Destruction of interstellar COMs by collisions with He^+: the case of dimethyl ether and methylformate

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KIDA
KINETIC DATABASE FOR ASTROCHEMISTRY

Astrochemical conference KIDA2017
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Outline

- Introduction
  - Ionic astrochemistry
  - relevance for DME / MF abundances
- Experimental methodology
  - Guided ion beam Mass Spectrometry
- Results
  - Experimental absolute cross sections *vs* collision energy
  - theoretical modelling
  - estimates of k(T)
- Conclusions

Ionic astrochemistry

Chemistry of the Early Universe

Diffuse and dark clouds

Protostars

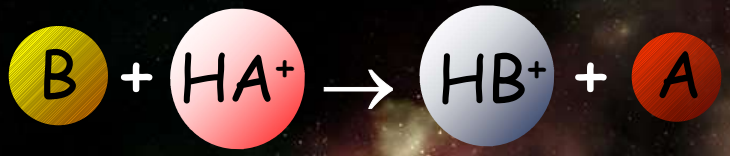
Planetary ionospheres

....

Outcomes of (cat)ion-molecule collisions

Charge Transfer

Proton transfer

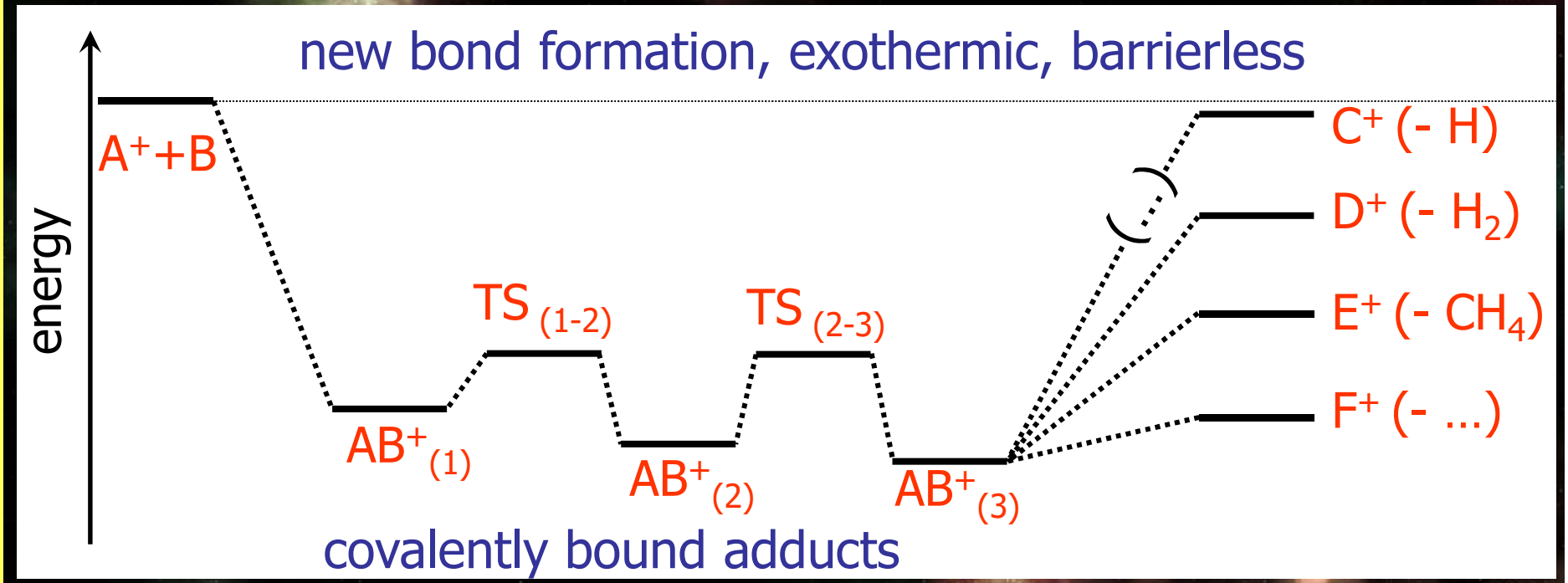


Bond Forming

Our interest / past work

Bond Forming
(C-C, C-N)

Growth of complex molecules

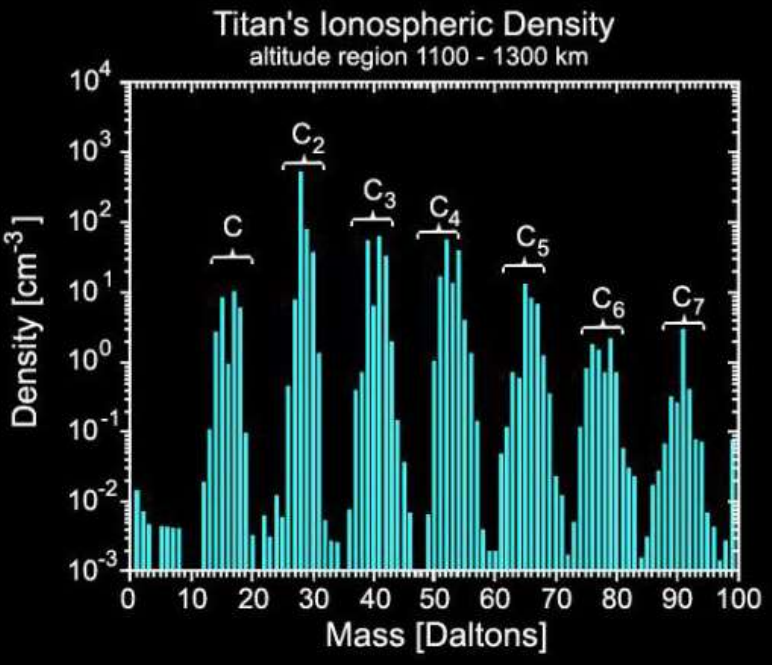


Our interest / past work

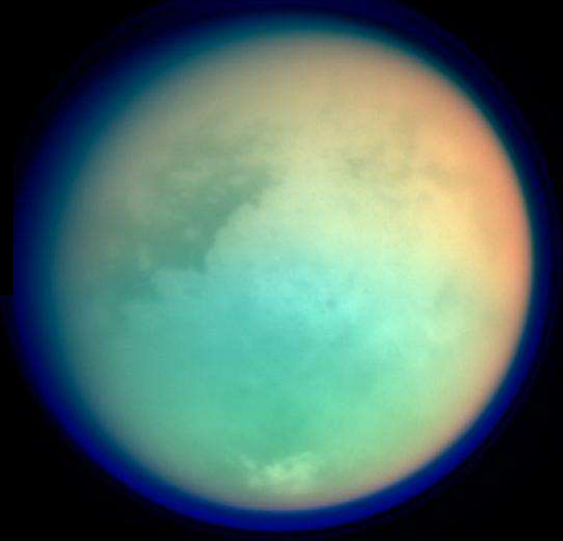
Bond Forming
(C-C, C-N)

Growth of complex molecules

Modelling the chemistry of Titan's upper atmosphere, as probed by the



Cassini-Huygens mission



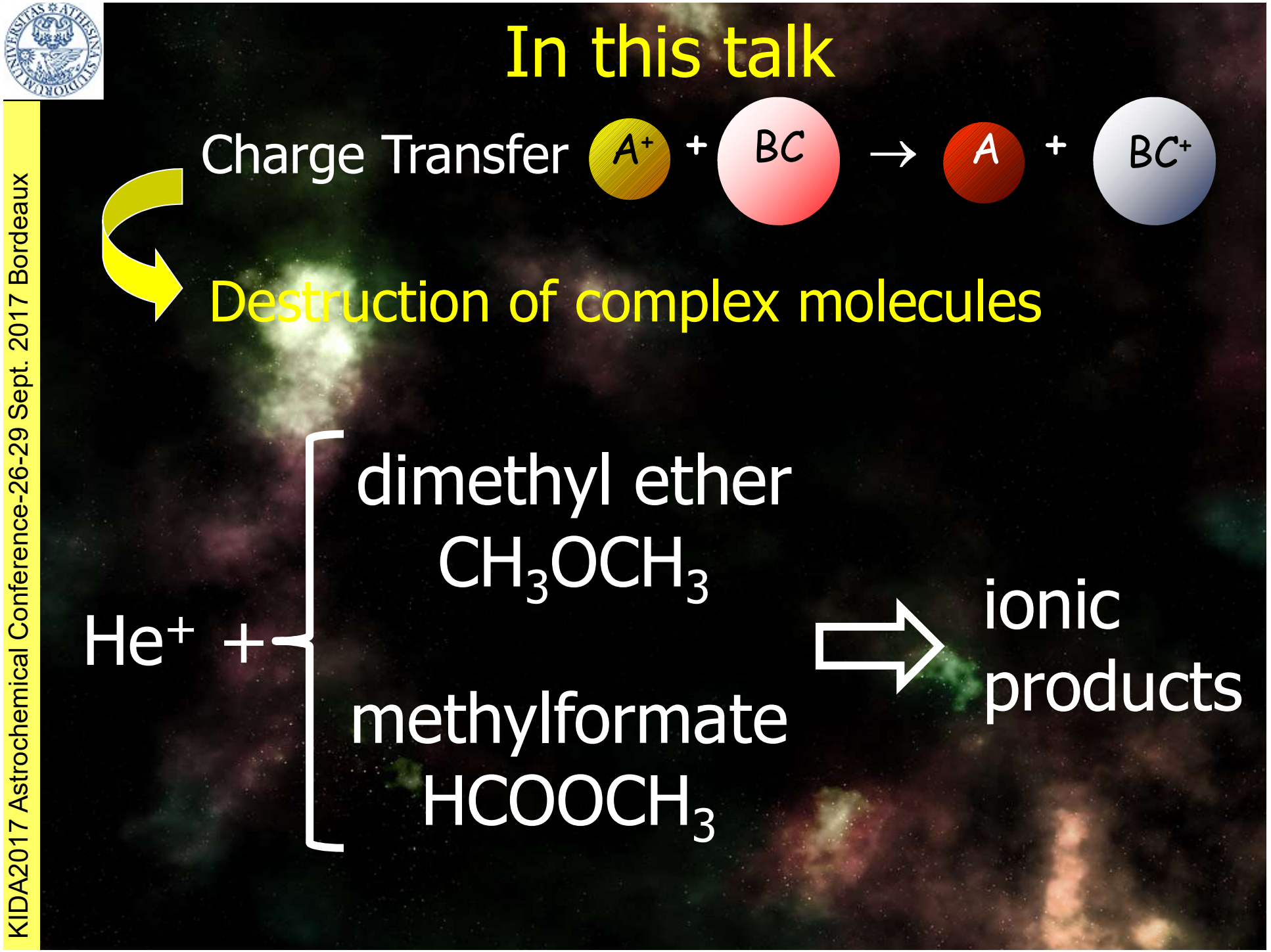
Studied systems

- $CH_3^+ + CH_3CCCH_3$ A. Cernuto et al. JCP 2017, 147, 154302
- $CH_2CN^+ + CH_4/C_2H_2$ C_2H_6 P. Fathi et al. Mol.Astr. 2016; P. Fathi et al. IJMS 2016
- $CH_2CNH^{+\bullet}/CH_3CN^{+\bullet} + C_2H_4$ M. Polasek et al. JPCA 2016
- $C_{10}H_7^+/C_{12}H_9^+ + C_6H_6$ J. Aysina et al. JCP 2013; D. Ascenzi et al. JCP 2010

Also in collaboration with:

SOLEIL SYNCHROTRON

Ch. Alcaraz CERISES set-up

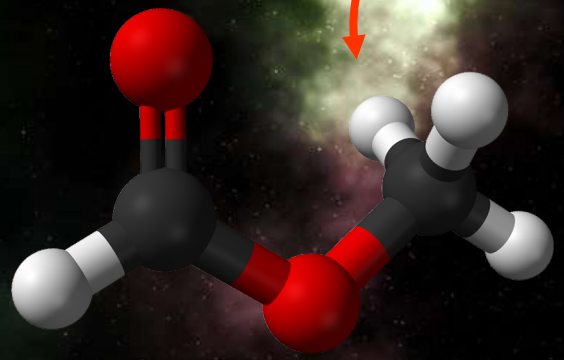

In this talk
Charge Transfer
A+ + BC → A + BC+
Destruction of complex molecules
He+ +
dimethyl ether
CH3OCH3
methylformate
HCOOCH3
ionic
products

DME and MF: ubiquitous COMs

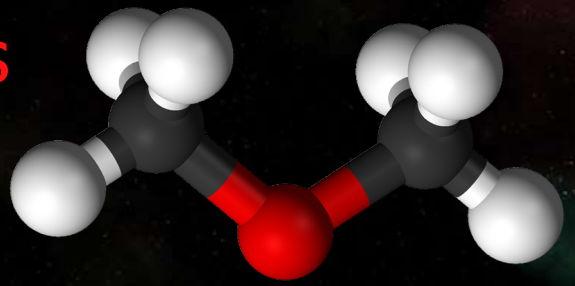
List of interstellar molecules (NASA Goddard, July 2014)

Number of atoms, *N*

N = 2	*N* = 3	*N* = 4	*N* = 5	*N* = 6	*N* = 7	*N* = 8	*N* = 9	*N* = 10	*N* = 11	*N* = 12	*N* = 13
H_2	H_2O	NH_3	CH_4	CH_3OH	$CH_2CH(OH)$	CH_3COOH	$(CH_3)_2O$	$(CH_2)_2CO$	$H(CC)_4CN$	C_6H_6	$H(CC)_5CN$
CO	H_2S	H_2CO(?)	SiH_4	CH_3SH	*c* - C_3H_2O	$HC(O)OCH_3$	CH_3CH_2CN	$HOCH_2CH_2OH$	CH_3C_6H	$CH_3CH_2CH_2CN$	
CSi	HCN	H_2CS	CH_2NH	C_2H_4	$HC(O)CH_3$	$HOCH_2C(O)H$	CH_3CH_2OH	$H_3CCH_2C(O)H$	$HC(O)OCH_2CH_3$		
CP	HNC	C_2H_2	NH_2CN	$H(CC)_2H$	H_3C-CC-H	H_3C-CC-CN	CH_3C_4H	$CH_3(CC)_2CN$			
CS	CO_2	HNCO	CH_2CO	CH_3CN	CH_3NH_2	H_2C_6	$H(CC)_3CN$				



Potential precursors of sugars and biopolymers



- warm and inner regions of protostars (hot cores and corinos) $T \geq 30K$
- galactic center clouds
- dark cold pre-stellar cores $T \leq 10K$

DME & MF: formation mechanisms

GAS PHASE
reactions in the gas phase, often started by injection of hydrogenated molecules formed on grains (H_2CO, CH_3OH)

In vogue 1991-2003/5

Millar, Herbst, Charnley, ApJ 1991; Charnley, Tielens, Millar ApJ 1992; Caselli, Hasegawa, Herbst ApJ 1993

GRAIN SURFACE warm-up scenario
Radical recombination reactions on the grain surface (T≥30K) + ejection in gas phase during warm-up phase (T> 100K)

In vogue until 2012/13

Garrod&Herbst A&A 2006; Garrod, Weaver, Herbst ApJ 2008; Chang&Herbst ApJ 2014; Taquet, Ceccarelli, Kahane A&A 2012

GAS - GRAIN MODEL non thermal desorption
Ion-neutral + radical – radical gas phase reacts with precursors formed on grains and ejected by non-thermal processes (reactive desorption…)

The latest fashion

Vasyunin, Caselli, Dulieu, Jimenez-Serra ApJ 2017; Chang&Herbst ApJ 2016; Balucani, Ceccarelli, Taquet MNRAS 2015; Reboussin, Wakelam, Guilloteau, Hersant MNRAS 2014; Vasyunin, Herbst ApJ 2013

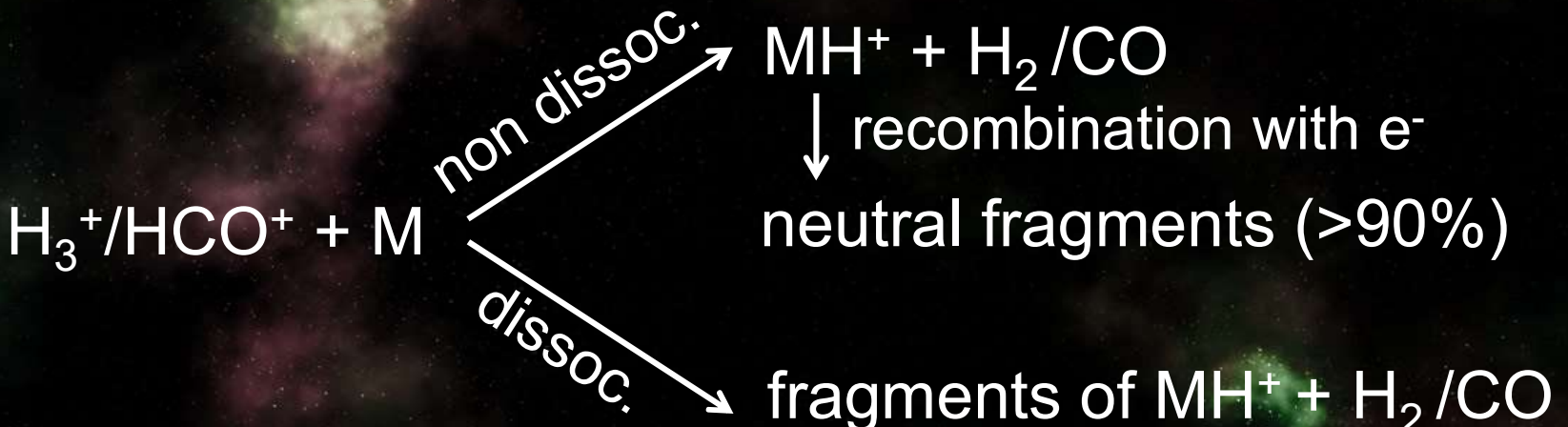
new gas phase reactions + improved RD + reactions and diffusion at the surface

credits to Cecilia Ceccarelli

DME & MF: destruction processes

- UV photons
- Cosmic rays
- Reactions with IONS (H^+ - He^+ - H_3^+ - HCO^+)

H_3^+ / HCO^+ react by **proton transfer (dissociative)**



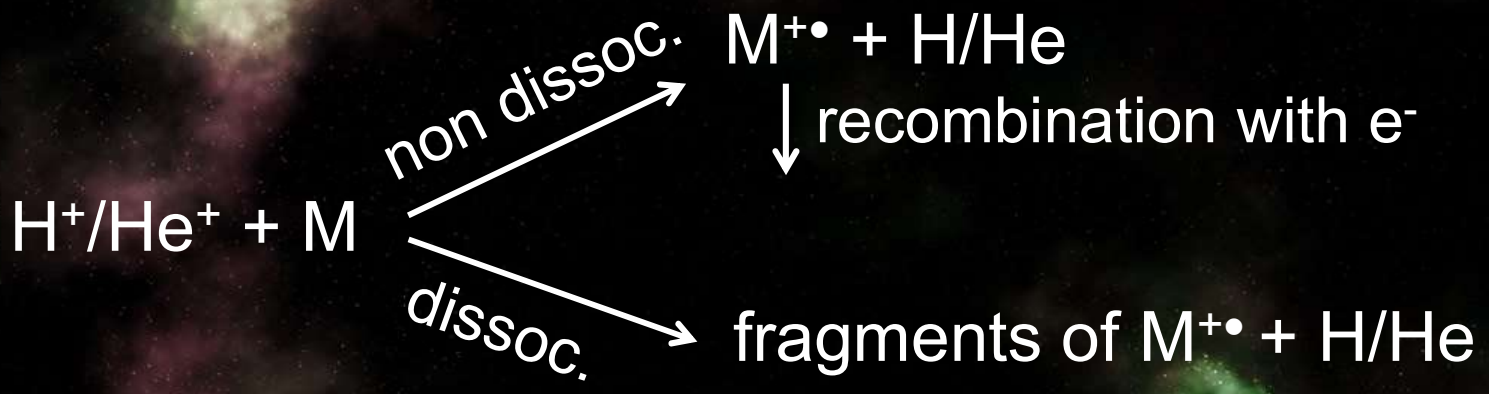
Fragmentation is more pronounced with H_3^+ than HCO^+ (due to higher exotermicity)

Lee, Drucker, Adams IJMS 1992; Hamberg A&A 2010; Lawson JPC-A 2012; Tanner IJMS 1979

DME & MF: destruction processes

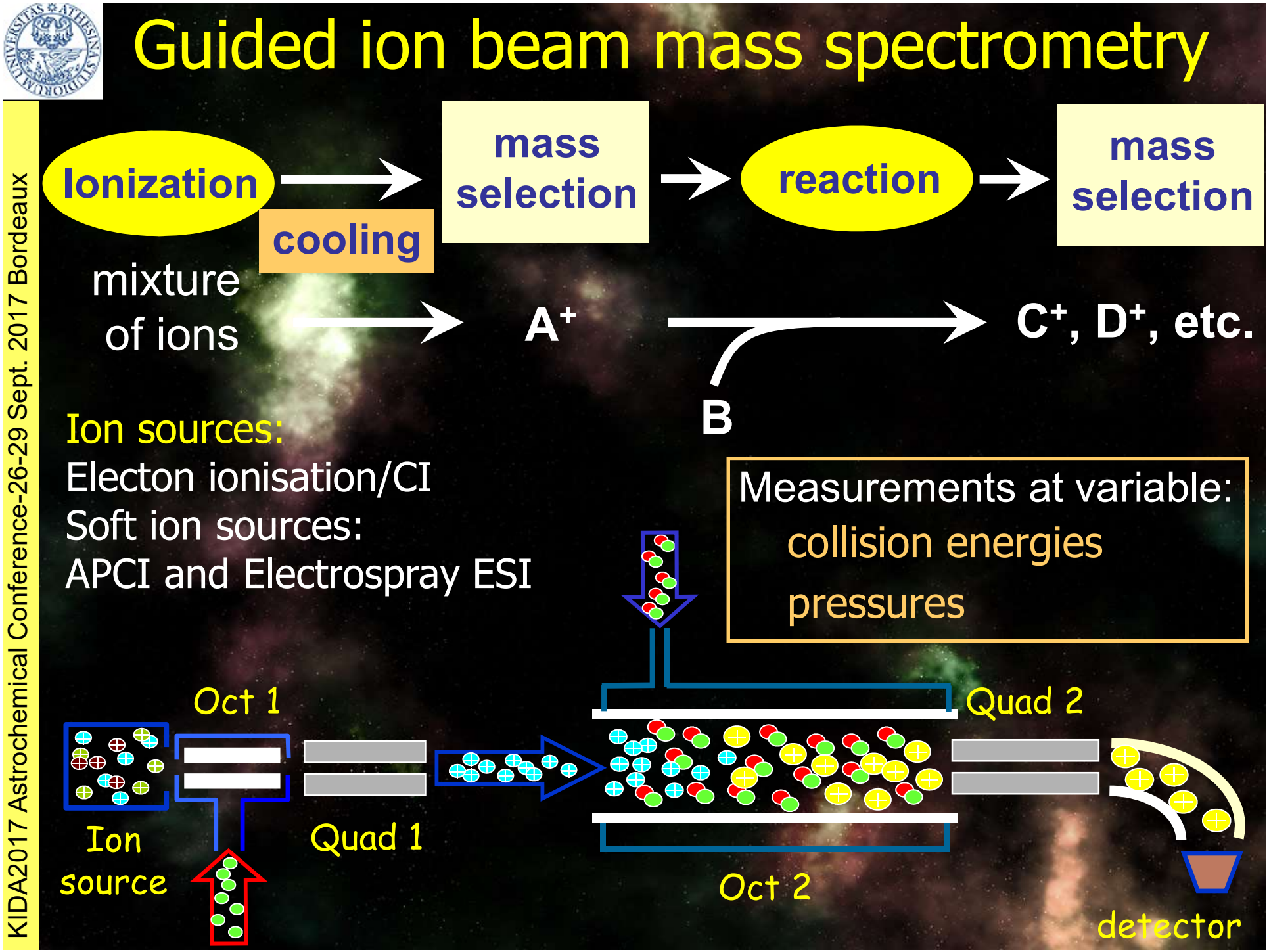
- UV photons
- Cosmic rays
- Reactions with IONS (H^+ - He^+ - H_3^+ - HCO^+)

H^+ / He^+ react by **charge exchange (dissociative)**

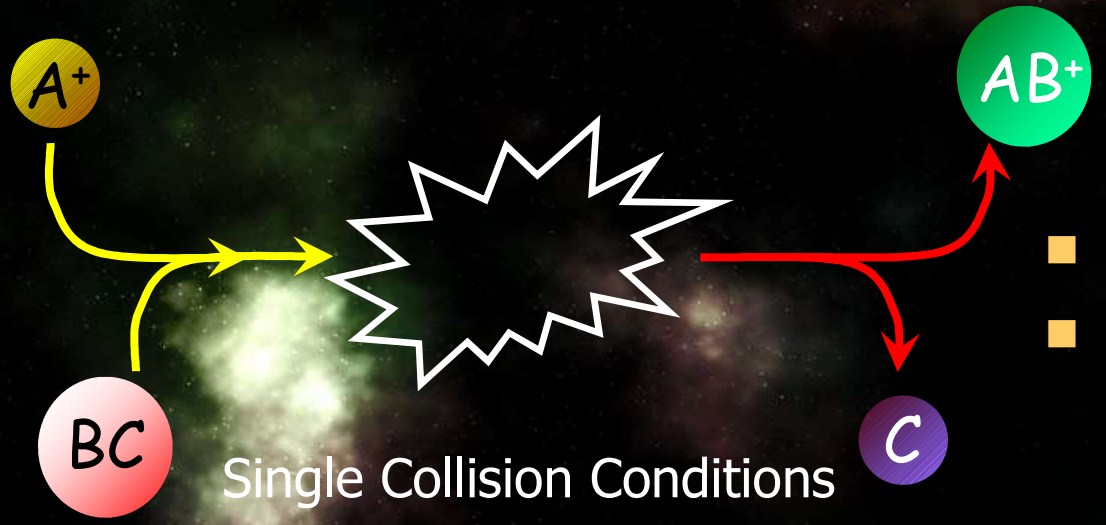


Fragmentation should be more pronounced with He^+ than H^+ (due to higher exotermicity)

No experimental $\sigma(E)$ or $k(T)$ measurements are available for reactions of He^+ with DME & MF


Guided ion beam mass spectrometry
Ionization
cooling
mass selection
reaction
mass selection
mixture of ions
A+
B
C+, D+, etc.
Ion sources:
Electon ionisation/CI
Soft ion sources:
APCI and Electrospray ESI
Measurements at variable:
collision energies
pressures
Oct 1
Quad 2
Ion source
Quad 1
Oct 2
detector
KIDA2017 Astrochemical Conference-26-29 Sept. 2017 Bordeaux

Reactive scattering experiments



- Collision Energy E_{CM}
- Internal Energy (quantum state)

Talk from S. Le Picard

The experimental observables:

Branching Ratios, $BR = 100*P_i/\sum P_i$

$$A^+ + B \rightarrow P_1 + P_2 + \ldots + P_N$$

Absolute integral reactive cross section $\sigma_i(E_{CM})$

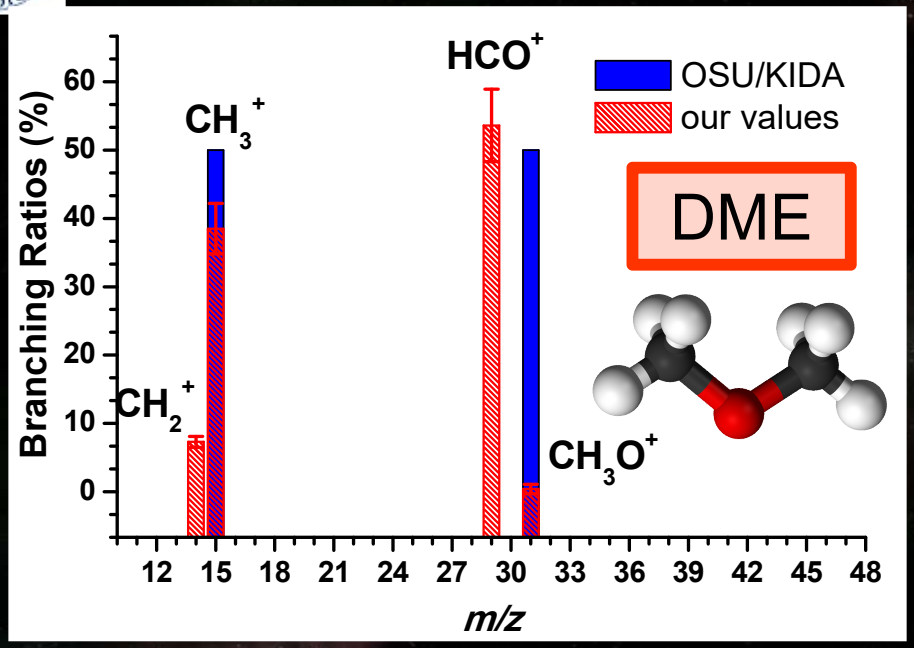
$$I = I_0(1-e^{-\mathcal{L}\sigma\rho})$$ Lambert-Beer law

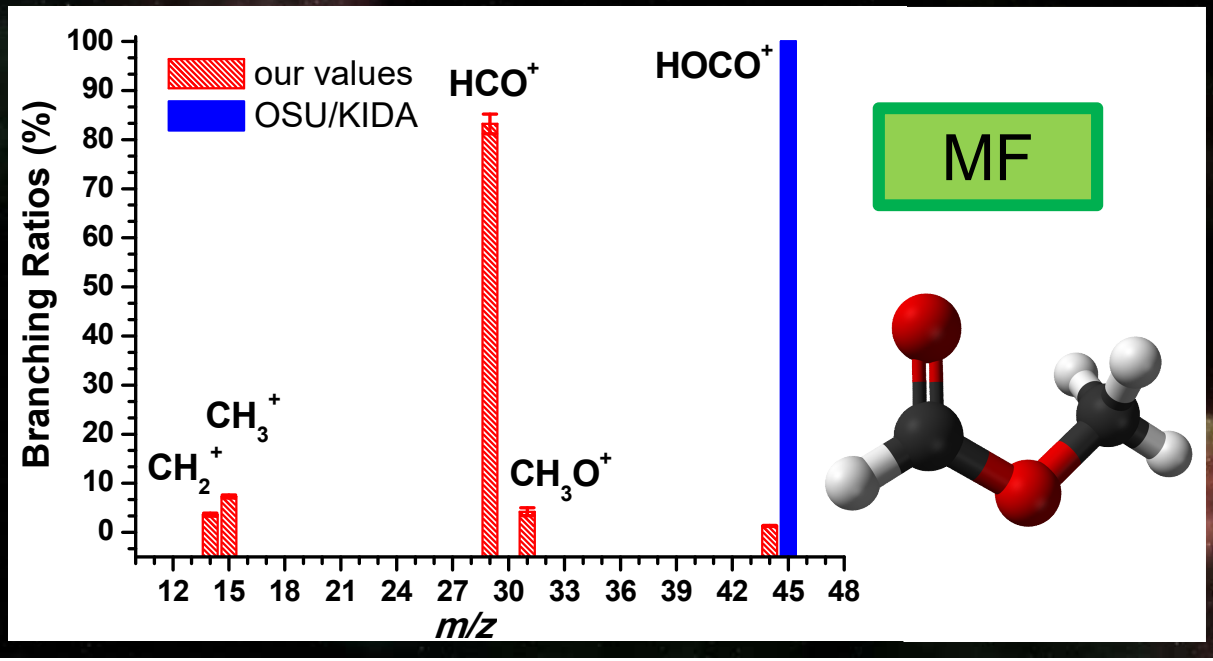
I = product intensity I_0 = reagent ion intensity

$\mathcal{L}$ = effective length of the scattering cell

ρ = density of B

He^+ + DME/MF: experimental BRs





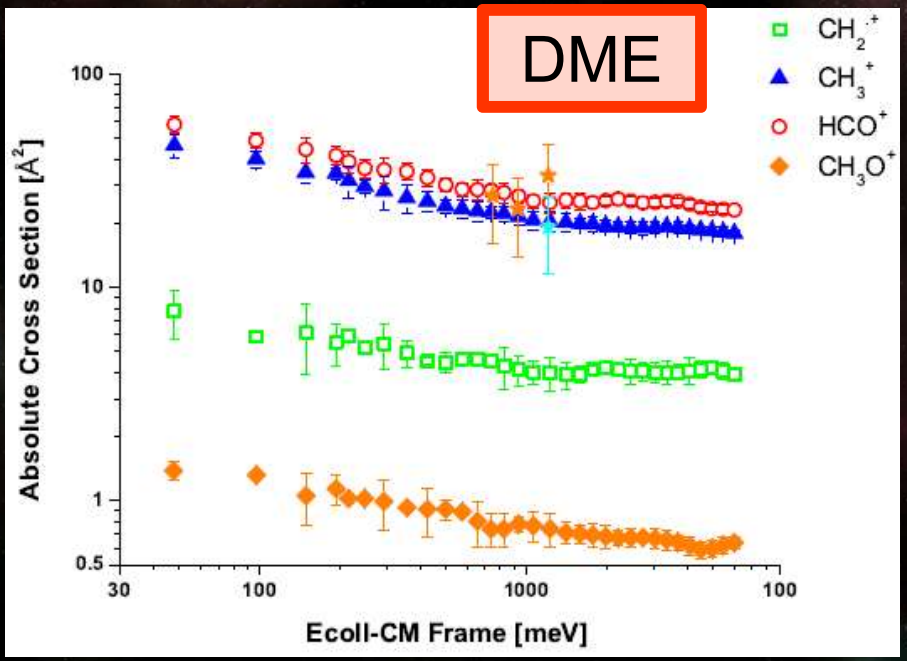
- charge exchange is 100% DISSOCIATIVE (no $M^{+\bullet}$ peaks detected)
- Experimental BRs are (quite!) different from estimates in astrochemical databases

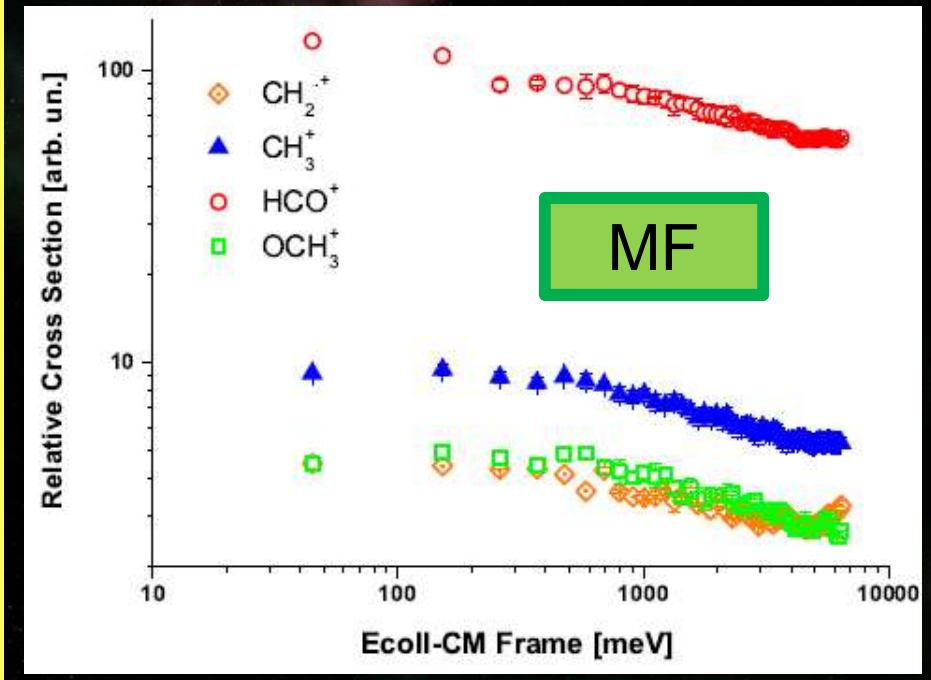
Dissociation products (HCO^+) can further react

Realistic BRs are important for correct modelling

He^+ + DME/MF: cross sections

- Cross sections decrease with increasing collision energy (hyperthermal energy range)
- BRs remain practically constants



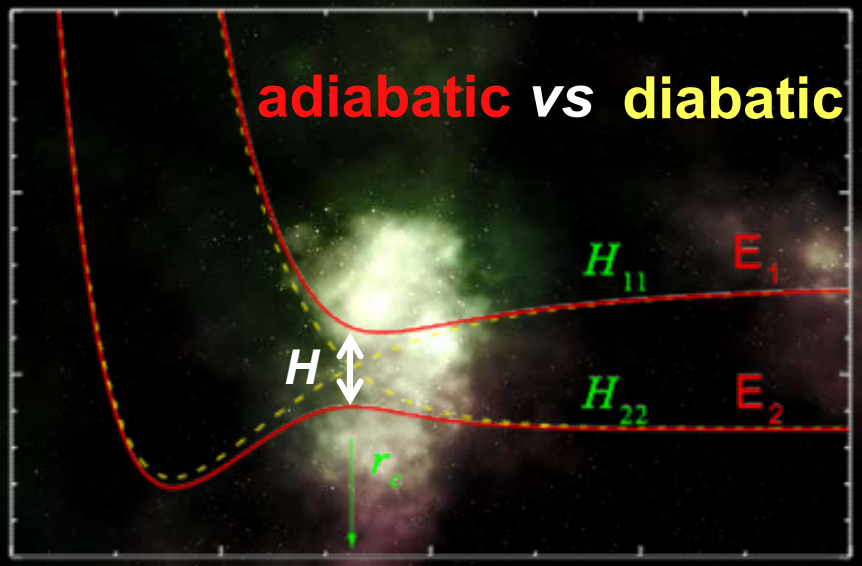


10meV ~ 116 K

Can we use our experimental data for «reasonable» estimates of rate constants at T relevant for ISM?

For DME see A. Cernuto *et al.* PCCP 2017

Theoretical model: charge exchange



$$A^+ + B \rightarrow A + B^+$$

- Electron exchange at crossings of potential energy curves (diabatic representation)

- Semi-classical Landau-Zener model for the non-adiabatic single passage probability

$$p(E,l) = \exp\left(-\frac{2\pi H^2}{\hbar v_r \Delta}\right)$$

E collision energy

l orb. angular momentum quantum number

v_r radial velocity

H non-adiabatic coupling

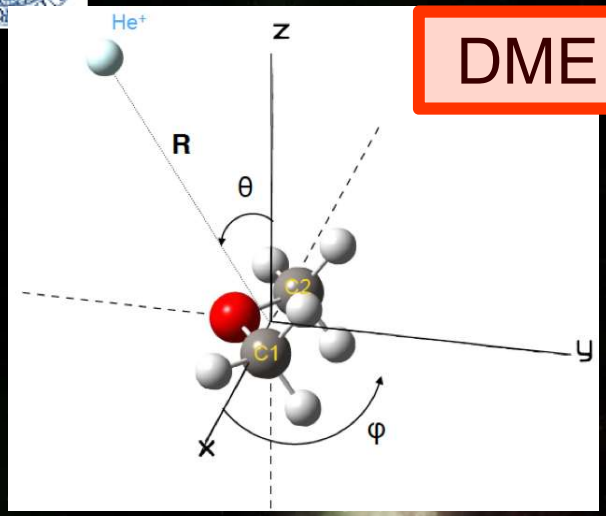
Δ slope difference $|H_{11}\text{-}H_{22}|$ at r_c

$k = 2\pi\mu v_r/h$

Total charge exchange cross section

$$\sigma(E) = \frac{\pi}{k^2}\sum_l P(l)(2l+1)$$

The Potential Energy Surface



DME

$V(R, \theta, \varphi)$

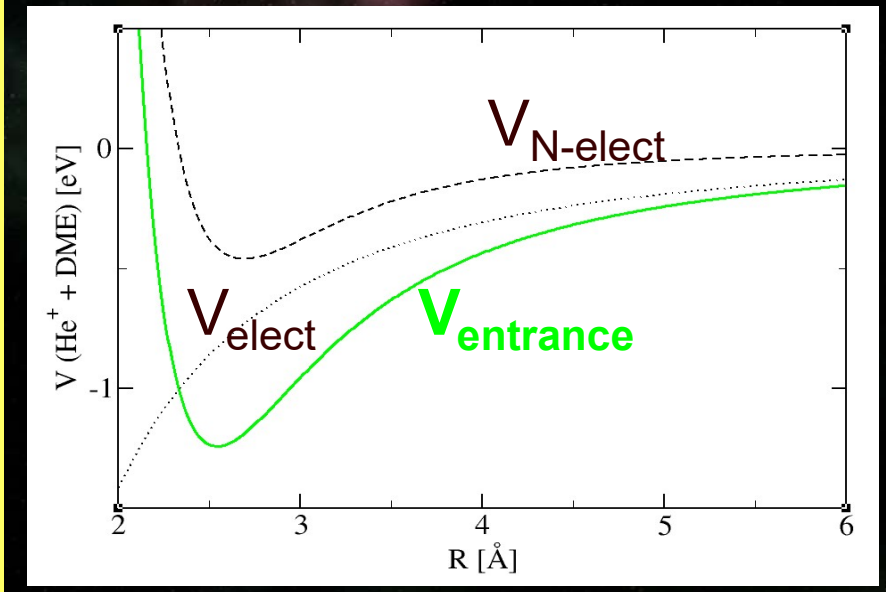
V_{elect}: Coulomb terms He^+/partial charges on O, C1,C2

$V_{N\text{-}elect}$: induction+dispersion+size repulsion (Improved LJ model)

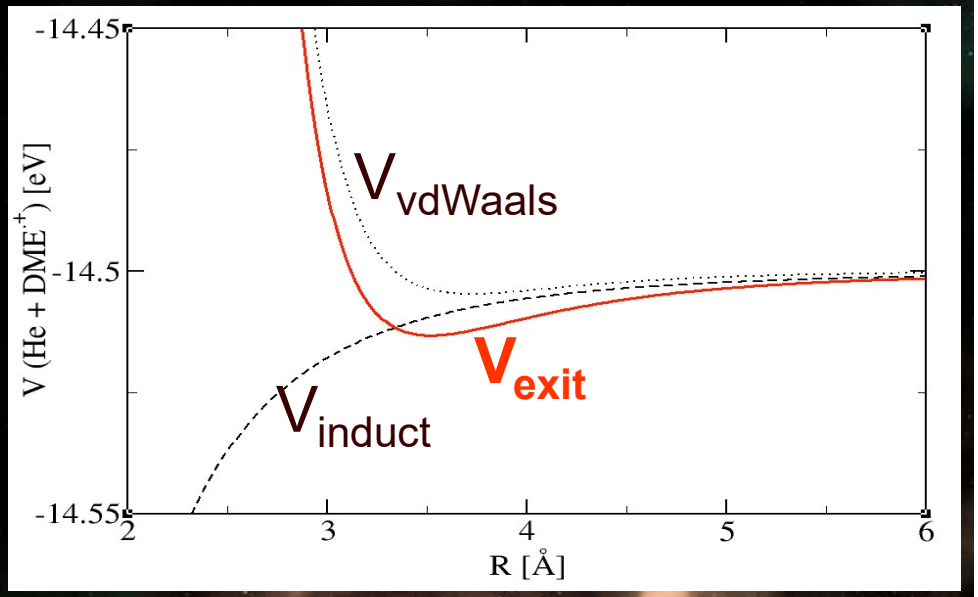
$V_{vdWaals}$: dispersion+size repulsion (ILJ)

V_{induct}: point charge interacting with He

Entrance channel: He^++DME

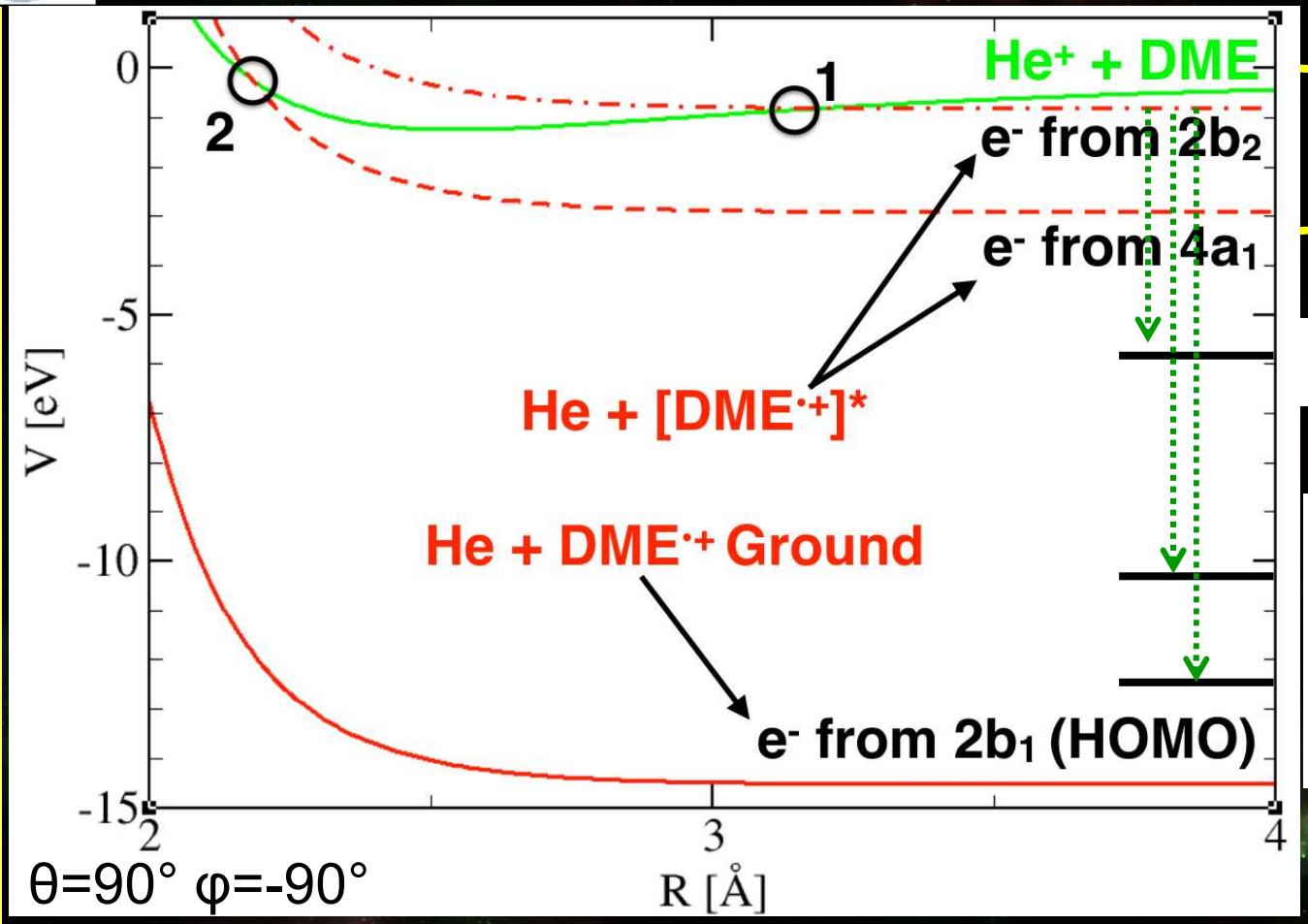


Exit channel: He + $DME^{\bullet+}$



Cuts of the PESs at θ=90° φ=-90° (He^+ approaching on the O- side)

He^+ plus DME: PES modelling



inner valence orbitals of DME

$CH_2^+ + H + CH_3O + He$

$CH_3O^+ + CH_3 + He$

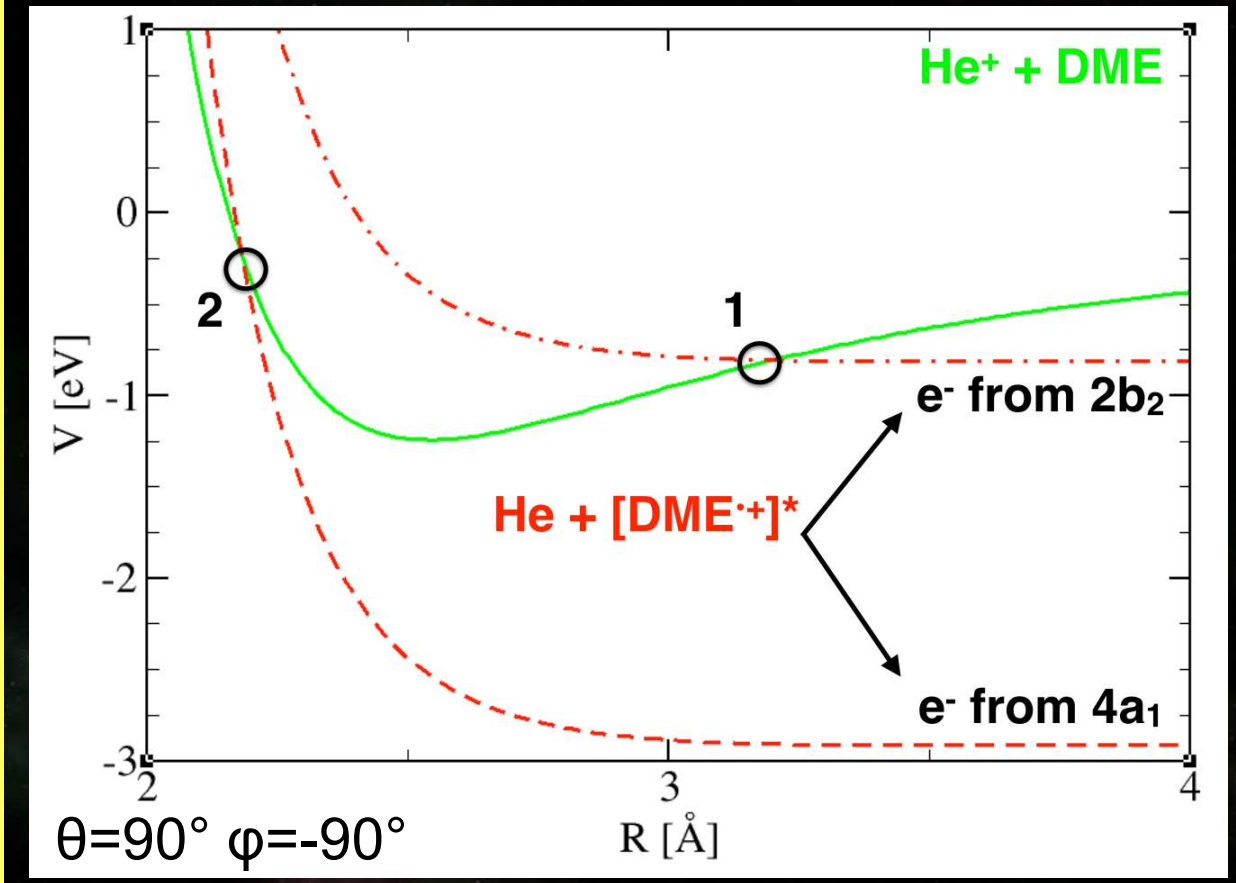
$CH_3^+ + CH_2O + H + He$

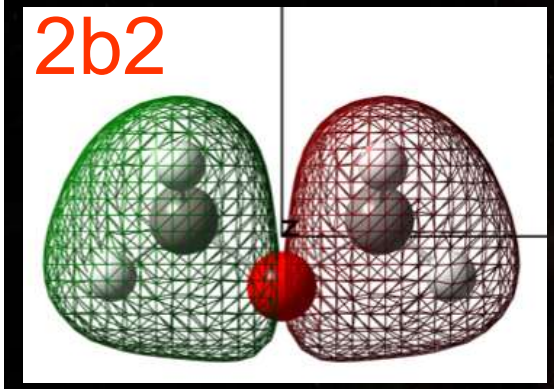
$HCO^+ + H_2 + CH_3 + He$

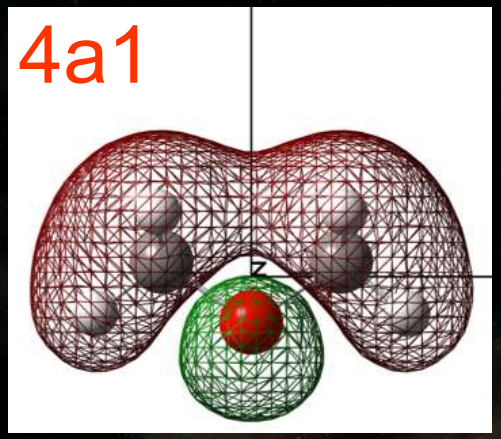
$HCO^+ + H + CH_4 + He$

- No curve crossing with the ground electronic state of $DME^{+\bullet}$
- Electron is removed from an inner valence orbital → $[DME^{+\bullet}]^*$ → exothermic fragmentation

Crossings and MO symmetries

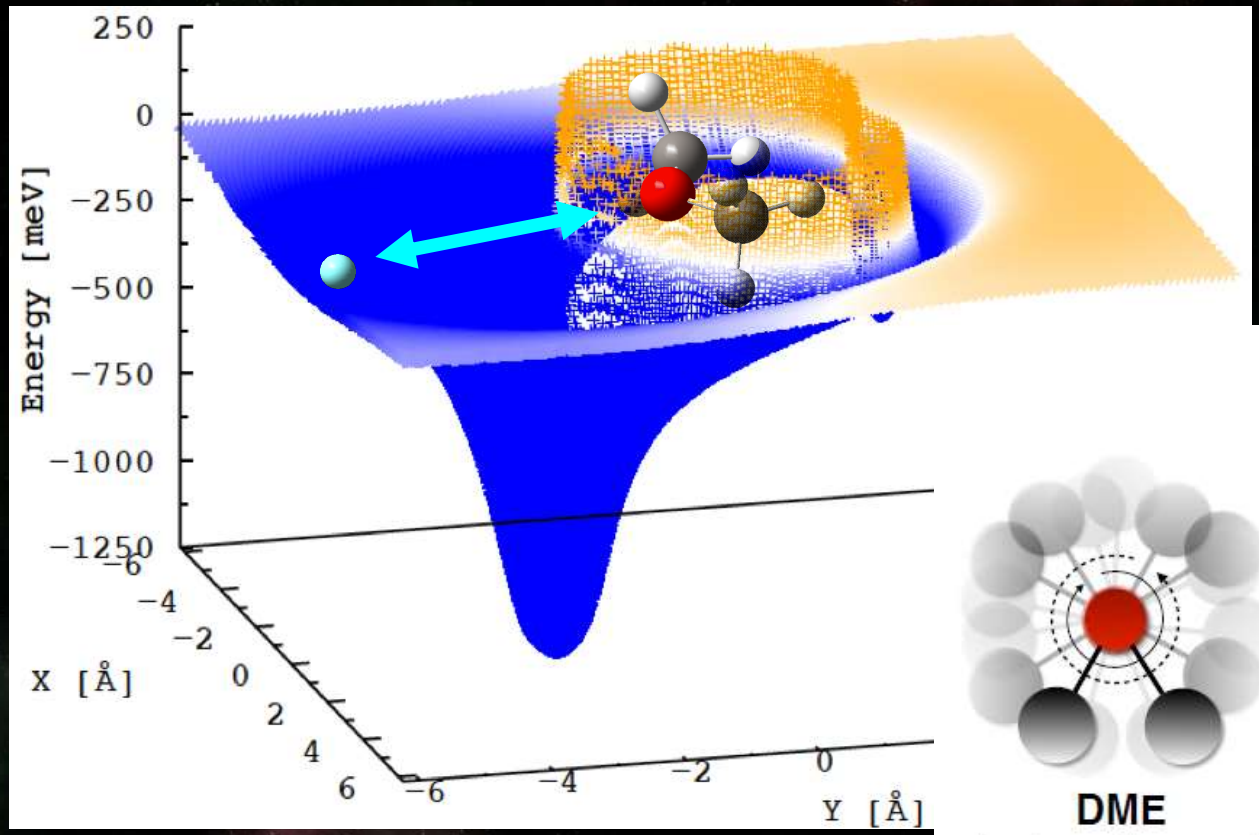


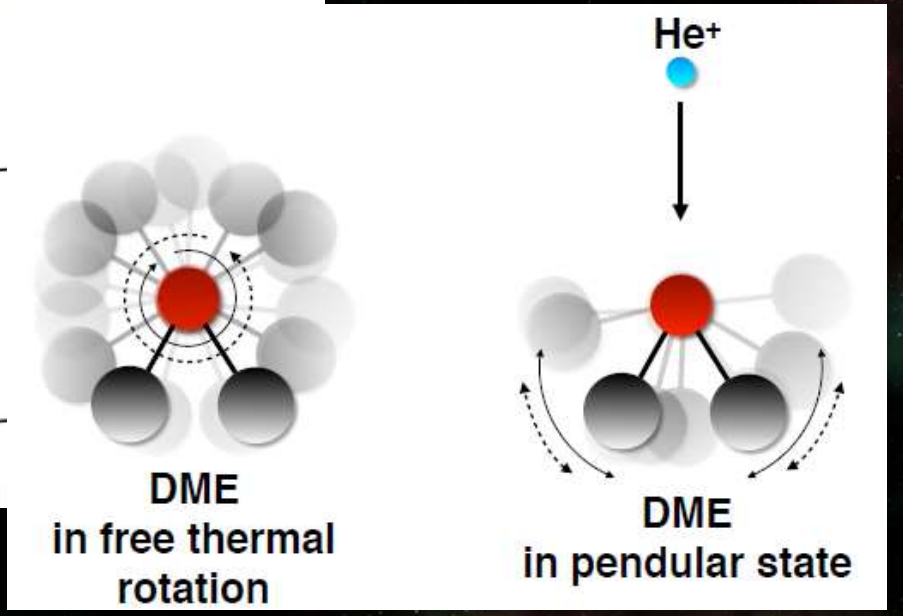




- Crossing 1 (with 2b2 MO) mostly contributes to the cross section (energy consideration)
- Different symmetries for the electron density distributions of 2b2 and 4a1

Strong anisotroy of the PES

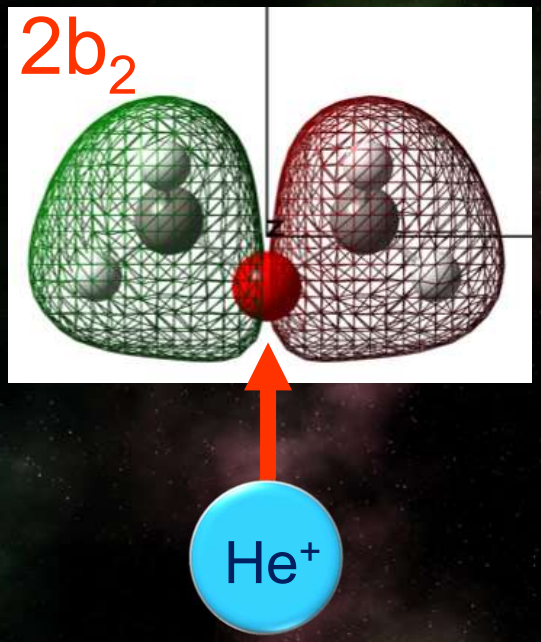




- Stereochemical effects drive the colliding system into the most attractive geometry
- Already operative at large distances and more significant at low collision energies

$E_{rot} \sim \Delta V$ at 15 Å

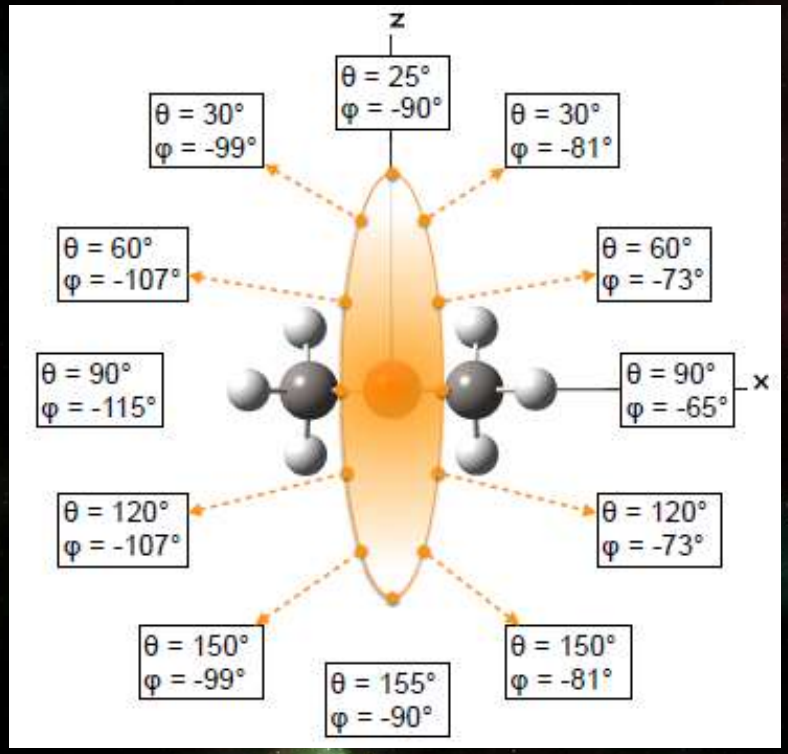
Stereochemistry + MO symmetries



- The most attractive geometry is also the less reactive due to unfavourable orbital overlap
- Improved L.Z.: correction factors are introduced in the non-adiabatic coupling term (*H*)
- The coupling (*H*) depends on the collision energy and on the orientation of the collision pair
- Reaction driven by Coriolis coupling in the most attractive geometries

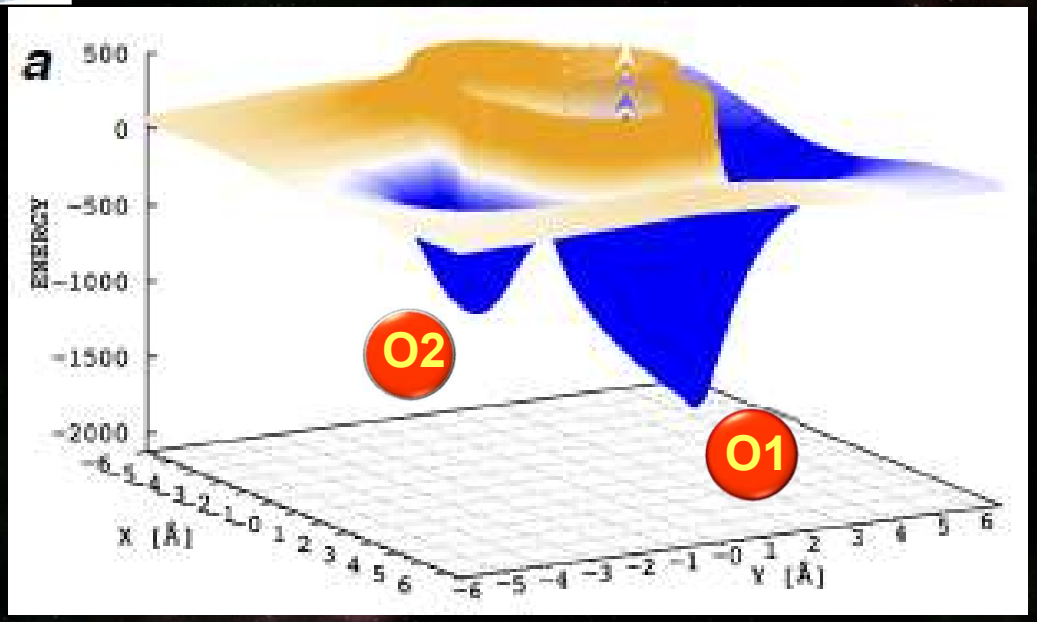
Stereochemistry + MO symmetries

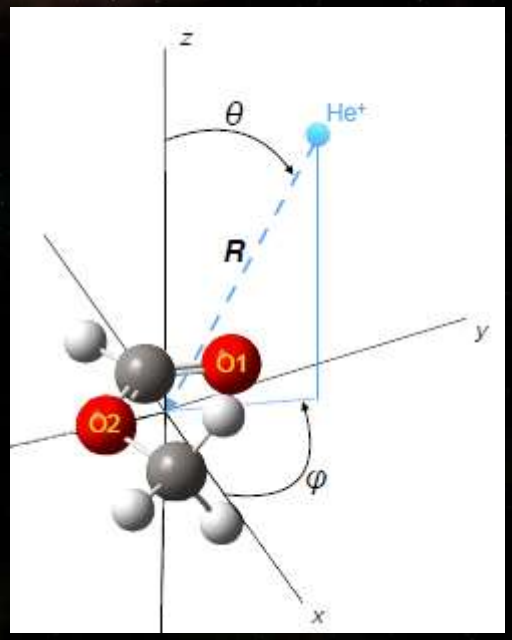
- Cross sections are calculated from configurations falling within an «effective cone for reaction»
- The cone is asymmetric due to CH_3 repulsions



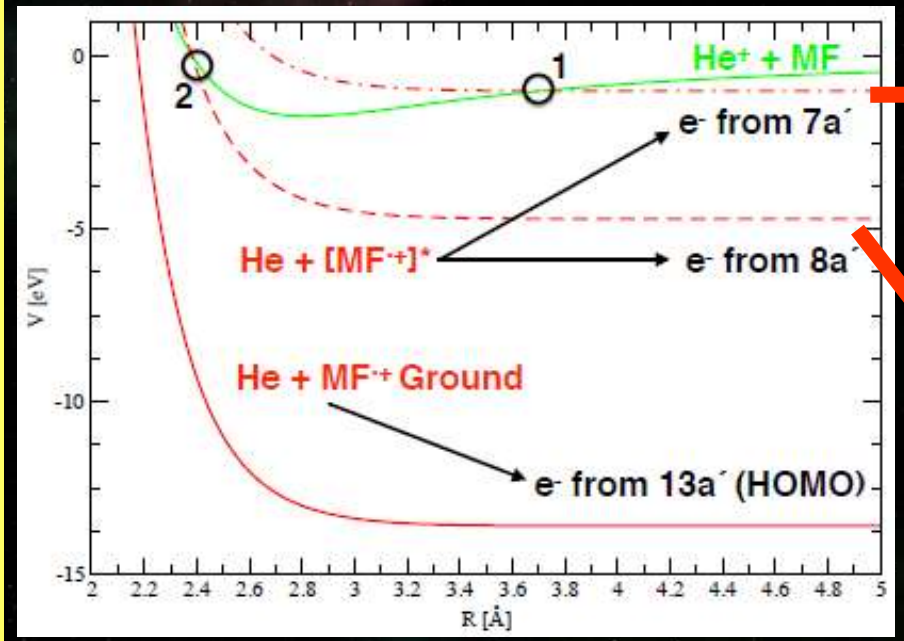
For details on the model see A. Cernuto *et al.* PCCP 2017 and Andrea Cernuto, PhD Thesis, University of Trento 2017

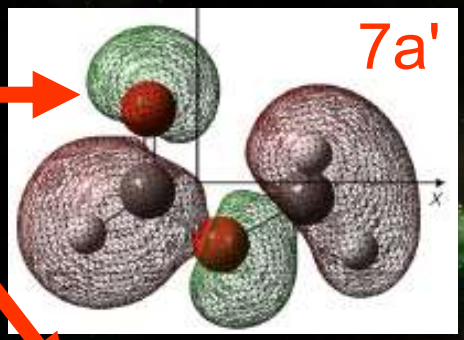
The model for He^+ with MF

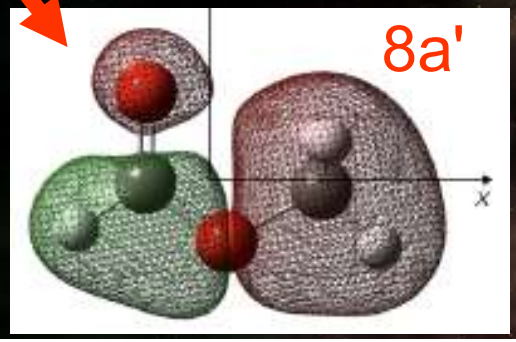




MF



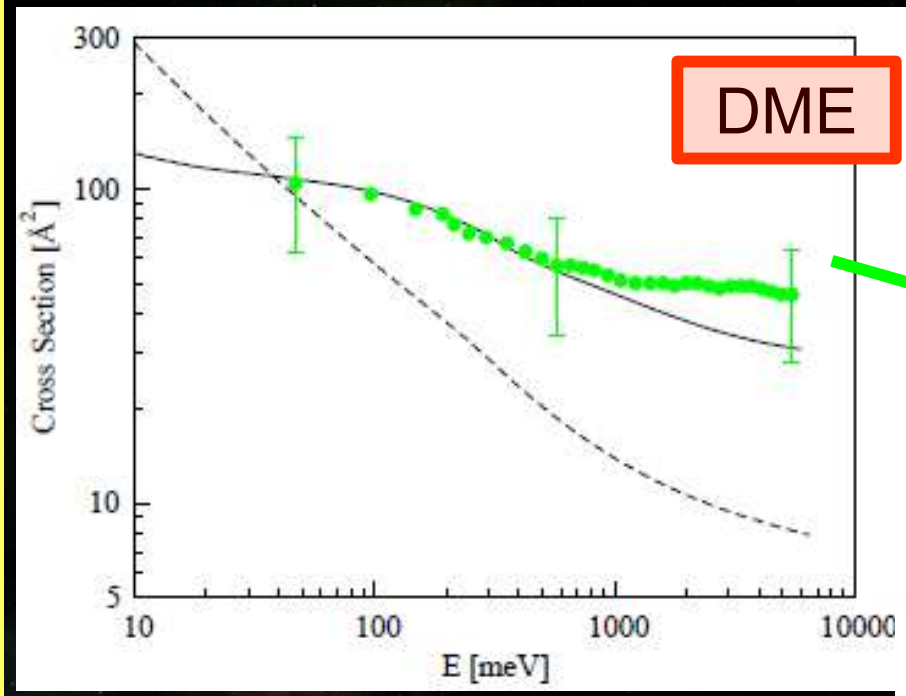




Two most attractive configurations

Two «effective cones»

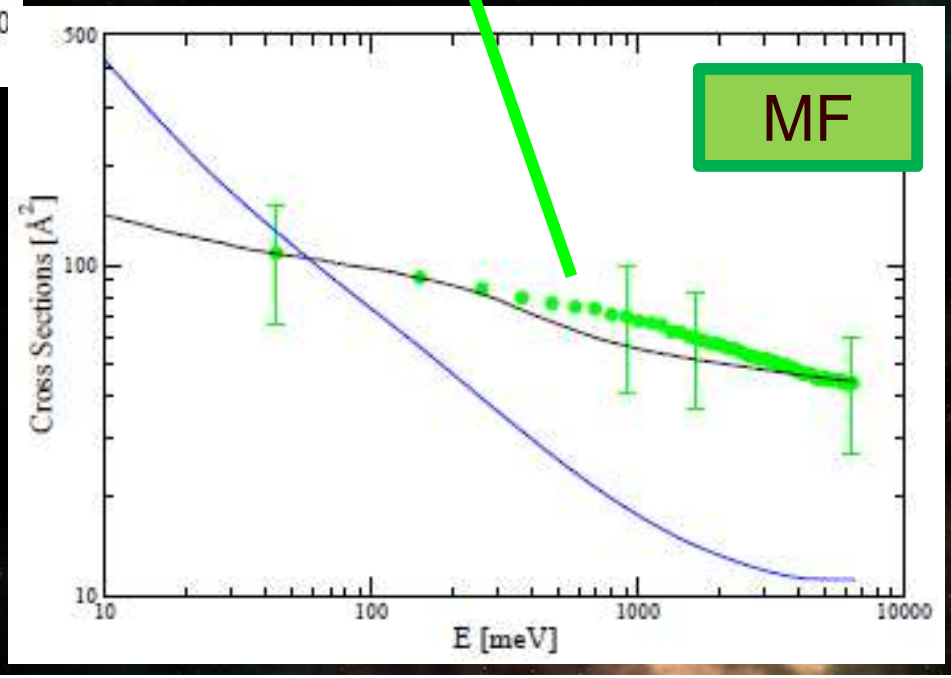
Experimental results *vs* model



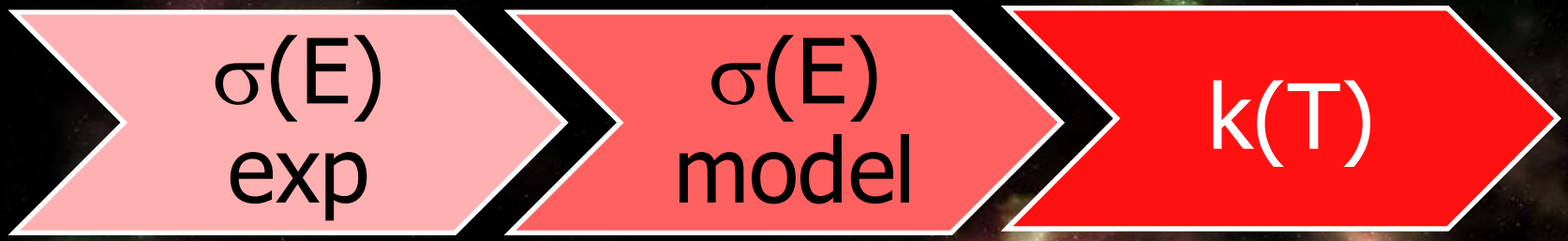
Total absolute cross sections

present model

no orientation



Can we use our model (validated by experiments at hyperthermal energies) to estimate rate constants at low T ???



k(T) from astrochemical databases

KIDA – OSU2009 gas phase chemistry model

$$k(T) = \alpha \cdot (T/300)^{\beta} \cdot e^{-\gamma/T} \ cm^3 \cdot s^{-1}$$

Modified Arrhenius equation

α	β	γ	
$2.64 \cdot 10^{-9}$	-0.5	0	He^+ - DME
$3.54 \cdot 10^{-9}$	-0.5	0	He^+ - MF

UDfA database (UMIST)

$$k(T) = k_{300K} \cdot (T/300)^{\beta} \ cm^3 \cdot s^{-1}$$

Arrhenius equation rescaled to measured/estimated values at 300K

k_{300K}	β	
$2.00 \cdot 10^{-9}$	-0.5	He^+- DME
$3.00 \cdot 10^{-9}$	-0.5	He^+ - MF

k(T) from astrochemical databases

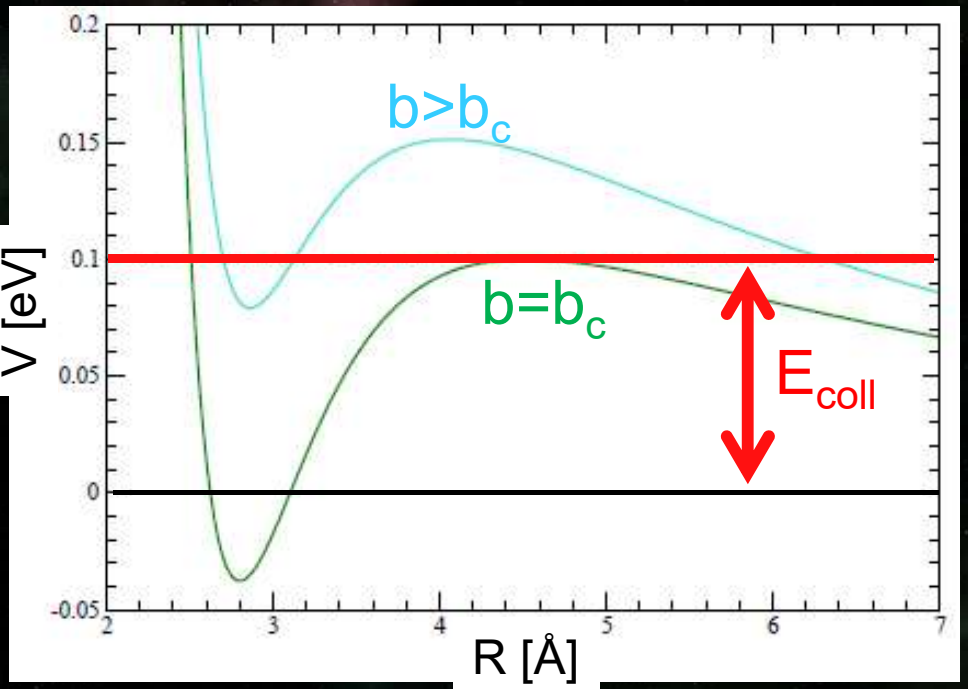
Su &Chesnavich 1982

Parametrization from a classical trajectory method

$$k(T) = c_1 + c_2 T^{-0.50} \text{cm}^3\cdot\text{s}^{-1}$$

$$c_1 = 0.62 k_L \quad ; \quad c_2 = 2.1179 \frac{\mu_D e}{\sqrt{\mu k_B}}$$

k_L Langevin rate
μ_D dipole moment
μ reduced mass



Capture model for ion-molecule reactions

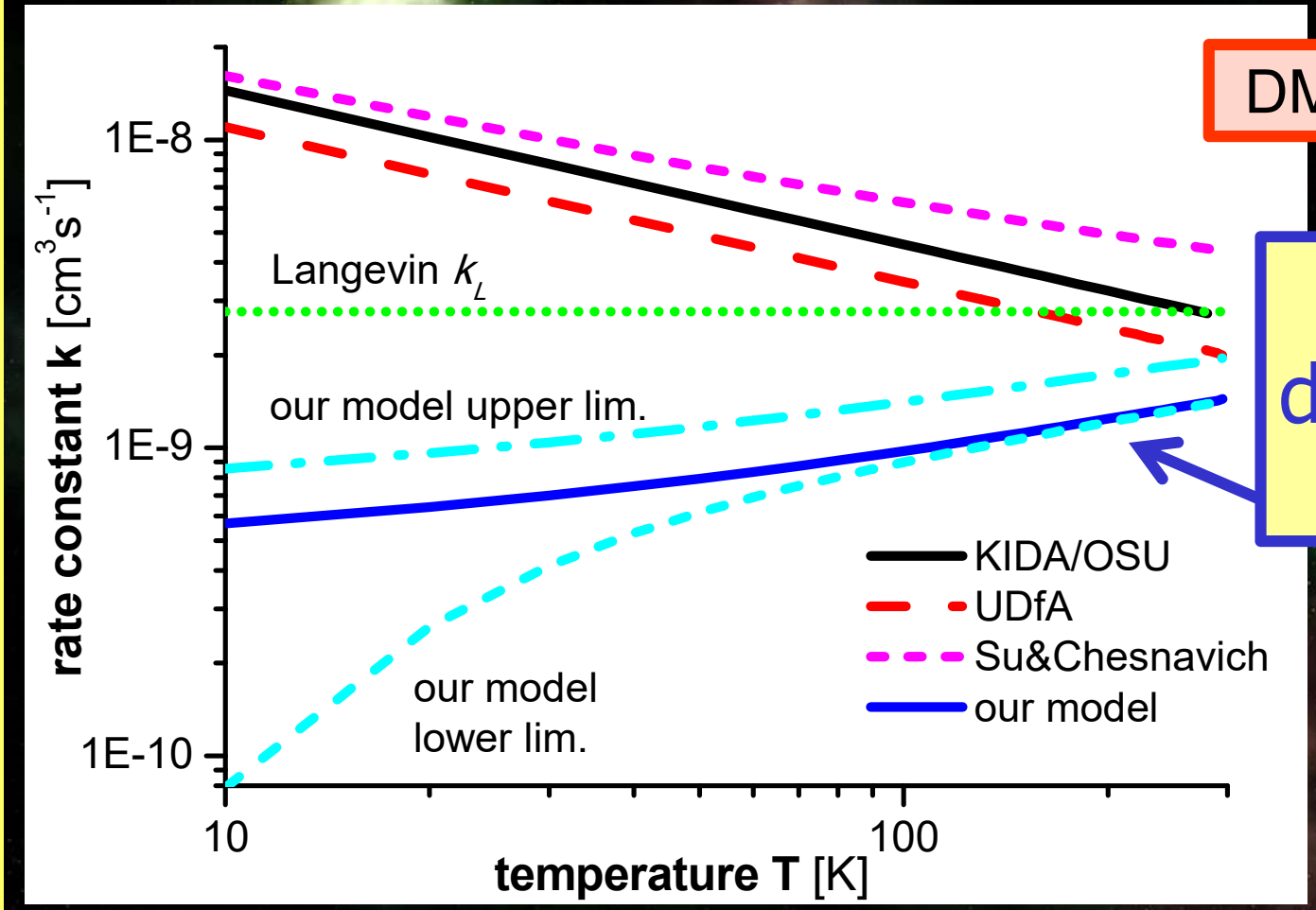
Collisions with impact parameters $b \leq b_c$ will overcome the centrifugal barrier and give reaction with unit probability

From σ(*E*) to rate constants k(T)

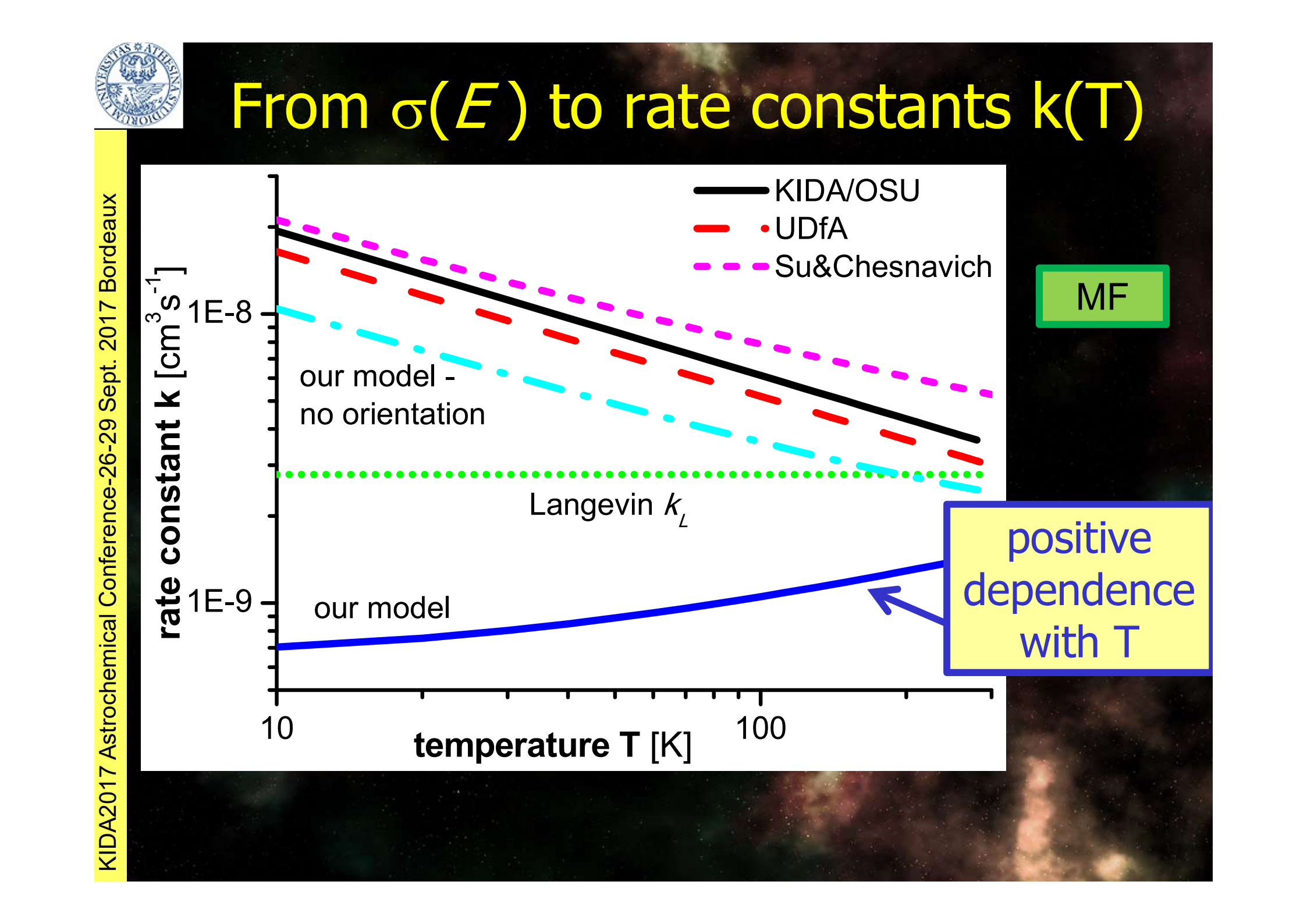
- our model extended down to 0.1 meV

$$k(T) = \left(\frac{1}{\pi\mu}\right)^{1/2} \cdot \left(\frac{2}{k_B T}\right)^{3/2} \cdot \int_0^{\infty} \sigma(E) \cdot E \cdot e^{-E/k_B T} dE$$

Talk from S. Le Picard



positive dependence with T


From σ(E) to rate constants k(T)
KIDA2017 Astrochemical Conference-26-29 Sept. 2017 Bordeaux
KIDA/OSU
UDfA
Su&Chesnavich
MF
our model -
no orientation
Langevin k_L
our model
positive dependence with T
rate constant k [cm^{3}s^{-1}]
1E-8
1E-9
10
100
temperature T [K]

Summary / Take-home message

- Absolute cross sections and BRs for He^+ - DME/MF collisions: dominated by dissociative charge exchange
- Theoretical model: orientation drives the charge exchange dynamics in ion-dipolar molecule collisions + MO symmetries
- Experimental results are necessary to test theoretical predictions and improve astrochemical models

Desiderata:

Measurements of k(T) at low T to validate our model

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