = 24.0 \text{ meV}. (2)$





Temperature dependence

 $\begin{array}{ll} \mathrm{OH^-} + \mathrm{D_2} \longrightarrow \mathrm{OD^-} + \mathrm{HD}, & \Delta H = -17.2 \ \mathrm{meV}, \ (1) \\ \mathrm{OD^-} + \mathrm{H_2} \longrightarrow \mathrm{OH^-} + \mathrm{HD}, & \Delta H = 24.0 \ \mathrm{meV}. \ \ (2) \end{array}$



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LOW-TEMPERATURE ION TRAP STUDIES OF $\mathrm{N}^+(^3P_{ja}) + \mathrm{H}_2(j) \rightarrow \mathrm{NH}^+ + \mathrm{H}$

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$$N^{+}(^{3}P_{ja}) + H_{2}(j) \rightarrow NH^{+} + H$$





 $k = f(\zeta_0 k_{1,0} + \zeta_1 k_{1,1}) + (1 - f)(\zeta_0 k_{0,0} + \zeta_1 k_{0,1})$

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LOW-TEMPERATURE ION TRAP STUDIES OF $N^+({}^3P_{ja}) + H_2(j) \rightarrow NH^+ + H$

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$N^{+}(^{3}P_{ja}) + H_{2}(j) \rightarrow NH^{+} + H$





 $k = f(\zeta_0 k_{1,0} + \zeta_1 k_{1,1}) + (1 - f)(\zeta_0 k_{0,0} + \zeta_1 k_{0,1})$

Part 4B

De Broglie wave length

$$\lambda = \frac{h}{p} = \frac{h}{mv} \sqrt{1 - \frac{v^2}{c^2}}$$

$$\lambda_e(4K) \sim 540 A \sim 54 x 10^{-9} m$$

$$\lambda_e(1eV) \sim 11.6A \sim 1.16x10^{-9}m$$

$$\lambda_e(mK) \sim 3x10^4 A \sim 3x10^{-6} m$$

•



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

Understanding plasma

Collisions Classification of collisions

elastic inelastic

The concept of collision cross-section $\delta I = -N\sigma I_{\pi} \delta x$ $I_{P} = I_{0} \exp(-\sigma N x)$ Hypothetical gas of rigid spheres of cross section σ

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

 \rightarrow

 \rightarrow

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

Collisions of electrons with atoms – Ramsauer's method

Lenard 1903 Akesson 1916 Ramsauer 1921

ATENUATION METHOD

 $\frac{\delta I = -N \sigma I_p \delta x}{I_p = I_0 \exp(-\sigma N x)}$



Cross sections - details



ФИГ. 14.8. Сечение столкновения с передачей импульса для электронов в аргоне. [Из работы: Frost L. S., Phelps A. V., Phys. Rev., 136, A1538 (1964).]



ФИГ. 14.3. Сечение столкновения с передачей импульса для электронов в гелии при є ≤ 6 эВ. (Кривая построена по данным табл. 14.2.)



ФИГ. 14.5. Сечение столкновения с передачей импульса для электронов в неоне при ε ≤ 7 эВ. (Кривая построена по данным табл. 14.4).

Frequencies of elastic collisions

 $\delta I = -NQI_{p} \delta x$ $I_{p} = I_{0} \exp(-QNx)$ $I_{0}(v) \qquad N.x \qquad I_{p}$ Q(v)

a₀=0.53x10⁻⁸cm~0.5A Radius of the first Bohr orbit of H atom











расчетах [24]

Total collision cross sections comparison



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.

This is for recombination ??!1 be careful





Franck-Condon Factors

$$P \sim \langle \psi_{\text{initial.}} \psi_{\text{final}} \rangle^{2}$$

Interaction of Electrons with Molecular ions

Electron – molecule collision calculations using the R-matrix method

Jonathan Tennyson Department of Physics and Astronomy University College London



Dissociation of H₂









Processes: at low impact energies

Elastic scattering $AB + e \longrightarrow AB + e$ **Electronic excitation** $AB + e \longrightarrow AB^* + e$ Vibrational excitation $\overline{AB}(v''=0) + e \longrightarrow \overline{AB}(v') + e$ **Rotational excitation** $\overline{AB(N'')} + e \longrightarrow \overline{AB(N') + e}$ **Dissociative attachment / Dissociative recombination** $AB + e \longrightarrow A^- + B$ \rightarrow A + B⁻ Impact dissociation $AB + e \longrightarrow A + B + e$ All go via (AB⁻)**. Can also look for bound states Electron impact dissociation of H₂ Important for fusion plasma and astrophysics

Low energy mechanism: $e^- + H_2(X \ ^1\Sigma_g) \longrightarrow e^- + H_2(b \ ^3\Sigma_u) \longrightarrow e^- + H + H$

R-matrix calculations based on adiabatic nuclei approximation extended to dissociation Including nuclear motion (within adiabatic nuclei approximation) in case of dissociation

 Excess energy of incoming e⁻ over dissociating energy can be split between nuclei and outgoing e⁻ in any proportion.



- Fixed nuclei excitation energy changes rapidly with bondlength
- Tunnelling effects significant

Determine choice of Tmatrices to be averaged

The energy balance method



D.T. Stibbe and J. Tennyson, New J. Phys., 1, 2.1 (1999).



Explicit adiabatic averaging over T-matrices using continuum functions
Need to Calculate:

- Total cross sections, σ(E_{in})
- Energy differential cross sections, dσ(E_{in})
 dE_{out}
- Angular differential cross sections, d<u>σ(E_{in})</u> dθ
- Double differential cross sections, d²σ(E_{in}) dθdE_{out}

Required formulation of the problem

C.S. Trevisan and J. Tennyson, J. Phys. B: At. Mol. Opt. Phys., 34, 2935 (2001)

Collisional dissociation

New Journal of Physics 1 (1998) 2.1–2.9 Near-threshold electron impact dissociation of H₂ within the adiabatic nuclei approximation

Darian T Stibbe † and Jonathan Tennyson †

$$e + H_2(X \ ^1\Sigma_g^+) \rightarrow H_2^*(b \ ^3\Sigma_u^+) + e \rightarrow H(1s) + H(1s) + e.$$





Figure 1. The molecule is excited from the X ${}^{1}\Sigma_{g}^{+}$ to the b ${}^{3}\Sigma_{u}^{+}$ state and then dissociates as it falls down the potential curve. Also shown are the ground state v = 0 nuclear wavefunction (dashed black) and continuum wavefunctions (ranging from red to blue) for different asymptotic kinetic energies of the dissociating molecule ($E_{\rm ke}$). The figure can be downloaded as an XMGR file (see Appendix A) from the article multimedia page.

Collisional dissociation



Figure 1. The molecule is excited from the X ${}^{1}\Sigma_{g}^{+}$ to the b ${}^{3}\Sigma_{u}^{+}$ state and then dissociates as it falls down the potential curve. Also shown are the ground state v = 0 nuclear wavefunction (dashed black) and continuum wavefunctions (ranging from red to blue) for different asymptotic kinetic energies of the dissociating molecule ($E_{\rm ke}$). The figure can be downloaded as an XMGR file (see Appendix A) from the article multimedia page.





Dissociation cross section as a function of incoming electron energy, *E*in, and initial vibrational state, *v*.

Dissociation rate as a function of electron temperature and initial H_2 vibrational level. Note the log rate scale.

Collisional dissociation



Figure 1. The molecule is excited from the X ${}^{1}\Sigma_{g}^{+}$ to the b ${}^{3}\Sigma_{u}^{+}$ state and then dissociates as it falls down the potential curve. Also shown are the ground state v = 0 nuclear wavefunction (dashed black) and continuum wavefunctions (ranging from red to blue) for different asymptotic kinetic energies of the dissociating molecule ($E_{\rm ke}$). The figure can be downloaded as an XMGR file (see Appendix A) from the article multimedia page.







FIG. 13.4. Apparent cross-section, $Q_{\rm diss}$, for dissociation of $\rm H_2$ into neutral H atoms by electron impact as observed by Corrigan. • Experimental points. — best fit to experimental points. — — estimated true $Q_{\rm diss}$ for electron energies beyond the ionization threshold.

Electron impact dissociation of H₂ Effective threshold about 8 eV for H₂(v=0) Thermal rates strongly dependent on initial H₂ vibrational state

For v=0: Excess energy largely converted to Kinetic Energy of outgoing H atoms For v > 0: Source of cold H atoms ?

Rotational and vibrational excitation - H_3^+ + e

Mon. Not. R. Astron. Soc. 405, 1195-1202 (2010)

doi:10.1111/j.1365-2966.2010.16522.x

Calculation of rate constants for vibrational and rotational excitation of the H^+_3 ion by electron impact

Viatcheslav Kokoouline,^{1,2*} Alexandre Faure,³ Jonathan Tennyson⁴ and Chris H. Greene⁵

ABSTRACT

We present theoretical thermally averaged rate constants for vibrational and rotational (de-)excitation of the H_3^+ ion by electron impact. The constants are calculated using the multichannel quantum-defect approach. The calculation includes processes that involve a change $|\Delta J| \le 2$ in the rotational angular momentum J of H_3^+ . The rate constants are calculated for states with $J \le 5$ for rotational transitions of the H_3^+ ground vibrational level. The thermal rates for transitions among the lowest eight vibrational levels are also presented, averaged over the rotational structure of the vibrational levels. The conditions for producing non-thermal rotational and vibrational distributions of H_3^+ in astrophysical environments are discussed.

Key words: molecular data - molecular processes - plasmas - ISM: molecules.

How is $o/p-H_3^+$ produced in H_2 plasma $o/p-H_2^+ + o/p-H_2 \rightarrow o/p-H_3^+ + H$







3 atomic molecule H_3^+



PHYSICAL REVIEW A 68, 012703 (2003)

Unified theoretical treatment of dissociative recombination of D_{3h} triatomic ions: Application to H_3^+ and D_3^+

Viatcheslav Kokoouline and Chris H. Greene Department of Physics and JILA, University of Colorado, Boulder, Colorado 80309-0440, USA (Received 14 March 2003; published 9 July 2003)





State specific recombination $H_3^+(v=0)$





Rotational levels for v_2



Absorption spectroscopy $H_3^+(v=0)$









overtone band $v_2=3 \leftarrow 0$ at 1.4 µm

Rotational and vibrational excitation - H_3^+ + e

Mon. Not. R. Astron. Soc. 405, 1195-1202 (2010)

doi:10.1111/j.1365-2966.2010.16522.x

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We present theoretical thermally averaged rate constants for vibrational and rotational (de-)excitation of the H_3^+ ion by electron impact. The constants are calculated using the multichannel quantum-defect approach. The calculation includes processes that involve a change $|\Delta J| \le 2$ in the rotational angular momentum J of H_3^+ . The rate constants are calculated for states with $J \le 5$ for rotational transitions of the H_3^+ ground vibrational level. The thermal rates for transitions among the lowest eight vibrational levels are also presented, averaged over the rotational structure of the vibrational levels. The conditions for producing non-thermal rotational and vibrational distributions of H_3^+ in astrophysical environments are discussed.

Key words: molecular data - molecular processes - plasmas - ISM: molecules.



Figure 1. Probabilities of rovibrational excitation of the H_3^+ ion calculated using the full rovibrational frame transformation. Only transitions from the ground vibrational level $\{00^0\}$ are shown. The $\{00^0\} \rightarrow \{01^1\}$ probabilities oscillate a lot below 3000 cm^{-1} and become less energy-dependent above. The oscillations are due to the strong rotational coupling between individual rotational levels of the initial and final states of the ion. When averaged over the initial and summed over the final rotational states and averaged over the appropriate energy distribution, the resulting probabilities are similar in magnitude to the probabilities shown in Fig. 2. The labels on top of the figure indicate different rovibrational ionization limits. Note that the zero of energy in the figure is set to the energy of the forbidden rovibrational level $\{00^0\}(00)$.

Rotational and vibrational excitation - H_3^+ + e



Figure 1. Probabilities of rovibrational excitation of the H_3^+ ion calculated using the full rovibrational frame transformation. Only transitions from the ground vibrational level $\{00^0\}$ are shown. The $\{00^0\} \rightarrow \{01^1\}$ probabilities oscillate a lot below 3000 cm^{-1} and become less energy-dependent above. The oscillations are due to the strong rotational coupling between individual rotational levels of the initial and final states of the ion. When averaged over the initial and summed over the final rotational states and averaged over the appropriate energy distribution, the resulting probabilities are similar in magnitude to the probabilities shown in Fig. 2. The labels on top of the figure indicate different rovibrational ionization limits. Note that the zero of energy in the figure is set to the energy of the forbidden rovibrational level $\{00^0\}(00)$.

Figs 1 and 2 compare our calculations with and without rotational structure included, for the probabilities of rovibrational and vibrational (de-)excitation of the ion. Fig. 1 shows in detail the rovibrational transitions from the ground to the first excited vibrational level {01¹} with $J_{tot} = 2$ in para-H₃⁺. In order to compare with the results in Fig. 2, one would need to take a sum over final quanta and average over initial J and K, and account for all possible J_{tot} and K_{tot} similar as it is done in equation (2). This would mean that to achieve a converged result at reasonably high energy (~2000 cm⁻¹) calculations would be needed for all J_{tot} up to 10. This would require a tremendous numerical effort if the fully quantum approach was to be applied.



Figure 2. Probabilities of vibrational excitation from the ground vibrational level $\{00^0\}$ to several excited vibrational levels calculated using the vibrational frame transformation only. Energies of vibrational thresholds are labelled with arrows and the corresponding vibrational quantum numbers.

Vibrational excitation - H_3^+ + e



Figure 2. Probabilities of vibrational excitation from the ground vibrational level $\{00^0\}$ to several excited vibrational levels calculated using the vibrational frame transformation only. Energies of vibrational thresholds are labelled with arrows and the corresponding vibrational quantum numbers.

The thermally averaged rate constant $\alpha_{th}(T)$ (in a.u.) is obtained from the energy-dependent cross-section $\sigma(E)$ as

$$\alpha_{\rm th}(T) = \frac{8\pi}{(2\pi kT)^{3/2}} \int_0^\infty \sigma(E_{\rm el}) {\rm e}^{-\frac{E_{\rm el}}{kT}} E_{\rm el} {\rm d}E_{\rm el} \,, \tag{4}$$

where *T* is the temperature. Temperature dependencies $\alpha_{\text{th}}(T)$ for different rovibrational transitions $v \rightarrow v'$ obtained using equation (4) are shown in Fig. 3 as solid lines.

For further discussion, it is convenient to represent the cross-section $\sigma(E_{\rm el})$ in the form

$$\sigma(E_{\rm el}) = \frac{\pi}{k^2} P(E_{\rm el}), \qquad (5)$$

where k is the wave vector of the incident electron, $P(E_{el})$ is the probability for vibrational (de-)excitation at collision energy E_{el} .



Figure 3. Thermally averaged rate constants for several (de-)excitation transitions obtained by direct integration using equation (4) (solid lines) and the approximate formula of equation (7) (dashed line). The averaged probabilities for vibrational (de-)excitations are listed in Table 1.

Rotational excitation - H_3^+ + e

4 RATE CONSTANTS FOR ROTATIONAL (DE-)EXCITATION

Rotational excitation - H_3^+ + e



Figure 4. Thermally averaged rate constants for several rotational (de-)excitation transitions $(JK) \rightarrow (J'K')$ of the H₃⁺ ion (solid lines). The vibrational level, $\{00^0\}$, is the same in the initial and final state of the ion. The dotted lines show a few examples of the numerical fit using equation (9).

Vibrational excitation - $H_3^+ + e$



Figure 3. Thermally averaged rate constants for several (de-)excitation transitions obtained by direct integration using equation (4) (solid lines) and the approximate formula of equation (7) (dashed line). The averaged probabilities for vibrational (de-)excitations are listed in Table 1.

Rotational excitation - calculations

Electron-impact rotational excitation of symmetric-top molecular ions

4.1. H_3^+ and D_3^+

 H_3^+ is the simplest polyatomic molecule, consisting of only three protons (fermions) and two electrons. As a consequence of the Pauli principle, which demands that the total wavefunction be antisymmetric with respect to permutation, the J = K = 0 state of the vibrational ground state cannot be occupied (Oka 1992). Therefore, the ground rotational state of H_3^+ is the (J = 1, K = 1) state and the next level is (J = 1, K = 0) (Pan and Oka 1986). Moreover, like the NH₃ molecule, H_3^+ has both ortho- and para-modifications, with K = 3n ortho and $K = 3n \pm 1$ para. On the other hand, D_3^+ is composed by three bosons and its lowest rotational level is (J = 0, K = 0).

In summary, propensity rules in H₃⁺/D₃⁺-electron collisions are found to be

if
$$K \neq 0$$
, $\Delta J = \pm 1, \pm 2$
and $\Delta K = 0$, (25)
if $K = 0, \Delta J = \pm 2$

which correspond to the quadrupolar selection rules derived from the CB theory (see section 2.1). It should be noted that radiative selection rules for the forbidden rotational transitions in H_3^+ are (Pan and Oka 1986)

$$\Delta J = 0, \pm 1 \qquad \text{and} \qquad \Delta K = \pm 3. \tag{26}$$

A Faure¹ and Jonathan Tennyson

J. Phys. B: At. Mol. Opt. Phys. 35 (2002) 3945-3956

Electron collisional selection rules are found to be consistent with the CB theory. In particular, dominant transitions are those for which $\Delta J \leq 2$ and $\Delta K = 0$.



Figure 1. Rotational excitation cross sections for transitions with $\Delta J = 1, 2$ and $\Delta K = 0$ in ortho-, para-H₃⁺ and D₃⁺ by electron impact. The *T*-matrix results, with and without threshold correction, are represented by the solid and dot–dashed curves, respectively. The long-dashed curve denotes the CB results.

Rotational excitation - calculations

Electron-impact rotational excitation of symmetric-top molecular ions





A Faure¹ and Jonathan Tennyson

J. Phys. B: At. Mol. Opt. Phys. 35 (2002) 3945-3956





Figure 2. Rotational excitation cross sections for transitions with $\Delta J = 1, 2, 3, 4$ and $\Delta K = 0, 3$ in ortho- and para-H₃⁺ by electron impact.

Rate coefficients

ABSTRACT

Molecular **R**-matrix calculations are performed to obtain rotational excitation rate coefficients for electron collisions with the symmetric-top ions H_3^+ and H_3O^+ up to electron temperatures of 10000 K. De-excitation rates and critical electron densities are also given. It is shown that short-range interactions, which are ignored in the standard Coulomb–Born theory, are crucial for studying electron-impact rotational excitation of molecular ions. In particular, our calculations show that electron collisions could help to create and maintain the predicted population inversion between the (J, K) = (4, 4) and (3, 1) levels of H_3^+ and populate the rotational levels of H_3O^+ up to the (4, 1) level.



Mon. Not. R. Astron. Soc. 340, 468-472 (2003)

Rate coefficients for electron-impact rotational excitation of H_3^+ and H_3O^+

Alexandre Faure* and Jonathan Tennyson†





Dissociative recombination of NO⁺ NO⁺ important ion in ionosphere of Earth and thermosphere of Venus

Mainly destroyed by $NO^+ + e^- \longrightarrow N^- + O$

Need T-dependent rates for models

Recent storage ring experiments show unexplained peak at 5 eV

Calculations:

resonance curves from R-matrix calculation

nuclear motion with multichannel quantum defect theory

NO⁺ dissociation recombination: potential energy curves



NO⁺ dissociation recombination: Direct and indirect contributions



NO⁺ dissociation recombination: comparison with storage ring experiments



IF Schneider, I Rabadan, L Carata, LH Andersen, A Suzor-Weiner & J Tennyson, J. Phys. B, 33, 4849 (2000)

NO⁺ dissociation recombination: Temperature dependent rates



Electron temperature, T_e (K)

Conclusion

- R-matrix method provides a general method for treating low-energy electron collisions with neutrals, ions and radicals
- Results should be reliable for the energies above 100 meV (previous studies of Baluja *et al* 2001 on OCIO).
- Total elastic and electron impact excitation cross sections.
- Being extended to intermediate energy and ionisation.



Chiara Piccarreta

Jimena Gorfinkiel

Iryna Rozum

End for 11. 03. 2025

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 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 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).

Maxwell distribution and excitation

0,25





Energy [eV]

End of part 2A

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 ???

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

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




Multiple ionization

Several theoretical models describing the low-energy behavior of atomic single and multiple ionization cross sections have been discussed in the literature. The most frequently cited model is the Wannier model [7] which is based on arguments from classical physics and which describes the electron impact ionization cross section $\sigma(E)$ in the near-threshold region as a function of the electron energy *E* by a power law

$$\sigma(E) = \text{constant}(E - E_T)^{\mu/2 - 1/4}$$
(1)

with

 $\mu(n) = (1/2)[(100Z - 9)/(4Z - 1)]^{1/2}$

where Z denotes the charge state of the final ion and E_T refers to its AE (threshold energy). This yields the well known Wannier threshold law for the case of single ionization of a neutral atom by an electron (originally developed for hydrogen [7])

(2)

$\sigma(E) = \sigma_o (E - ET)^{1.127}.$ (3)

It is important to note that this law predicts the cross sectional behavior starting at the threshold, but does not give the energy range over which it is valid.

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 µs. The current of the parent ion beam was measured simultaneously in a Faraday cup.

Binding energy value of about 11 eV

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

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

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

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

Ionization of fullerene

Scaling behavior of cross-sections for electron-impact multiple-ionization of negatively-charged fullerene ions

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Fig. 1. Absolute cross-sections $\sigma_{-1,1}$ for electron-impact double ionization of C_{60}^- (circles), C_{70}^- (squares) and C_{84}^- (triangles) ions. Error bars indicate total experimental uncertainties.



Fig. 3. Same as in Fig. 1 for quadruple ionization. Open circles: absolute cross-sections for quadruple ionization of C_{60}^{-} subtract a contribution of C_{20}^{+} (for more details see text).

Received 16 November 1999; in final form 17 January 2000



Fig. 2. Same as in Fig. 1 for triple ionization.

Ionization of clusters



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



Dissociative attachment

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

Resonances in Electron Impact on Atoms and Diatomic Molecules

George J. Schulz

Reprinted from Reviews of Modern Physics Vol. 45, No. 3, pp. 378-486, July 1973



FIG. 11. The energy dependence of the total cross section for dissociative attachment in H₂, HD, and D₂ near 3.7 eV. The process shows a very large isotope effect and proceeds via the Σ_{μ}^{+} states of H₂⁻. Part (a) shows the experimental results of Schulz and Asundi (1967) and part (b) shows the unfolded cross sections as reported by Chen and Peacher (1968a). It should be noted that the experimental curves of Schulz and Asundi, shown on the left side of the diagram, have peak cross sections differing by orders of magnitude (1.6×10⁻²¹ cm² for H2, 1×10-22 cm2 for HD, and 8× 10^{-24} cm² for D₂). Whereas the H⁻/H₂ cross section was obtained with an electron energy distribution of 0.1 eV the curves for HD and D₂ had to be taken with an energy distribution of 0.45 eV in order to gain sensitivity. This accounts for the difference in the threshold behavior. The rising portion of the D^{-}/D_{2} cross section, indicated by dashes, is real having been reproduced by Ziesel and Schulz (unpublished). It could result partially from the wings of the Σ_0^+ resonance near 10 eV.



FIG. 6. The real and imaginary parts of the potential energy curves for the ${}^{2}\Sigma_{u}^{+}$ and ${}^{2}\Sigma_{g}^{+}$ states of H₂⁻. On the left-hand side are shown the potential energy curves for H₂ (---), and the potential energy curves for H₂⁻ derived by Bardsley *et al.* (1966a) and by Chen and Peacher (1968a). The dotted curve indicates the real part of the potential curve for the ${}^{2}\Sigma_{u}^{+}$ state which is needed to obtain agreement with the vibrational cross section of Ehrhardt, *et al.* (1968). The repulsive curve for H₂⁻ (${}^{2}\Sigma_{g}^{+}$) of Chen and Peacher (1968a) is in very good agreement with the curve derived by Eliezer, Taylor, and Williams (1967), which is shown in Fig. 25(a). The potential energy curves for the lowest states of H₂(${}^{2}\Sigma_{g}^{+}$ and ${}^{2}\Sigma_{g}^{+}$) are taken from Kolos and Wolnicwicz (1965). The right-hand side of the figure shows the calculated widths of the ${}^{2}\Sigma_{u}^{+}$ and ${}^{2}\Sigma_{g}^{+}$ states. [From Chen 1969.]

Hydrogen



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





Fig. 11. The energy dependence of the total cross section for dissociative attachment in H2, HD, and D2 near 3.7 eV. The process shows a very large isotope effect and proceeds via the Σ_{μ}^{+} states of H₂⁻. Part (a) shows the experimental results of Schulz and Asundi (1967) and part (b) shows the unfolded cross sections as reported by Chen and Peacher (1968a). It should be noted that the experimental curves of Schulz and Asundi, shown on the left side of the diagram, have peak cross sections differing by orders of magnitude (1.6×10⁻²¹ cm² for H₂, 1×10^{-22} cm² for HD, and $8 \times$ 10^{-24} cm² for D₂). Whereas the H⁻/H₂ cross section was obtained with an electron energy distribution of 0.1 eV the curves for HD and D2 had to be taken with an energy distribution of 0.45 eV in order to gain sensitivity. This accounts for the difference in the threshold behavior. The rising portion of the D^-/D_2 cross section, indicated by dashes, is real having been reproduced by Ziesel and Schulz (unpublished). It could result partially from the wings of the Σ_0^+ resonance near 10 eV.



Hydrogen









FIG. 15. Isotope effect in dissociative attachment in the neighborhood of 10 eV in H₂, HD, and D₂. [Taken from Rapp, Sharp, and Briglia (1965).]



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).]

Excitation function







Resonances in Electron Impact on Atoms and Diatomic Molecules

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Reprinted from Reviews of Modern Physics Vol. 45, No. 3, pp. 378-486, July 1973

Resonances George	in J.	Electron Schulz.	Impact	on 	Atoms	1
Resonances George	in J.	Electron Schulz	Impact	on 	Diatomic Molecules	47

Experiments



FIG. 3. Schematic overview of experiments which are useful for the study of resonances in atoms and molecules.



FIG. 4. Schematic diagram of a typical electrostatic monochromator with electrostatic analyzer. Angular distribution can be obtained by rotating the analyzer with respect to the monochromator. Elastic and inelastic differential cross sections can be obtained with such an instrument. [From Pavlovic, Boness, Herzenberg, and Schulz (1972).]



-GAS IN

PUMP OUT 2

FIG. 6. Schematic arrangement of a modified Ramsauer apparatus for the measurement of total scattering cross section. [From Golden and Bandel (1965).]

SCATTERING

CHAMBER

DROPPING

CHANNEL

GRID-

COLLECTOR

CATHODE



FIG. 7. Schematic diagram of a trapped-electron experiment and potential distribution at the axis of the tube. F is the filament, P2 is the retarding electrode, G is the cylindrical grid forming the collision chamber, M is the cylinder for collection of trapped electrons, E is the electron beam collector, V_A is the accelerating voltage, and W is the depth of the well. The double line in (b) indicates the energy of the electron beam and the arrow indicates the energy lost by an electron in an inelastic collision. The electron energy in the collision chamber is (V_A+W) . [From Schulz (1959).]

Excitation function





FIG. 13.50. Excitation function for metastable states of N $_2$ observed by Olmsted, Newton, and Street.

Vibr. excitation of N₂ 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+.*

Ionization of N₂ fine structure



FIG. 13.46. Potential energy curves for some electronic states of N_2 and N_2^+ .





Excitation N₂ and other diatomic



Fig. 11.30, Momentum-transfer cross-section for electrons in N₂, ---- derived by Engolnardt, Phelps, and Risk from analysis of swarn data. ------ derived by Pack and Phelps from analysis of their drift velocity observations. ---------derived from drift velocity observations of Crompton and Sutten. ---- total cross-section measured by Rumsauer method.





FIG. 10.21. Total collision cross-sections of diatomic molecules for slow electrons (a) H₂, N₂, O₂, CO, (b) HCl, NO.

Partial cross section for excitation





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

Molecular Oxygen Cross Sections

Molecular Oxygen Cross Sections

- · O2 cross section consistent with electron transport data
- · Metastable excitation and dissociation dominate at modest electron energies.



Next \rightarrow IONIZATION

Swarm Analyzed Cross Section Set: Argon

Comparison of calculated and measured ionization coefficients for several Ar cross section sets



How is $o/p-H_3^+$ produced in H_2 plasma $o/p-H_2^+ + o/p-H_2 \rightarrow o/p-H_3^+ + H$



Fig. 1: Rotational energy levels of H₃⁺ in the ground vibrational state.¹





Energy levels of H_2 D_3^+ in K Rotational excitation



ortho para



3 atomic molecule H_3^+







PHYSICAL REVIEW A 68, 012703 (2003)

Unified theoretical treatment of dissociative recombination of D_{3h} triatomic ions: Application to H_3^+ and D_3^+

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State specific recombination $H_3^+(v=0)$





Rotational levels for v_2



Absorption spectroscopy $H_3^+(v=0)$









overtone band $v_2=3 \leftarrow 0$ at 1.4 µm

Measured transitions in NIR – second overtone



How is o/p-H₃⁺ thermalised











Energy levels Rotational states

1eV corresponds to ~ 11604K

106 EXCITATION, DISSOCIATION, AND ENERGY TRANSFER



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-H₂), the nuclear spins are parallel; for the para version $(p-H_2)$, the nuclear spins are antiparallel. [From Shimamura (1984).]

Potential curves N₂, N₂⁺

Vibrational states Electronic states Ionisation



28

26

24

22

20

12 3

8°2'

+* (†P)

14.5eV

15 YI HN YD

HCN / HNC NIR spectra



<u>Ion traps</u>



Photoelectron spectrum



Date: 23 Apr 2010 Satellite: Hubble Space Telescope Depicts: Detail of the Carina Nebula

