LECTURE 5

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| Bond Formation Processes | | Typical rate coefficient (cm ³ s ⁻¹) |
|---|--|---|
| Radiative association | $X + Y \to XY + h\nu$ | $10^{-17} - 10^{-14}$ |
| Associative detachment | $X^- + Y \rightarrow XY + e$ | $\sim 10^{-9}$ |
| Bond Destruction Processes | | |
| Dissociative recombination | $XY^+ + e \rightarrow X + Y$ | $10^{-7} - 10^{-6}$ |
| Bond Rearrangement Processes | | |
| Ion–molecule exchange Charge–transfer Neutral–neutral | $\begin{array}{l} X^+ + YZ \rightarrow XY^+ + Z \\ X^+ + YZ \rightarrow X + YZ^+ \\ X + YZ \rightarrow XY + Z \end{array}$ | $10^{-9} - 10^{-8}$ 10^{-9} $10^{-11} - 10^{-9}$ |

- Gas-phase chemistry
- Photochemistry (this class)
- Cosmic rays induced chemistry (next class)
- Grain-surface chemistry (future classes)
- Ion-neutral reactions drive the chemistry (k~10⁻⁹ cm³s⁻¹)
- From where the ions come?
- Photons and/or cosmic-ray!

CHEMISTRY IN THE ISM (REMIND)

- Photoreactions are unimolecular reactions!
- Very important in many different envs (shocks, diffuse clouds, planetary atmospheres...)

1. $A + B \rightarrow P$ (two-body reactions) 2. $A + photon \rightarrow P$ (photo-reactions) 3. $A + B + C \rightarrow P$ (three-body reactions)

$$\frac{dn_{\rm P}}{dt} = k(T)n_{\rm A}n_{\rm B} \qquad (1) \quad \text{units of } k(T): \ \mathrm{cm}^3 \ \mathrm{s}^{-1}$$
$$\frac{dn_{\rm P}}{dt} = k(T)n_{\rm A} \qquad (2) \quad \mathrm{units of } k(T): \ \mathrm{s}^{-1}$$
$$\frac{dn_{\rm P}}{dt} = k(T)n_{\rm A}n_{\rm B}n_{\rm C} \qquad (3) \quad \mathrm{units of } k(T): \ \mathrm{cm}^6 \ \mathrm{s}^{-1}$$

ASTROCHEMISTRY



N_H (cm⁻²)

| | Diffuse Atomic | Diffuse Molecular | Translucent | Dense Molecular |
|--------------------------------------|-----------------------|---|--|--------------------|
| Defining Characteristic | $f^{n}_{H_{2}} < 0.1$ | $f^{n}_{H_{2}} > 0.1 f^{n}_{C^{+}} > 0.5$ | $f^{n}_{C^{+}} < 0.5 f^{n}_{CO} < 0.9$ | $f^{n}_{CO} > 0.9$ |
| A _V (min.) | 0 | ~0.2 | ~1-2 | ~5-10 |
| Typ. $n_{\rm H}$ (cm ⁻³) | 10–100 | 100–500 | 500-5000? | >10 ⁴ |
| Тур. Т (К) | 30–100 | 30–100 | 15-50? | 10–50 |
| Observational | UV/Vis | UV/Vis IR abs | Vis (UV?) IR abs | IR abs |
| Techniques | H I 21-cm | mm abs | mm abs/em | mm em |

Interaction matter-radiation

- Determines
 - the physical state of interstellar gas (phase transitions)
 - its chemical and ionization state (photochemistry)
 - its thermal state (photoelectrons)
 - re-radiation of energy at longer wavelengths (dust)
 - radiation pressure (dynamical effects)

Interstellar Radiation Field

- Galactic synchrotron radiation from relativistic electrons
- The cosmic microwave background radiation
- FIR and IR from dust grains heated by starlight
- Plasma emission (10⁴ K) free-free, free-bound, and bound-bound
- <u>Starlight</u>
- X-ray emission from hot plasma (10⁵ to 10⁸ K)

RADIATION SOURCES

The ISM is permeated by various photon fields, which influence the physical and chemical state of the gas and dust.



► Diffuse X-rays (> 124 eV)

mean intensity in units of erg cm $^{-2}~{\rm s}^{-1}~{\rm Hz}^{-1}~{\rm sr}^{-1}$



► EUV (10.25 – 124 eV)

mean intensity in units of erg cm $^{-2}$ s $^{-1}$ Hz $^{-1}$ sr $^{-1}$



FUV (6.2 – 13.6 eV, including Ly- α edge)

mean intensity in units of erg cm $^{-2}~{\rm s}^{-1}~{\rm Hz}^{-1}~{\rm sr}^{-1}$



► IR (0.0012 - 1.2 eV)

Starlight

- HI regions: radiation is mainly emitted below 13.6 eV
- Photons in between 13.6 and 100 eV are strongly absorbed by H and He
- FUV radiation very important in the neutral ISM
 - Photoexcitation, photodissociation (particularly H₂)
 - Photoionization of heavy elements
 - Ejection of photoelectrons from dust grains

Starlight



- Habing (1968) early estimate of the intensity of UV radiation
- 4 x 10⁻¹⁴ erg cm⁻³ at 1000 Angstroms, i.e. E = 12.4 eV

$$\chi \equiv \frac{(\nu u_{\nu})_{1000 \text{ Å}}}{4 \times 10^{-14} \text{ erg cm}^{-3}}$$

Starlight



- Habing flux is good in between 10-13.6 eV
- If we integrate the Habing's UV spectrum in between 6 and 13.6

 $u_{\text{Hab}}(6 - 13.6 \,\text{eV}) = 5.29 \times 10^{-14} \,\text{erg}\,\text{cm}^{-3}$

$$G_0 \equiv \frac{u(6 - 13.6 \,\mathrm{eV})}{5.29 \times 10^{-14} \,\mathrm{erg} \,\mathrm{cm}^{-3}}$$

Standard Interstellar Radiation Field

- It is the standard UV field measured in the solar vicinity
- With energy < 13.6 eV



 $\mathcal{N}_{\rm ISRF} = 8.530 \times 10^{-5} \lambda^{-1} - 1.376 \times 10^{-1} \lambda^{-2} + 5.495 \times 10^{1} \lambda^{-3} \rm cm^{-2} \rm s^{-1} \rm Hz^{-1} \rm sr^{-1}$

$$I_E^{\text{Draine}} = \left(1.658 \times 10^6 \left(\frac{E}{\text{eV}} \right) - 2.152 \times 10^5 \left(\frac{E}{\text{eV}} \right)^2 + 6.919 \times 10^3 \left(\frac{E}{\text{eV}} \right)^3 \right)$$
(5.30)

In any astrophysical region where UV photons can penetrate the following processes can occur:

- 1. photoionization
- 2. photodissociation
- 3. heating of the medium
- 4. secondary ionizations

PHOTOPROCESSES

$$\begin{array}{rrrr} A^{+n} & + & h\nu \rightarrow A^{+(n+1)} + e^{-} \\ AB & + & h\nu \rightarrow AB^{+} + e^{-} \\ AB & + & h\nu \rightarrow A + B \end{array}$$

A molecule has to be excited above its dissociation energy $(D_e \text{ or } E_0)$.

| Bond | (KJ/mol) | Bond | (KJ/mol) | Bond | (KJ/mol) |
|------|----------|--------------|----------|--------------|----------|
| H-H | 436 | O-H | 463 | C=C | 614 |
| C-H | 413 | 0-0 | 146 | $C \equiv C$ | 839 |
| C-C | 348 | S-H | 339 | C=N | 615 |
| C-N | 293 | S-S | 266 | $C \equiv N$ | 891 |
| C-O | 358 | S=O | 523 | C=O | 799 |
| C-S | 259 | $S \equiv S$ | 418 | $C \equiv O$ | 1072 |
| N-H | 391 | | | N=N | 418 |
| N-N | 163 | | | $N \equiv N$ | 941 |
| N-O | 201 | | | O=O | 495 |

Table 1: Average bon enthalpies (1 KJ/mol = 120 K = 0.01 eV)

PHOTO-IONIZATION

| Ionization potential | | | | |
|----------------------|----------------------------|------|----------------------------|--|
| Atom | <i>E</i> ₀ (eV) | Atom | <i>E</i> ₀ (eV) | |
| HI | 13.6 | OI | 13.61 | |
| Hel | 24.6 | OII | 35.1 | |
| Hell | 54.4 | Sil | 8.1 | |
| CI | 11.2 | Sill | 16.3 | |
| CII | 24.4 | Fel | 7.9 | |



 $I_{H_2} = 15.44 \,\mathrm{eV}$ $I_{CO} = 14.01 \,\mathrm{eV}$ $I_{CH} = 10.64 \,\mathrm{eV}$

PHOTODISSOCIATION MECHANISMS

- Direct photodissociation (most of molecules e.g. H₂O)
- Pre-dissociation (CO, and N₂)
- Two steps dissociation (H₂)

energy

DIRECT PHOTODISSOCIATION



- a molecule absorbs a photon into an excited electronic state that is repulsive with respect to the nuclear coordinate.
- spontaneous emission back to the ground state is a slow process (A ~ 10⁹ s⁻¹)
- ► dissociation times of 10¹³ s⁻¹
- virtually all of the absorptions lead to dissociation of the molecule.

energy

PRE-DISSOCIATION



- initial absorption occurs into a bound excited electronic state
- non-radiatively interaction with a nearby repulsive electronic state
- ► e.g. spin-orbit coupling between states of different spin multiplicity (pure quantum mechanics → let's avoid details)

energy

TWO-STEPS PHOTODISSOCIATION



- if the excited bound states are not predissociated
- emission of photons into the continuum of a lower-lying repulsive state
- emission into the vibrational continuum of the ground electronic state

CROSS-SECTIONS: CONTINUUM VS LINE



- direct: H₂+, OH, H₂O pre-diss: CO 2-steps diss: H₂
- Continuum absorption Intensity $k_{\rm pd}^{\rm cont} = \int_{\lambda_{\rm H}}^{\lambda_{\rm d}} \sigma(\lambda) I(\lambda) d\lambda \ {\rm s}^{-1}$
- Line absorption for one line (one needs to sum over all the transitions)



oscillator strength

Population of the lower level I

Dissociation probability

| Bond Formation Processes | | Typical rate coefficient (cm ³ s ^{-1}) |
|---|--|--|
| Radiative association | $X+Y \to XY + h\nu$ | $10^{-17} - 10^{-14}$ |
| Associative detachment | $X^- + Y \rightarrow XY + e$ | $\sim 10^{-9}$ |
| Bond Destruction Processes | | |
| Photodissociation Dissociative recombination | $\begin{array}{l} XY+h\nu \rightarrow X+Y \\ XY^{+}+e \rightarrow X+Y \end{array}$ | $10^{-10} - 10^{-8} \text{ s}^{-1}$ $10^{-7} - 10^{-6}$ |
| Bond Rearrangement Processes | | |
| Ion–molecule exchange Charge–transfer Neutral–neutral | $\begin{array}{l} X^+ + YZ \rightarrow XY^+ + Z \\ X^+ + YZ \rightarrow X + YZ^+ \\ X + YZ \rightarrow XY + Z \end{array}$ | $10^{-9} - 10^{-8}$ 10^{-9} $10^{-11} - 10^{-9}$ |

UNITS AND USEFUL LINKS

Phidrates website: phidrates.space.swri.edu

Leiden database: <u>home.strw.leidenuniv.nl/~ewine/photo</u>

Verner database: https://www.pa.uky.edu/~verner/photo.html

$$k_{\rm pd} = [{\rm s}^{-1}]$$
$$E = [{\rm eV}]$$
$$I(\nu) = I(E) = \left[\frac{{\rm eV}}{{\rm cm}^2 \,{\rm s} \,{\rm Hz} \,{\rm sr}}\right]$$
$$\sigma(E) = [{\rm cm}^2]$$

ANALYTIC FITS

Verner database: https://www.pa.uky.edu/~verner/photo.html

$$\sigma_{pe}(E) = \sigma_0 F(y), \quad x = \frac{E}{E_0} - y_0, \quad y = x^2 + y_1^2,$$

where
$$F(y) = \left[(x - 1)^2 + y_w^2 \right] y^{0.5P - 5.5} \left(1 + \sqrt{\frac{y}{y_a}} \right)^{-P}$$

 $\sigma_0, E_0, y_0, y_1, y_w, y_a, P$ These parameters are given in the database

Units of sigma are given in $Mb = 10^{-18} \text{ cm}^2$

ANALYTIC FITS

Verner database: https://www.pa.uky.edu/~verner/photo.html

Photoionization cross sections

This site:

Atomic data for astrophysics. II. New analytic fits for photoionization cross sections of atoms and ions. D. A. Verner, G. J. Ferland, K. T. Korista, and D. G. Yakovlev, 1996, ApJ, 465, 487

Abstract. We present a complete set of analytic fits to the non-relativistic photoionization cross sections for the ground states of atoms and ions of elements from H through Si, and S, Ar, Ca, and Fe. Near the ionization thresholds, the fits are based on the Opacity Project theoretical cross sections interpolated and smoothed over resonances. At higher energies, the fits reproduce calculated Hartree-Dirac-Slater photoionization cross sections. <u>PostScript</u> 653.1 K, including figures and table.

- Table 1. Fit parameters for photoionization cross sections. <u>Description</u> (1.2 K), <u>ASCII</u> (17.8 K),
- Fortran subroutine which implements these fits and fits from Verner & Yakovlev (1995, A&AS, 109, 125). Includes all necessary parameters as BLOCK DATA.
- <u>Version 1</u> (January 3, 1996; 219.9 K).
 - Version 2 (March 25, 1996; 209.9 K).







- Can penetrate through thick clouds
- Are principal source of ionization in MCs
- Contribute to the heating of the gas (~10-20 eV per ionization)
- Produce gamma-rays and light element isotopes via spallation
- Control the coupling of B with the gas (electrical resistivity)



WHAT COSMIC RAYS ARE AND FROM WHERE THEY COME?

- Energetic charged particles (E > 100 eV)
- Vast majority are protons
- But also electrons, positrons and He-nuclei

COSMIC RAYS SPECTRUM



$$\phi \propto E^{-2.7}$$

- Power-law
- Below 1 GeV difficult to measure: lowenergy particles deflected by solar winds (modulation)
- Produced by SNRs for E < 10⁷ GeV
- E > 10⁷ GeV extragalactic (SMBHs, AGN)

LONG STORY

ALL STARTED IN 1785 WITH COULOMB

HOW DOES AN ELECTROSCOPE WORK?

- used to detect the presence of electric charge (or ionizing radiation)
- due to the Coulomb electrostatic force on it

Negative charge usually given to the electroscope









A BIT OF HISTORY OF COSMIC RAYS: IT STARTED WITH RADIOACTIVITY

- Some elements are able to spontaneously emit charged particles
- These can in turn cause discharge of the electroscopes
- The discharge rate was used to measure radioactivity
- > The dominant opinion was that all the high-energy radiation was coming from the soil

H. Becquerel & P. Curie & M. Curie



1896-1898



COMMON IDEA

- Ionization is generated by radioactive materials on the Earth's crust.
- Calculations showed that this radiation should have then decreased with height
- Electroscopes at that time where difficult to transport and not very sensitive

A BIT OF HISTORY OF COSMIC RAYS: FATHER WULF

- Theodor Wulf, German Jesuit Priest
- Built a accurate electroscope in 1908-1909
- Sensitivity of 1 V and transportable




FATHER WULF EXPERIMENT (1909-1910)

- Idea: measure radioactivity on top of Eiffel Tower (~300 m)
- He did it during an Easter holiday
- Expected reduction (if the radiation comes only from the soil) but results not conclusive



BALLOON EXPERIMENTS: ALBERT GOCKEL

- Idea: improving Wulf's measurements going higher
- > 1909: first balloon experiments (Berwitz and Gockel)
- Up to 4000 m, Gockel found that radiation did not decrease with altitude
 Gockel concluded that: penetrating is a set of the set of th



Gockel concluded that: penetrating radiation in the atmosphere independent on radioactive source

Die erhaltenen Resultate würden in Übereinstimmung stehen mit dem, was auch Pacini¹) aus seinen Beobachtungen auf dem Meere und Mache²) aus denen in Innsbruck folgert, daß nämlich ein nicht unbeträchtlicher Teil der durchdringenden Strahlung unabhängig ist von der direkten Wirkung der in den obersten Erdschichten enthaltenen aktiven Substanz. Befriedigend stimmen mit meinen Resultaten auch die von Wulf³) auf dem Eiffelturm erhaltenen überein, besonders

DOMENICO PACINI: FUNDAMENTAL CONTRIBUTION (NOT RECOGNIZED)

- Meteorologist in Rome, and professor in Bari
- June 1911: bringing an electroscope
 3 m deep in the sea
- Experiment repeated at the Lake of Bracciano





Fig. 4. The cacciatorpediniere "Fulmine", used by Pacini for his measurements of (courtesy of the Marina Militare Italiana).

DOMENICO PACINI: FUNDAMENTAL CONTRIBUTION (NOT RECOGNIZED)

- Published: "Penetrating radiation at the surface of and in water"
- > 20% reduction of the radioactivity

Coll'apparecchio alla superficie del mare si ebbe una perdita oraria di Volta:

- 13,2 12,2 12,1 12,6 12,5 13,5 12,1 12,7
- media 12,6 equivalente a ioni 11 per cm³ al 1". Coll'apparecchio immerso:

10,2 - 10,3 - 10,3 - 10,1 - 10,0 - 10,6 - 10,6.

media 10,3 equivalente a ioni 8,9 per cm³ al 1". La differenza fra questi due valori è di ioni 2,1.



PACINI CONCLUSIONS

"The explanation appears to be, due to the absorbing power of water and the minimum amount of radioactive substances in the sea, that radiation coming from the outside is absorbed when the apparatus is immersed. (Nuovo Cim., February 1912)"

Pacini concludes that "a sizable cause of ionization exists in the atmosphere, originating from penetrating radiation, independent of the direct action of radioactive substances in the ground."

Pacini's experiment marked the beginning of the underwater technique for CR studies

VICTOR HESS (1911-1912): NEW RESULTS

- Austrian scientist working in Wien and Graz
- Started using the Wulf's electroscope
- Expected reduction but results not conclusive
- 2 ascensions up to 1300 m in 1911





VICTOR HESS (1911-1912): FINAL FLIGHTS

- April-August 1912: 7 flights
- Reached 5200 m



VICTOR HESS (1911-1912): RESULTS

- After passing a minimum he found increase of ionization
- conclusions: radiation has extra-terrestrial origin





Gockel's results

PACINI-HESS: SCIENCE AT WORK

Exchange of letters between Pacini and Hess

Pacini to Hess, March 1920: ... [in your] paper entitled `The problem of penetrating radiation of extraterrestrial origin' ... the Italian measurement..., which take priority [for] the conclusions that you ... draw, are missing; and I am so sorry about this, because in my own publications I never forgot to mention and cite anyone...

Hess to Pacini, March 1920: ... My short paper ... is a report of a public conference, and therefore has no claim of completeness...

Pacini to Hess, April 1920: [...but] several authors are cited whereas I do not see any reference to my relevant measurements ... performed underwater in the sea and in the Bracciano Lake, that led me to the same conclusions that the balloon flights have later confirmed. ...

Hess to Pacini, May 1920: ... I am ready to acknowledge that certainly you had the priority in expressing ... in `Nuovo Cimento', February 1912, the statement that a non terrestrial radiation of 2 ions/cm³/s at sea level is present. However, the demonstration of the existence of a new source of penetrating radiation from above came from my balloon ascent to a height of 5000 meters on August 7 1912, in which I have discovered a huge increase in radiation above 3000 meters. ...



Hess and Eugster writes about the contribution of Pacini:

"The first who expressed some doubts as to the correctness of this view was D. Pacini, who, in 1910, from measurements over sea and on shores at Livorno concluded that part of the observed ionization might be due to sources other than the known radioactive substances."

Pacini, who died in 1934, was never nominated for the Nobel Prize. Hess was first nominated in 1931 and received the prize in 1936.

WERNER KOLHÖRSTER (1913-1914)

- Confirmed Hess's results
- Did a number of flights up to 9200 m







MILLIKAN AND CO

USA ARRIVED LATE BUT CLAIM THE DISCOVERY (WAR TIME)

MILLIKAN CONTRADICTION!

In the early 1920's the existence of hohenstrahlung was questioned.

Otis and Millikan Phys Rev 23 778 (1924)

62. The source of the penetrating radiation found in the earth's atmosphere. RUSSELL M. OTIS and R. A. MILLIKAN, California Institute of Technology.—Assuming, following Kolhorster's 1923 conclusions, a penetrating radiation of cosmic origin which produces 2 ions/cc/sec. at sea level and has an absorption coefficient per cm in water of 2.5×10^{-3} , we find that this radiation would produce 9 ions/cc/sec. on top of Pike's Peak (14100 ft). Inside our completely enclosing lead shield, 5 cm thick, it should produce 7.8 ions/cc/sec. The ionization in our apparatus contributed by the walls and the lead shield was found to be at least 7 ions/cc/sec., so that if there were no local radiation on Pike's Peak, the lowest obtainable value of the ionization in our shielded vessel should have been 14.8 ions/cc/sec. We observed as low as 11. We conclude, therefore, that there exists no such penetrating radiation as we have assumed. Second,

we found as a result of a snow-storm on the mountain as large a percentage change (about 10 per cent) in the ionization inside our 5 cm lead shield as outside it. We interpret this result also as meaning that the whole of the penetrating radiation is of local origin. How such quantities of radioactive material get into the upper air is as yet unknown.

1924: No penetrating radiation exists

1928: evidence claimed

Nature (suppl) 121, 19, (1928) Lecture at Leeds University

These facts, combined with the further observation made both before and at this time, that within the limits of our observational error the rays came in equally from all directions of the sky, and supplemented finally by the facts that the observed absorption coefficient and total cosmic ray ionisation at the altitude of Muir Lake predict satisfactorily the results obtained in the 15.5 km. balloon flight, all this constitutes pretty unambiguous 7 evidence that the high altitude rays do not originate in our atmosphere, very certainly not in the lower ninetenths of it, and justifies the designation ' cosmic rays,' the most descriptive and the most appropriate name yet suggested for that portion of the penetrating rays which come in from above. We shall discuss just how unambiguous the evidence is at this moment after having presented our new results.

MILLIKAN SURFING THE WAVE (1926)!



- Measurements of radiation depths in lake at high-altitudes
- Pacini's results reproduced
- He cloned the term "cosmic rays"
- This became a success of USA science
- Never mentioned Hess or Pacini pioneering works



HESS'S REACTION (1926)

Hess Phys Zeit 27 159 (1926) Not pleased with Millikan

Zu der eingangs zitierten Veröffentlichung von A. Millikan möchte ich vorerst bemerken, daß er die Geschichte der Entdeckung der Höhenstrahlung in einer Weise darstellt, die Mißverständnisse hervorrufen könnte³).

1) Physik. Zeitschr. 13, 1084, 1912; Wien, Ber. IIa, 121, 2001, 1912.

2) Physik. Zeitschr. 14, 610, 1913; Wien. Ber. IIa, 132, 1053, 1913.

3) Die neuerliche Feststellung der Existenz und der hohen Durchdringungskraft der Höhenstrahlung durch Millikan und seine Mitarbeiter wurde von amerikanischen naturwissenschaftlichen Zeitschriften wie "Science", "Scientific Monthly" zum Anlaß genommen, um für die Höhenstrahlung die Bezeichnung "Millikan-Strahlen" vorzuschlagen. Da es sich hier nur um die Bestätigung und Erweiterung der Ergebnisse der von Gockel, von mir und von Kolhörster 1910 bis 1913 ausgeführten Strahlungsmessungen im Ballon handelt, ist diese Benennung als irreführend und unberechtigt abzulehnen. Hess: Physik. Zeitschr. 27, 159, (1926)

As concerns the publication of Millikan, cited above, I would like to remark that he tells a story of the discovery of hohenstrahlung that could be easily misunderstood.

3) The recent determination by Millikan and his colleagues of the high penetrating power of hohenstrahlung has been an occasion for American scientific journals such as "Science" and "Scientific Monthly" to introduce the term "Millikan Rays". Millikan's work is only a confirmation and extension of the results obtained by Gockel, by myself, and by Kolhörster from 1910 to 1913 using balloon borne measurements of the rays. To refuse to acknowledge our work is an error and unjustified.

1936: The Nobel prize to Hess (& Anderson)

Hess was awarded the 1936 Nobel Prize in physics, shared with Anderson. Hess was nominated by Clay, Compton:

- The time has now arrived, it seems to me, when we can say that the socalled cosmic rays have their origin at remote distances from the Earth [...] and that the use of the rays has by now led to results of such importance that they may be considered a discovery of the first magnitude. [...] It is, I believe, correct to say that Hess was the first to establish the increase of the ionization observed in electroscopes with increasing altitude; and he was certainly the first to ascribe with confidence this increased ionization to radiation coming from outside the Earth



PHYSICS OF COSMIC RAYS DEVELOPED FURTHER

- Cosmic rays are important in particle physics, astrophysics, astrochemistry!
- Particularly in astrochemistry they drive ions-neutral reactions in MCs
- Low-energy CRs determine ionization of species in the ISM
- Unfortunately the CRIR is still an uncertain parameter

- Interstellar chemistry is driven by fast ion-molecule reactions
- Requires source of ionization
 - UV photons with E > 13.6 eV are absorbed by atomic H
 - Species with IP > 13.6 eV are primarily neutral
 - Species with IP < 13.6 eV are singly ionized</p>
- In diffuse and molecular clouds H and H₂ are ionized by CRs

INTERACTION WITH INTERSTELLAR GAS

- High energy (E > 280 MeV) cosmic ray protons create gamma-rays
- Lower energy cosmic rays ionize and heat the ISM

 Secondary electrons can cause additional ionization and heating, and can excite UV emissions from H and H2 (important in dense clouds where starlight is absent. The CRs spectrum is a power law spanning 12 dex in E and 30 dex in flux... but < 1 GeV poorly constrained</p>

- CRs ionization of H and H₂ is most efficient at keV to MeV energies
- Particle spectrum is measured above > 1GeV, but poorly constrained in energy range important for ionization
- Determination of ionization rate from molecular observations can add constraints to low-energy particle flux.

SOME IMPORTANT CONSIDERATION (SEE INDRIOLO+2013)

- Different ways to define CRIR
- > Primary ionization rate (ionization rate of H due only to protons and heavy nuclei) $\zeta_{\rm p}$
- > Total ionization rate per H (including further ionizations per secondary e) $\zeta_{\rm H}$
- Total ionization rate per H_2 ζ_{H_2}

$$\zeta_{\rm H} = 1.5 \zeta_{\rm p}$$
$$\zeta_{\rm H_2} = 2.3 \zeta_{\rm p}$$

COSMIC RAYS IN ASTROCHEMISTRY



EXAMPLES: DEUTERATION CHEMISTRY



SO FAR IN ASTROCHEMICAL MODELS

- We need the cosmic ray ionization rate (CRIR)
- Fundamental for the interpretation of observations
- Important in non-ideal MHD
- Normally a constant CRIR is assumed (valid only in local ISM)

$$\zeta_{CR} \sim 10^{-17} [\mathrm{s}^{-1}]$$

PROPERLY MODELING THE COSMIC RAYS

- The idea is that we could consider variation and effect of column density on the CRIR
- And the magnetic field coupling
- But unfortunately this is pretty expensive, it requires propagation of CRs which is similar to RT
- See Padovani&Galli 2011,2013, and Padovani+2009



MEASUREMENTS

COSMIC-RAYS MEASUREMENTS (NEUFELD'S TALK)

| Table 1 Classification of Interstellar Cloud Types | | | | | | | | | |
|---|--|--------------------------------------|--|------------------|--|--|--|--|--|
| | Diffuse Atomic | Diffuse Molecular | Translucent | Dense Molecular | | | | | |
| Defining Characteristic | $f^{n}_{H_{2}} < 0.1$ | $f^n_{H_2} > 0.1 f^n_{C^+} > 0.5$ | $f^{n}{}_{C^{+}} < 0.5 \ f^{n}{}_{CO} < 0.9$ | $f^n_{CO} > 0.9$ | | | | | |
| A _V (min.) | 0 | ~0.2 | ~1-2 | ~5-10 | | | | | |
| Typ. $n_{\rm H}$ (cm ⁻³) | 10–100 | 100-500 | 500-5000? | >10 ⁴ | | | | | |
| Тур. Т (К) | 30–100 | 30–100 | 15-50? | 10-50 | | | | | |
| Observational | UV/Vis | UV/Vis IR abs | Vis (UV?) IR abs | IR abs | | | | | |
| Techniques | H I 21-cm | mm abs | mm abs/em | mm em | | | | | |
| From OH ⁺ , H ₂ O ⁺ and ArH ⁺ $\zeta_p(H) = 2.2 \pm 0.3 \times 10^{-16} \text{ s}^{-1}$ From H and C RRL $\zeta_p(H) = 8 \times 10^{-17} \text{ s}^{-1}$ | | | | | | | | | |
| | From H_3^+ $\zeta_p(H) = 2.3$ (with margin | s ⁻¹ From HC & van Dis | ' O⁺ (van der Tak hoeck 2000) | | | | | | |



- Formation
 - $CR + H_2 \rightarrow H_2^+ + e^- + CR'$
 - $H_2^+ + H_2 \rightarrow H_3^+ + H$
- Destruction
 - $H_3^+ + e^- \rightarrow H + H + H$

- Dense Clouds
 - $H_3^+ + CO \rightarrow HCO^+ + H_2$
 - $H_3^+ + O \rightarrow OH^+ + H_2$
- Atomic Clouds
 - $H_2^+ + H \rightarrow H_2 + H^+$
 - $H_2^+ + e^- \rightarrow H + H$

CR + H₂

$$\zeta_2 n(H_2) = k(H_3^+ | e^-) n(H_3^+) n_e$$

$$\zeta_2 = k(\mathbf{H}_3^+|e^-) x_e n_{\mathbf{H}} \frac{N(\mathbf{H}_3^+)}{N(\mathbf{H}_2)}$$

- $k(H_3^+|e^-)$ measured in laboratory (2×10⁻⁷ cm³ s⁻¹)
- x_e approximated by $x(C^+)$ (1.5×10⁻⁴)
- $n_{\rm H}$ estimated from molecular observations (100 cm⁻³)
- *N*(H₂) measured or estimated (10²⁰-10²¹ cm⁻²)
- *N*(H₃⁺) determined from NIR observations

2
$$\zeta L = \left[\frac{\sum k_X n(X)}{n(H_2)}\right] N(H_3^+)$$

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| G034.3+00.15 | | | | | | | | | |
|----------------------------|---|---|--|----------------------------|--|--|--|--|--|
| v _{LSR} (km/s) | N(OH ⁺) (10 ¹³ cm ⁻²) | $N(H_2O^+)$ (10 ¹³ cm ⁻²) | N(H) (10 ²¹ cm ⁻²) | <i>f</i> (H ₂) | ζ _H (10 ⁻¹⁶ s ⁻¹) | | | | |
| [-12, 7] | 2.5 | 0.26 | 1.3 | 0.03 | 2.1 | | | | |
| [7, 18] | 3.0 | 0.67 | 2.1 | 0.06 | 2.8 | | | | |
| [18, 36] | 2.7 | 0.31 | >3.6 | 0.03 | <0.9 | | | | |
| [36, 44] | 1.7 | 0.21 | 2.4 | 0.03 | 0.9 | | | | |
| [44, 52] | 3.7 | 0.93 | 3.6 | 0.07 | 2.2 | | | | |
| [52, 70] | 4.2 | 1.2 | >5.2 | 0.08 | <2.0 | | | | |



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SUMMARY OF OBSERVATIONS (PADOVANI+)


DENSE CORES ESTIMATES ARE STRONGLY MODEL DEPENDENT

| | Diffuse Atomic | Diffuse Molecular | Translucent | Dense Molecular |
|--------------------------------------|-----------------------|---|--|------------------|
| Defining Characteristic | $f^{n}_{H_{2}} < 0.1$ | $f^n{}_{H_2} > 0.1 \ f^n{}_{C^+} > 0.5$ | $f^{n}_{C^{+}} < 0.5 f^{n}_{CO} < 0.9$ | $f^n_{CO} > 0.9$ |
| A _V (min.) | 0 | ~0.2 | ~1-2 | ~5–10 |
| Typ. $n_{\rm H}$ (cm ⁻³) | 10–100 | 100–500 | 500-5000? | >10 ⁴ |
| Тур. Т (К) | 30–100 | 30–100 | 15-50? | 10–50 |
| Observational | UV/Vis | UV/Vis IR abs | Vis (UV?) IR abs | IR abs |
| Techniques | H I 21-cm | mm abs | mm abs/em | mm em |

Table 1 Classification of Interstellar Cloud Types

Van der Tak & Van Dischoeck 2000: estimates based on models (0d) to match HCO⁺ obs.

Obtaining values of around 1.1 x 10⁻¹⁷ s⁻¹



Infinite amount of reactions neglected

Estimating CRIR from molecular observations:

$$\zeta_2 = \alpha \ k_{\rm CO}^{\rm H_3^+} \times \frac{X_{\rm CO}}{L} \times \frac{N(\rm oH_2D^+)}{3R_{\rm D}}$$

It is simply based on the idea that H_{3^+} is converted into its isotopologues in dense regions via deuterium fractionation



Analytical equation, α calibrated on simulations

Bovino+2020

ASTROCHEMISTRY

Obtained from deuterated species of H_3^+ (H_2D^+) with ALMA



Sabatini, Bovino, Redaelli, ApJ Letters 2023

76



Sabatini, Bovino, Redaelli, ApJ Letters 2023

SUMMARY

- Gas-phase chemistry is driven by fast ion-neutral reactions
- This requires a mechanism of ionization
- UV radiation (diffuse gas) and cosmic-rays (dense gas) provide with the necessary ions
- Both radiation and cosmic-rays also heat the gas
- Cosmic-rays are fundamental for the understanding of observational signatures
- Some processes generate secondary electrons which can induce further ionization
- CRIR still uncertain and inaccurate in models!