

Gas-phase Interstellar Chemistry & Its Reactions: Review and Particular Problems



ERIC HERBST

DEPARTMENTS OF PHYSICS,
CHEMISTRY AND ASTRONOMY
THE OHIO STATE UNIVERSITY

Gaseous interstellar and circumstellar molecules (149)

N=2		N=3		N=4	N = 5	N = 6	N = 7	N = 8	N = 9	N = 10
H ₂	AlCl	CH ₂	C ₂ S	NH ₃	CH ₄	CH ₃ OH	CH ₃ NH ₂	HCOOCH ₃	(CH ₃) ₂ O	(CH ₃) ₂ CO
CH	PN	H ₂ S	OCS	H ₂ CO	SiH ₄	CH ₃ SH	CH ₃ CCH	CH ₃ C ₂ CN	C ₂ H ₅ OH	CH ₃ C ₄ CN
NH	SiN	NH ₂	MgCN	H ₂ CS	CH ₂ NH	C ₂ H ₄	CH ₃ CHO	HC ₆ H	C ₂ H ₅ CN	CH ₃ CH ₂ CHO
OH	SiO	H ₂ O	MgNC	H ₂ CN	C ₅	H ₂ C ₄	c-CH ₂ OCH ₂	C ₇ H	CH ₃ C ₄ H	(CH ₂ OH) ₂
O ₂ (?)	SiS	HNO	NaCN	<i>l</i> -C ₃ H	<i>l</i> -C ₃ H ₂	CH ₃ CN	CH ₂ CHCN	HOCH ₂ CHO	C ₈ H	
HF	PO	C ₂ H	SO ₂	c-C ₃ H	c-C ₃ H ₂	CH ₃ NC	HC ₄ CN	CH ₃ COOH	HC ₆ CN	
C ₂	SH	HCN	N ₂ O	HCCH	H ₂ CCN	NH ₂ CHO	C ₆ H	H ₂ CCCHCN	CH ₃ CONH ₂	N = 11
CN	AlF	HNC	SiCN	HNCO	H ₂ NCN	H ₂ CCHO	H ₂ CCHOH	H ₂ C ₆	CH ₂ CHCH ₃	HC ₈ CN
CO	FeO	HCO	SiNC	HNCS	CH ₂ CO	C ₅ H		CH ₂ CHCHO		CH ₃ C ₆ H
CS	SiC	c-SiC ₂		HCCN	HCOOH	C ₅ N		C ₂ H ₆		
CP		MgCN		C ₂ CN	C ₄ H	HC ₄ N				
NO		MgNC		C ₃ O	HC ₂ CN	C ₅ S(?)				N = 12
NS		AiNC		C ₃ S	HC ₂ NC	HC ₄ H				C ₆ H ₆
SO		HCP	H ₃ ⁺	c-SiC ₃	C ₄ Si	CH ₂ CNH				
HCl	CH ⁺	C ₃	HCO ⁺	C ₃ N ⁻	HNCCC	HC ₂ CHO				
NaCl	CO ⁺	C ₂ O	HOC ⁺	H ₃ O ⁺		c-C ₃ H ₂ O				N = 13
KCl	SO ⁺	CO ₂	N ₂ H ⁺	HCNH ⁺	H ₂ COH ⁺					HC ₁₀ CN
N ₂ (?)	CF ⁺		HCS ⁺	HOCO ⁺	C ₄ H ⁻	HC ₃ NH ⁺	C ₆ H ⁻		C ₈ H ⁻	

Constraints

- Sources range from 10 K to >300 K including photon-dominated and shocked regions. **At lower temperatures, exothermic reactions without activation energy are dominant.**
- Binary collisions only except in protoplanetary disks
- Hydrogen dominant element; H₂ dominant molecule
- Ionization generally from cosmic ray flux, occasionally augmented by X-rays.
- Clouds are weak plasmas.

Reaction Classes: Gas-Phase

- Cosmic-ray processes
- Photoprocesses (external and internal)
- Ion-molecule reactions
- Dissociative recombination reactions
- Radical-neutral reactions
- Radiative association and *radiative attachment reactions*
- *Dissociative attachment reactions*
- *Associative detachment reactions*
- *Mutual neutralization reactions*

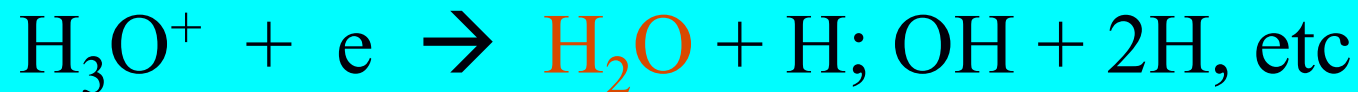
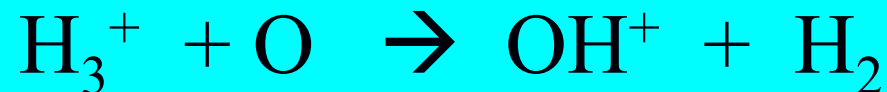
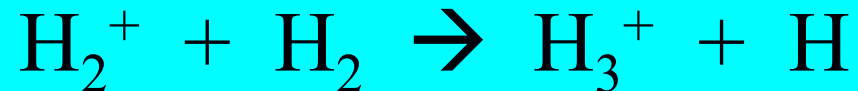


A Flavor of the Chemistry of Cold Dense Sources

FORMATION OF GASEOUS WATER



Elemental abundances: C,O,N = 10^{-4} wrt H



+ longer pathways to unsaturated organic species.....

Formation of CH_n and O₂



Warm/Hot Sources

- Evaporation of ice mantles leading to saturated gas-phase species such as methanol.
- High temperatures leading to roles for exothermic reactions with barriers and even endothermic reactions.

Assorted Chemical Complications

- Value of cosmic ray ionization rate ζ uncertain.
- Many reaction rates not measured or calculated in detail, so must be estimated. (Negative ions particularly poorly studied.)
- Non-thermal effects can be important (shock waves, ortho/para effects)
- (also astronomical problems concerning physical conditions and elements)



Classes of Reactions: Some Salient Problems

Ion-Molecule Reactions I

Hydrocarbon-ion H₂ reactions:



tend not to proceed past very unsaturated ions for $n > 2$. Past work for $n > 6$ mainly old ICR work that claims that only C_nH_2^+ can be formed.

Ion-Molecule Reactions II

- **Problems with ion-polar neutral T dependence:**
 - a) few low-temperature studies
 - b) no simple exact formula in 10-300 K range (not a central force problem)

Best simple pictures: $k = k_L \{ \alpha + \beta(T/300)^{-1/2} \}$
(trajectory-scaling and locked-dipole approaches)

- c) major networks ignore first term
- d) Rate06 (polar version) starts from measured or Langevin 300 K value while osu.2007 uses theoretical values.

Ion-Molecule Reactions III

- Extreme Discrepancy (300 K):

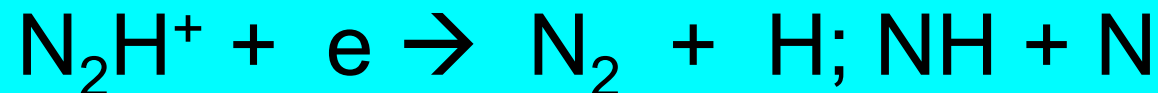


$$k (\text{osu.2007}) = 7.5 \cdot 10^{-9} (T/300)^{-1/2} \text{ cc/s}$$

$$k (\text{Rate06}) = 1.3 \cdot 10^{-9} (T/300)^{-1/2} \text{ cc/s}$$

Dissociative Recombination

- Storage-ring and bench-top experiments can disagree on product branching fractions
- New bench-top work from Adams group differs strongly from storage-ring results for



Neutral-Neutral Reactions

Unlike ion-molecule reactions, hard to generalize from detailed studies since reactions are strongly affected by:

a) Activation energy barriers

b) Number of potential surfaces that correlate with ground state reactants

but hear Ian Smith's talk....

Radiative Association



Most measurements are at high density, where three-body association dominates. Mechanism not applicable to low density. Low-density trap data uncommon.

Statistical theories can be used independently or can be used to convert experimental ternary values to radiative values.

Results: large inverse temperature dependence and high rate coefficients for large bond energy and large size of reactants. *Calculated rate coefficients range from collisional value to many orders of magnitude lower. **Order-of-magnitude accuracy all that can be expected.***

Two important reactions: $C + H_2$; $C + C_3$

Radiative Association II

- One problematic reaction:



theory: $k = 5.5 \cdot 10^{-12} (\text{T}/300)^{-1.7} \text{ cc/s}$

experiment: $k = 2.0 \cdot 10^{-12} \text{ cc/s}$

Herbst 1985; Luca et al. 2002

Radiative Association III

Hydrocarbon-ion H₂ reactions:



Need to be investigated more thoroughly *at low temperatures and densities*. For example, the existence of propylene (C₃H₆) might suggest that the C₃H₅⁺ + H₂ reaction occurs.

Negative Ion Formation

- Radiative attachment (Herbst 1981)



- Dissociative attachment (Petrie & Herbst 1997)



(normally endothermic unless neutral an unusual species such as a carbene)

Few experimental studies.....

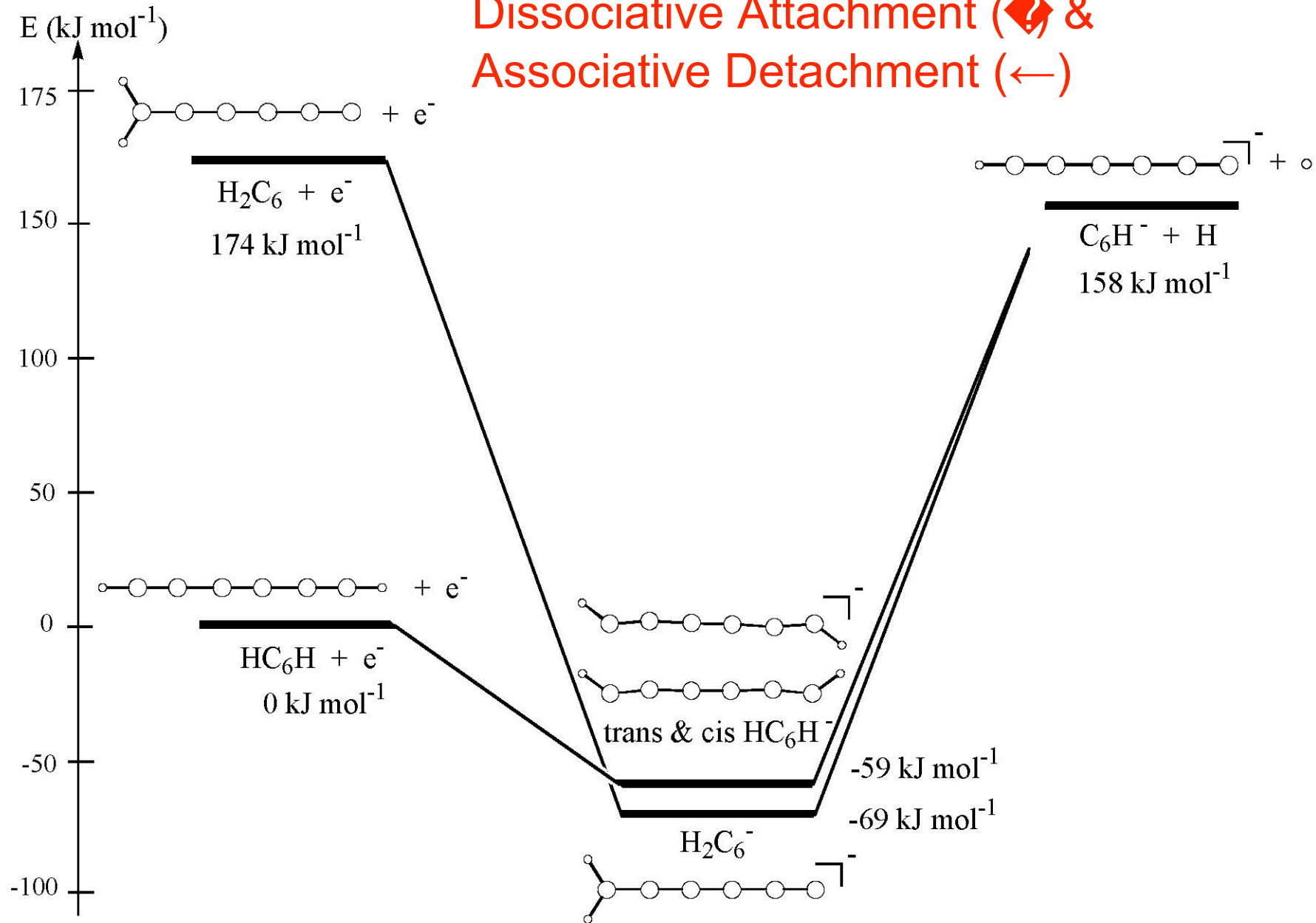
Destruction occurs by associative detachment, mutual neutralization, and photodetachment as well as ion-molecule reactions.....

Some calculated (phase-space) 300 K radiative attachment rate coefficients

SYSTEM	EA (eV)	k(cm ³ s ⁻¹)
C ₂ H + e	2.956	2.0(-15)
C ₃ N + e	4.37	2.6(-10)
C ₄ H + e	3.558	1.1(-08) XXXX
C ₆ H + e	3.809	6.2(-08)

More detailed approach may involve so-called dipole bound states. Statistical approach yields $T^{-1/2}$ rate coefficient dependence.

Dissociative Attachment (↙) &
 Associative Detachment (↔)



Herbst & Osamura

Mutual Neutralization



Adams et al. (2003) say that at 300 K:

$k = 2\text{-}6 \times 10^{(-8)}$ cc/s for molecular ions based on some experiments

Lepp & Dalgarno (1988) estimated $k = 7.3 \times 10^{(-8)}$ cc/s

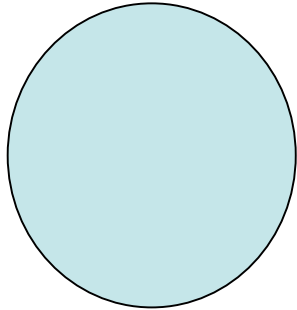
Wakelam & Herbst (2008) estimated $k = 1.2 \times 10^{(-8)}$ cc/s

The estimated T dependence is $T^{-1/2}$

SUMMARY

- In addition to more prosaic problems involving the uncertainty in our knowledge of rate coefficients, our ignorance of selected types of reactions can range from moderate to great. Further theoretical work and/or experimental studies may be needed to increase our understanding.

Cold Core



$T = 10 \text{ K}$

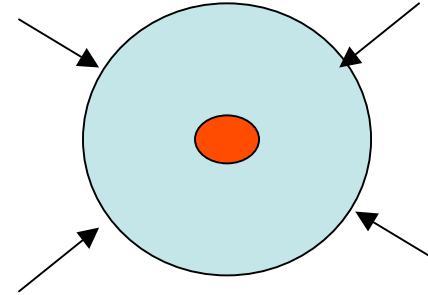
$n = 10^4 \text{ cm}^{-3}$

Low-mass Star Formation

Isothermal collapse



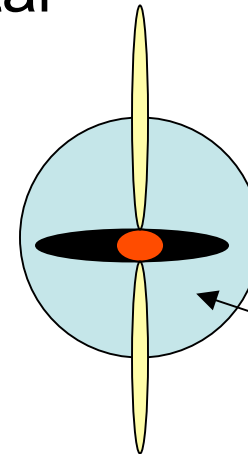
Pre-stellar Core



adiabatic



Protostar

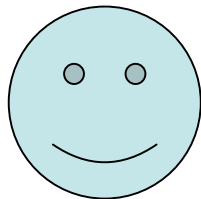


Cold envelope

hot core

100 K

Star + Disk



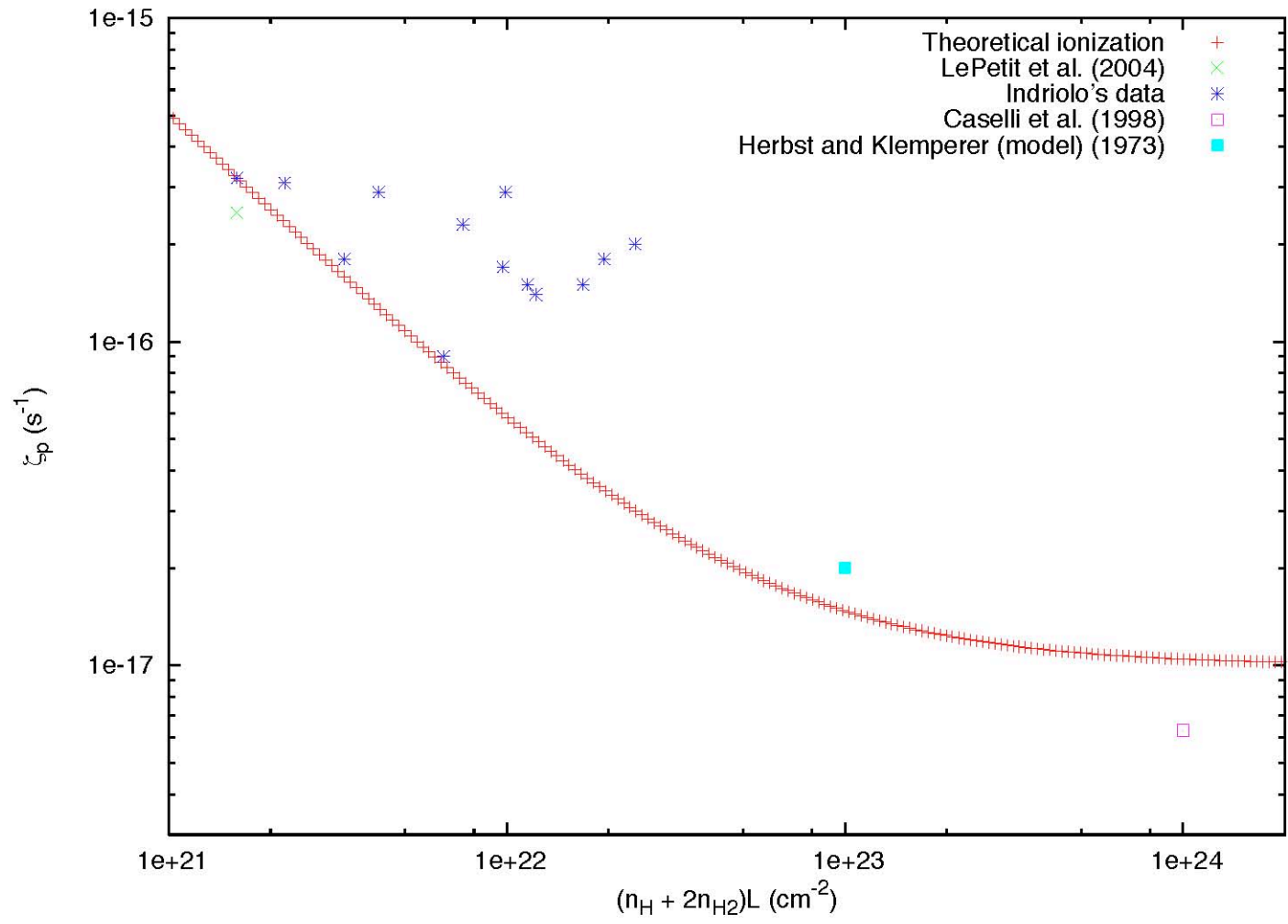
Molecules probes of physical conditions and history.

What is the value of ζ ?

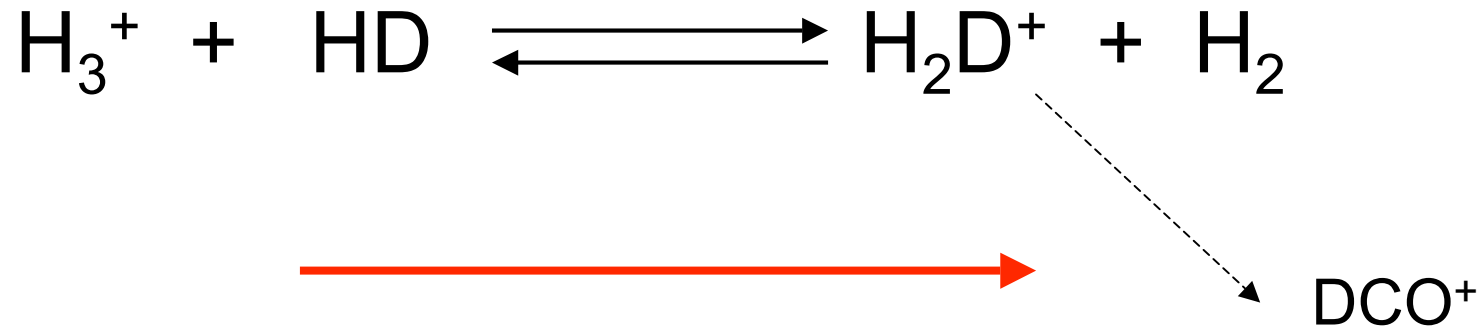
1. Obtained from solar-system measurements of cosmic ray flux, which may not be universal.
2. Depends on column of gas that cosmic rays travel through. (Rimmer & Herbst, in prep.)
3. Most commonly used value for dense clouds dates back to model fits from 1970's and 1980's.
4. New observational evidence that ζ larger by 1-2 orders of magnitude in diffuse clouds (agrees with 2.)

$$d[\text{H}_2]/dt = -\zeta[\text{H}_2]$$

1



Deuterium Fractionation



(1) $\text{D}/\text{H} = 10^{-5}$ BUT $\text{H}_2\text{D}^+/\text{H}_3^+ = 0.1$ in cold cores

(2) Fractionation even stronger in the centers of pre-stellar cores where chemical equilibrium is reached and D_3^+ dominates

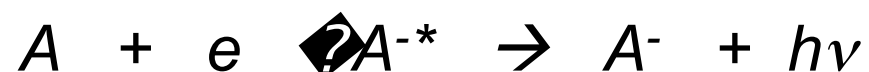
Deuterium Fractionation II

- But analysis depends on use of 230 K for exothermicity, implying that reactants and products are in lowest possible ortho/para/rotational states. Significant excitation can change results; e.g., for example, the $J=1$ (ortho) state of H_2 lies 170 K above $J=0$.

Negative Ions in Clouds

- Herbst (1981) considered the possible abundance of anions in cold regions of the ISM based on radiative attachment mechanism:
- $A + e \rightarrow A^- + h\nu$
- and estimated their maximum abundance to be 1% of the neutral counterparts in cold sources for species with large electron affinities and at least 4-5 atoms. Phase space theory used.

Radiative Attachment – Phase-Space Theory



$$k_{ra} = k_1 k_r / (k_{-1} + k_r)$$

Herbst 1981

k_1 : s-wave channel in partial wave expansion with unit probability

k_{-1} : microscopic reversibility

k_r : vibrational emission averaged over normal mode states

ANIONS AT LAST

- Three in family C_nH^- and most recently C_3N^-
- TMC-1, a cold interstellar core: $n=6, 8$ (*McCarthy et al.*; *Bruenken et al.*)
- (1-5% level)
- L1527, a lukewarm protostar: $n=4, 6$ (*Sakai et al.*)
- IRC+10216, an extended circumstellar envelope: C_nH^- ; $n = 4, 6, 8$ (*McCarthy et al.*; *Cernicharo et al.*; *Remijan et al.*; *Kasai et al.*) and, most recently, C_3N^- (*Thaddeus et al.*)

Dissociative Recombination II

- At what size if any does dissociative recombination go over to radiative recombination; e. g.,



Simple RRKM treatment by Bettens & Herbst (1995) suggests that $n=20$ is the dividing line.

Photodetachment

- Negative ions can undergo photodetachment for photons with energy ε equal to or greater than the electron affinity.
- Assumption:
$$\sigma = \sigma_0 [1 - EA/\varepsilon]^{0.5}$$
 where $\sigma_0 = 1.0(-17) \text{ cm}^2$
- Absolute measurements difficult and dependent on FC factors.