

Charge transfer processes in atom-molecule collision experiments

Paulo Limão-Vieira, F Ferreira da Silva and G García

Department of Physics, Universidade NOVA de Lisboa, Portugal
and

Consejo Superior de Investigaciones Científicas (CSIC), Madrid, Spain



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Vienna, 20 December 2016

The Atomic and Molecular Collisions Laboratory

Asst. Prof. Filipe Ferreira da Silva

Dr. Krystyna Regeta, Post-Doc

- Funding through several schemes:

PhD students:

Mr. Tiago Cunha, PT

Ms. Emanuele Lange, BR

Ms. Mónica Mendes, PT

Ms. Alexandra Loupas, PT

Ms. Rebeca Meißner, D

Technicians:

Mr. João Faustino

Mr. Afonso Moutinho



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Our most close collaborations

CSIC – Madrid, ES

Gustavo García

University of Innsbruck, AT

Paul Scheier

Stephan Denifl

Sophia University – Tokyo, JP

Hiroshi Tanaka

Masamitsu Hoshino

Flinders University, AU

Michael Brunger

Université de Lyon, FR

Marie Christine Bacchus

Czech Academy of Sciences, CZ

Juraj Fedor

Data for plasma applications

- Elastic DCS; ICS; Total Cross Sections (experiment and theory);
- Electronic Excitation (experiment and theory) / high-resolution VUV spectroscopy
- Japan-Portugal-Spain-Australia (from 2003):

GeF_4 ; SiF_4 , CF_4 ; BF_3 ; C_4F_6 ; CF_3Cl ; CF_2Cl_2 ; CFCI_3 ; 1,3- C_4F_6 , c- C_4F_6 and 2- C_4F_6 ; CCl_4 ; F_2CO ; C_2F_4

COS ; CS_2 ; H_2O ; CH_4 ; SiH_4 ; GeH_4 ; C_6H_6 ; CH_3F ; CH_3Cl ; CH_3Br ; CH_3I ; O_2

- UK-Portugal (2006):
 CF_3I , C_2F_4 and CF_x ($x = 1 - 3$) radicals

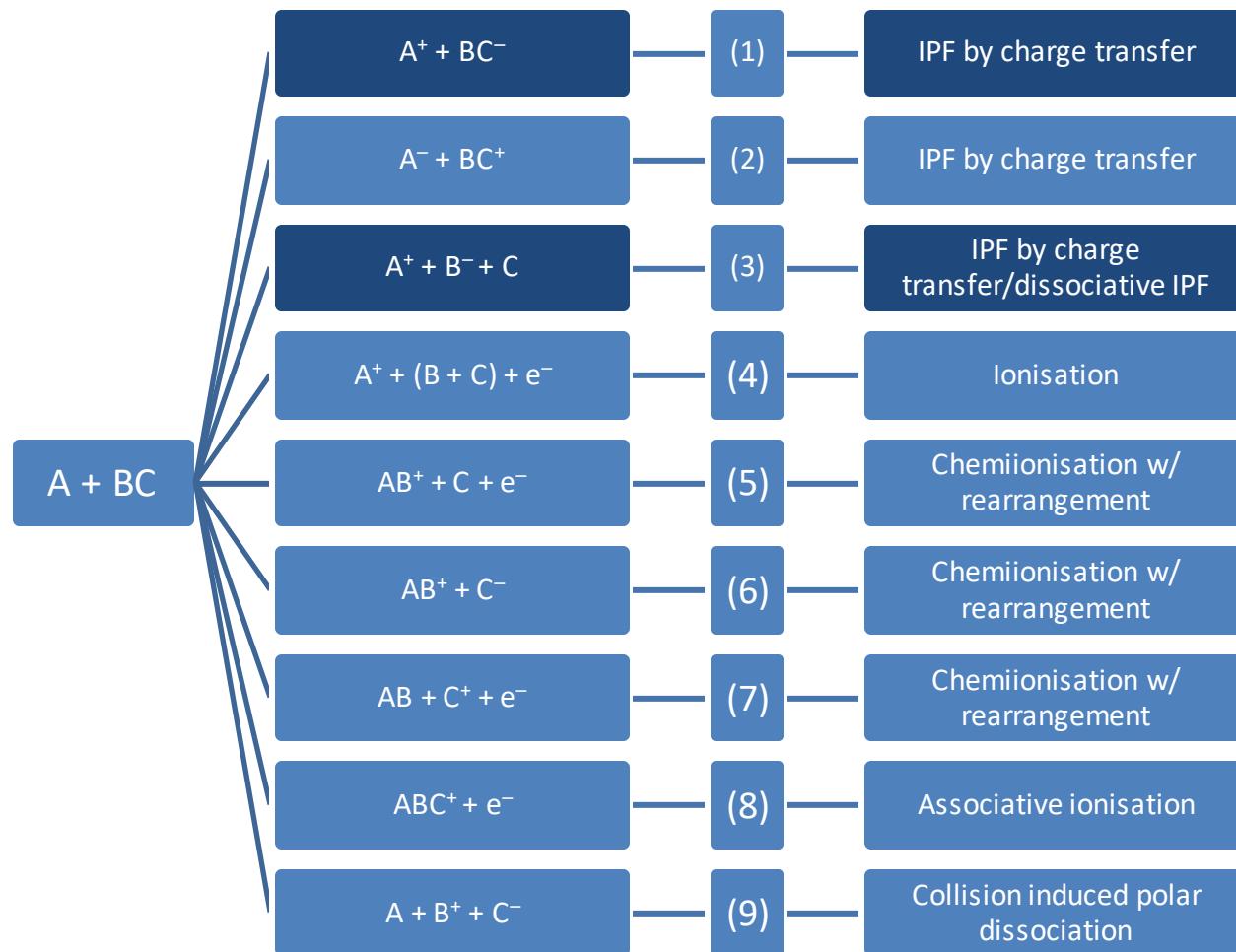
Overview

- Motivation
- Introduction
- Experimental set-up
- Results
- Conclusions

- Negative ion formation
- electron transfer
- ion-pair formation
- acetic acid
- pyrimidines
- nitromethane

Motivation

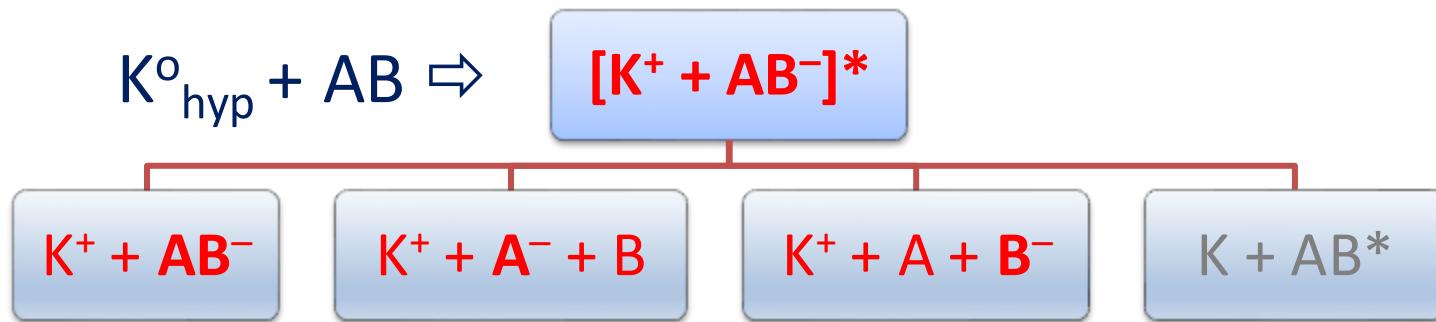
Collisional ionisation processes between atoms A and molecules BC



Motivation

Negative ions formation from molecular targets

Electron transfer in atom-molecule collisions:



- Studying chemical reactions – understand radiation induced damage;
- Collisional excitation and dissociation;
- Site- and bond-selectivity (pyrimidines, purines, imidazole);
- The role of the collision complex – pathways;
- Competitive (even concerted) fragmentation mechanisms in pyrimidines and purines.

Motivation

- access to parent molecular states which are not accessible in EA (states positive EA);
- role of vibrational excitation of the parent neutral molecule - collision dynamics

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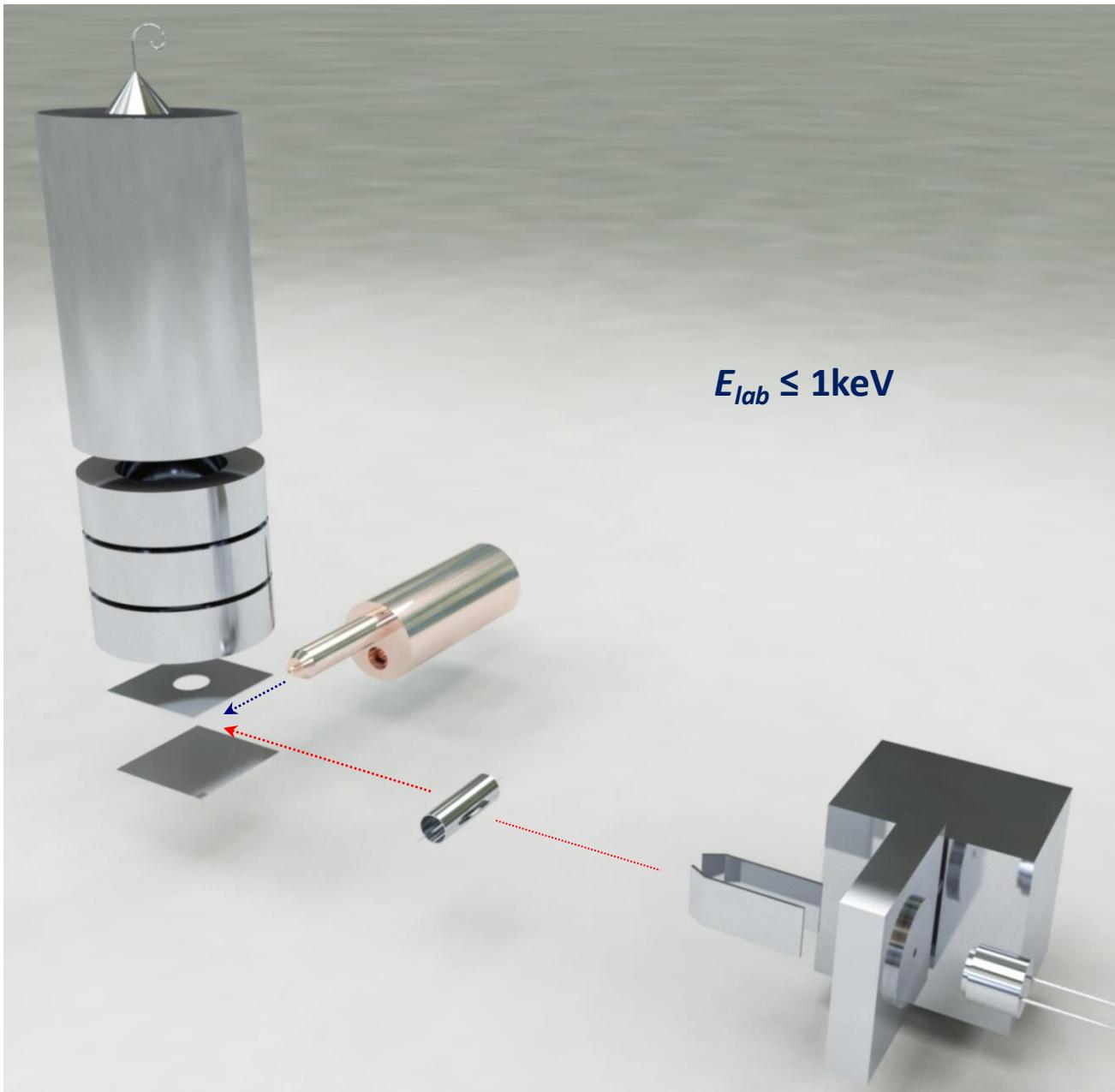
Kinetic-energy release distributions of fragment anions from collisions of potassium atoms with D-Ribose and tetrahydrofuran^{*,**}

André Rebelo¹, Tiago Cunha¹, Mónica Mendes¹, Filipe Ferreira da Silva¹, Gustavo García², and Paulo Limão-Vieira^{1,a}

¹ Laboratório de Colisões Atómicas e Moleculares, CEFITEC, Departamento de Física, Faculdade de Ciências e Tecnologia, Universidade NOVA de Lisboa, 2829-516, Caparica, Portugal

² Instituto de Física Fundamental, Consejo Superior de Investigaciones Científicas (CSIC), Serrano 113-bis, 28006 Madrid, Spain

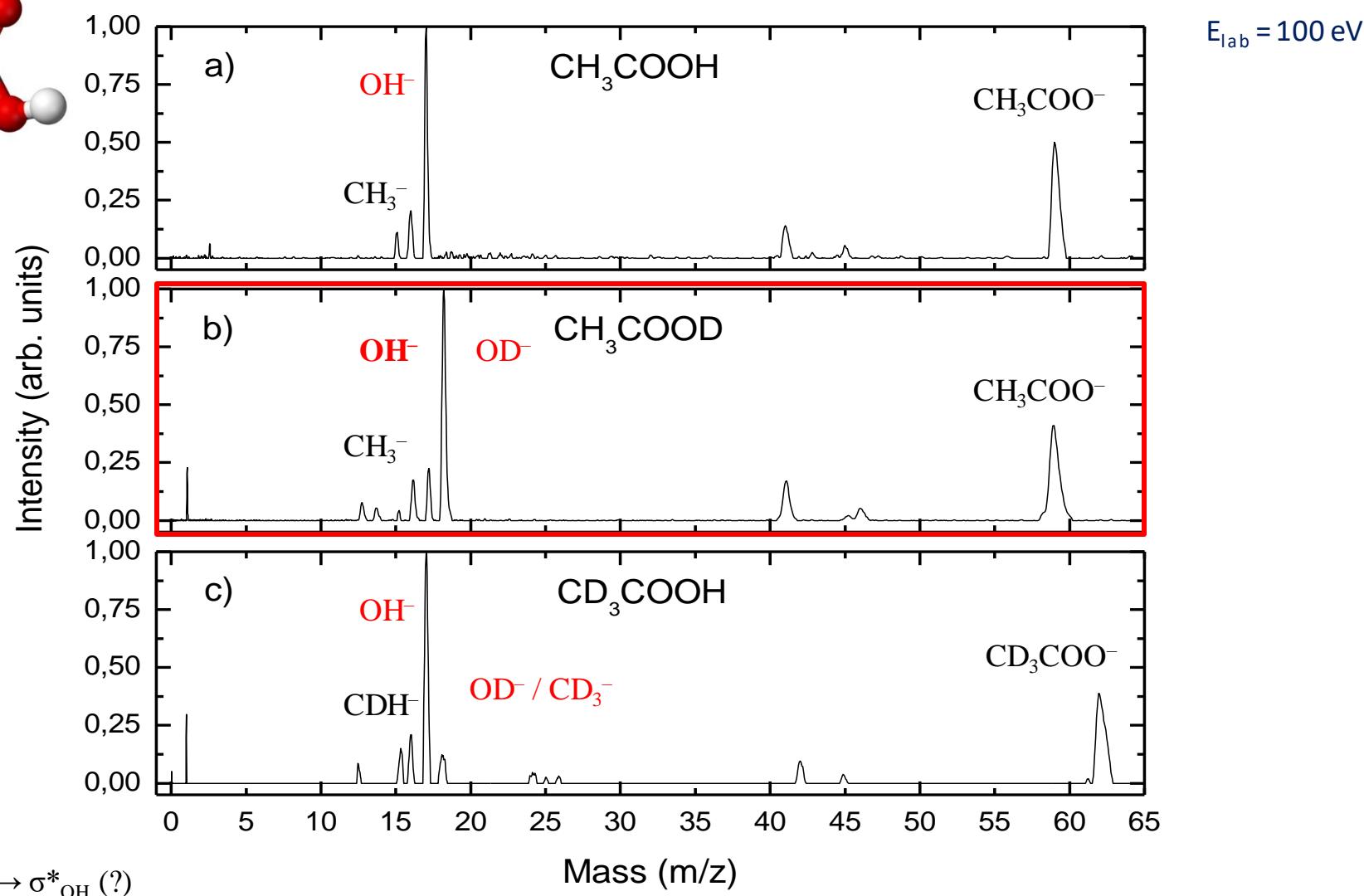
- DEA - resonances;
- direct and statistical dissociation;

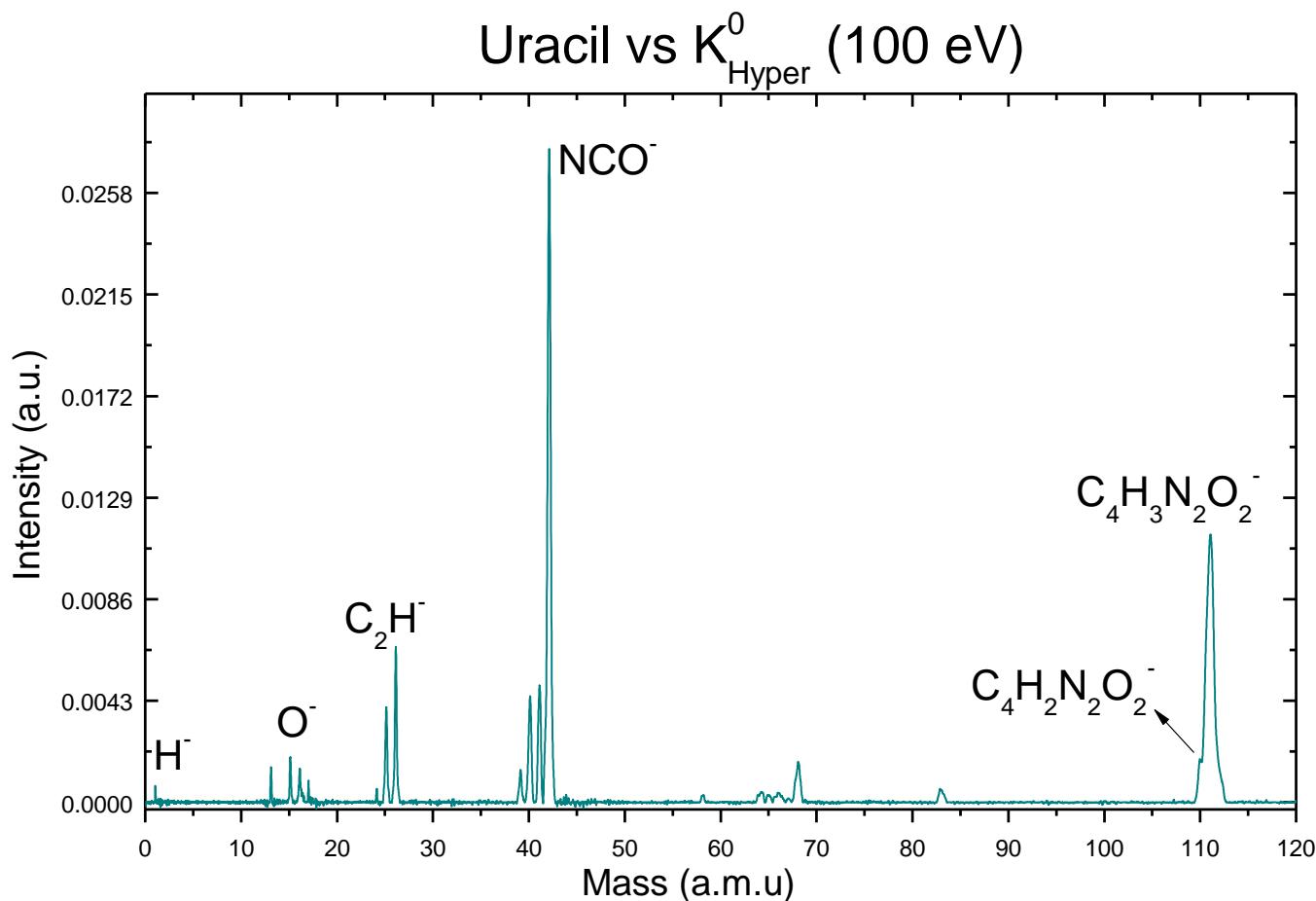


The crossed molecular beam setup in Lisbon



Complex internal rearrangement yielding OH⁻

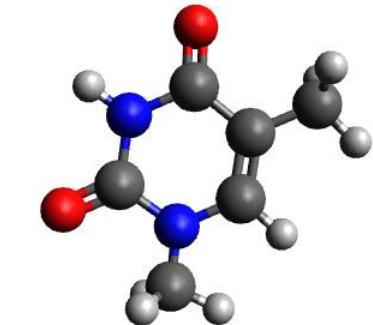
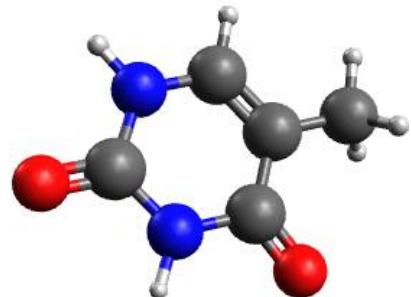




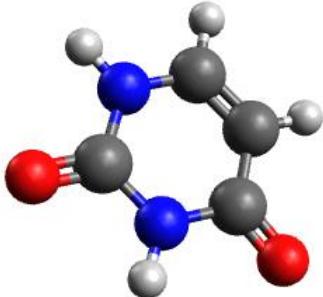
Bond	BE	EA	BE-EA
${}^1\text{N-H}$	4.29	3.40	0.89
${}^3\text{N-H}$	5.80	4.50	1.30
$\text{CH}_2\text{-H}$	4.54	1.82	2.23
${}^6\text{C-H}$	4.98	2.76	2.72

Almeida, Antunes, Martins, Eden, Silva, Nunes, Garcia and PLV
Phys. Chem. Chem. Phys. **13** (2011) 15657

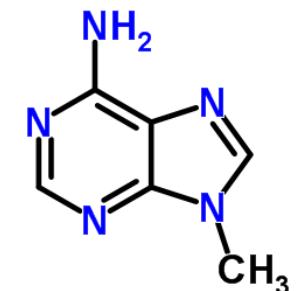
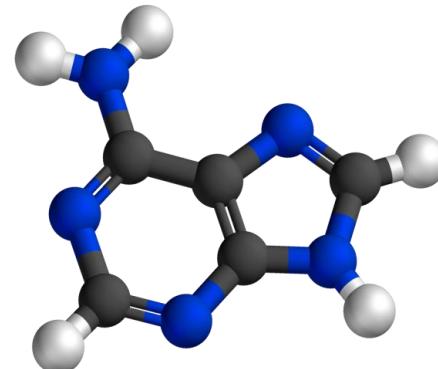
Site- and bond-selectivity



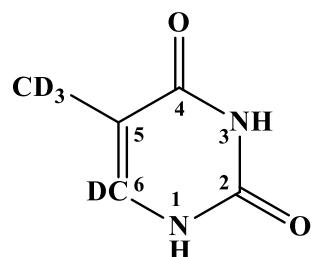
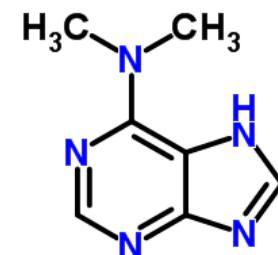
1-methyl thymine



3-methyl uracil

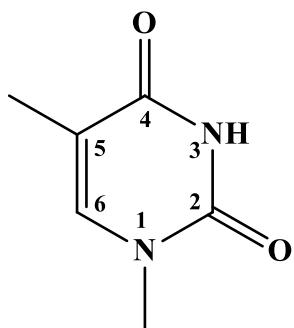


9-methyl adenine

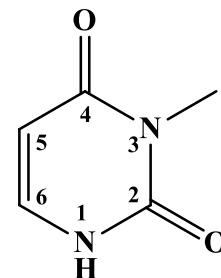
thymine- d_4 

6-dimethyladenine

Autodetachment suppression & Coulombic complex stabilization



1-methyl- thymine



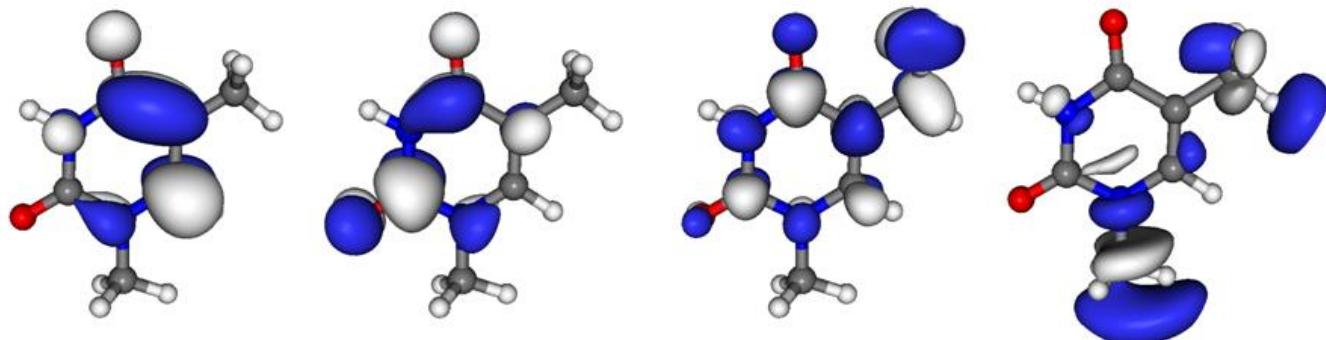
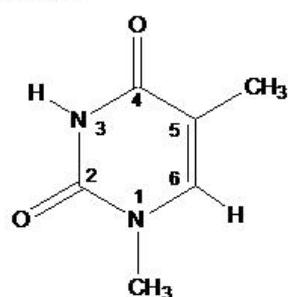
3-methyl-uracil

N-site de-methylation in pyrimidine bases as studied by low energy electrons and *ab initio* calculations

D. Almeida,^a D. Kinzel,^b F. Ferreira da Silva,^a B. Puschnigg,^c D. Gschliesser,^c P. Scheier,^c S. Denifl,*^c G. García,^{de} L. González^b and P. Limão-Vieira*^a

Cite this: *Phys. Chem. Chem. Phys.*, 2013,
15, 11431

1meT



3meU

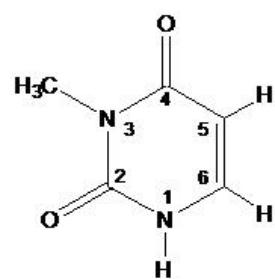
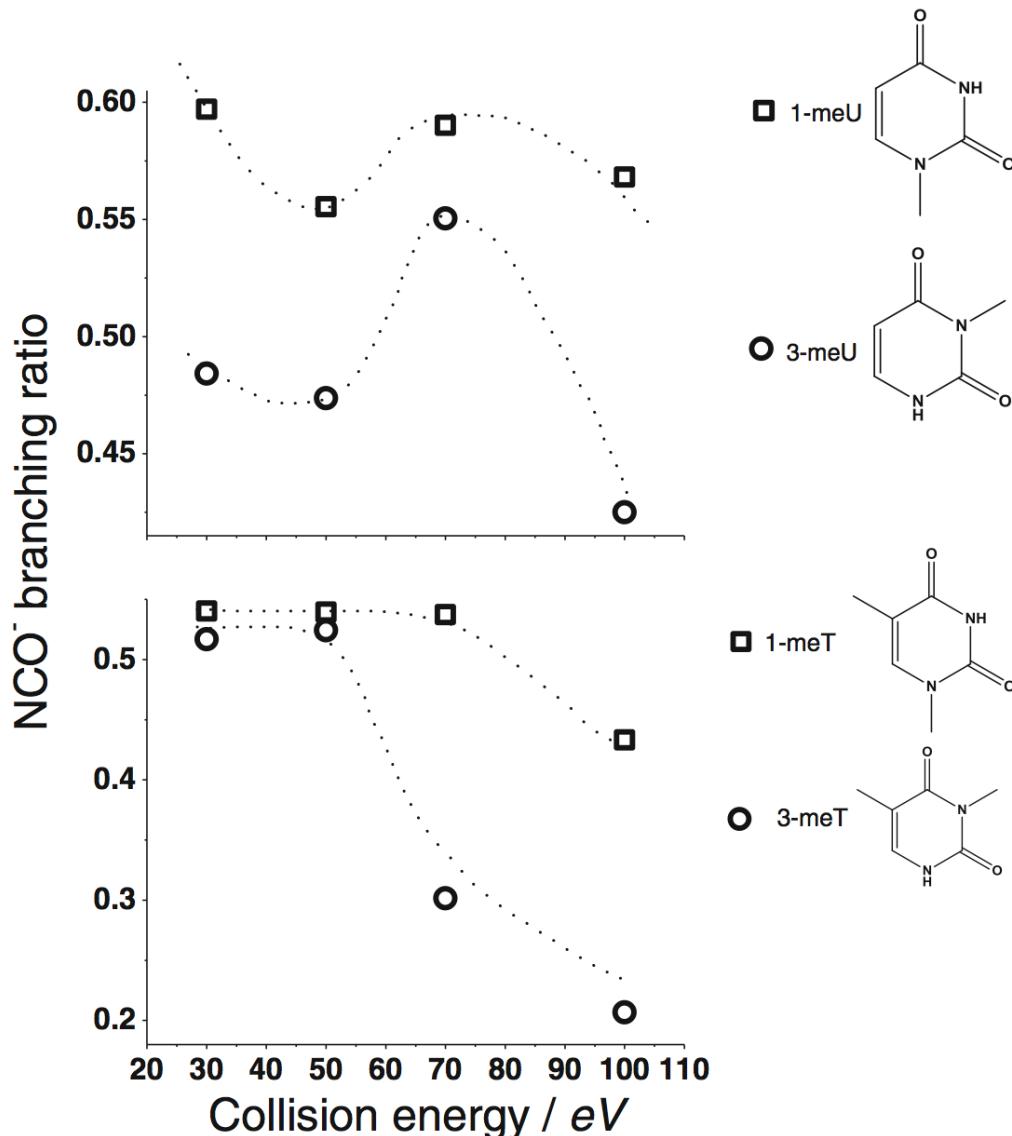


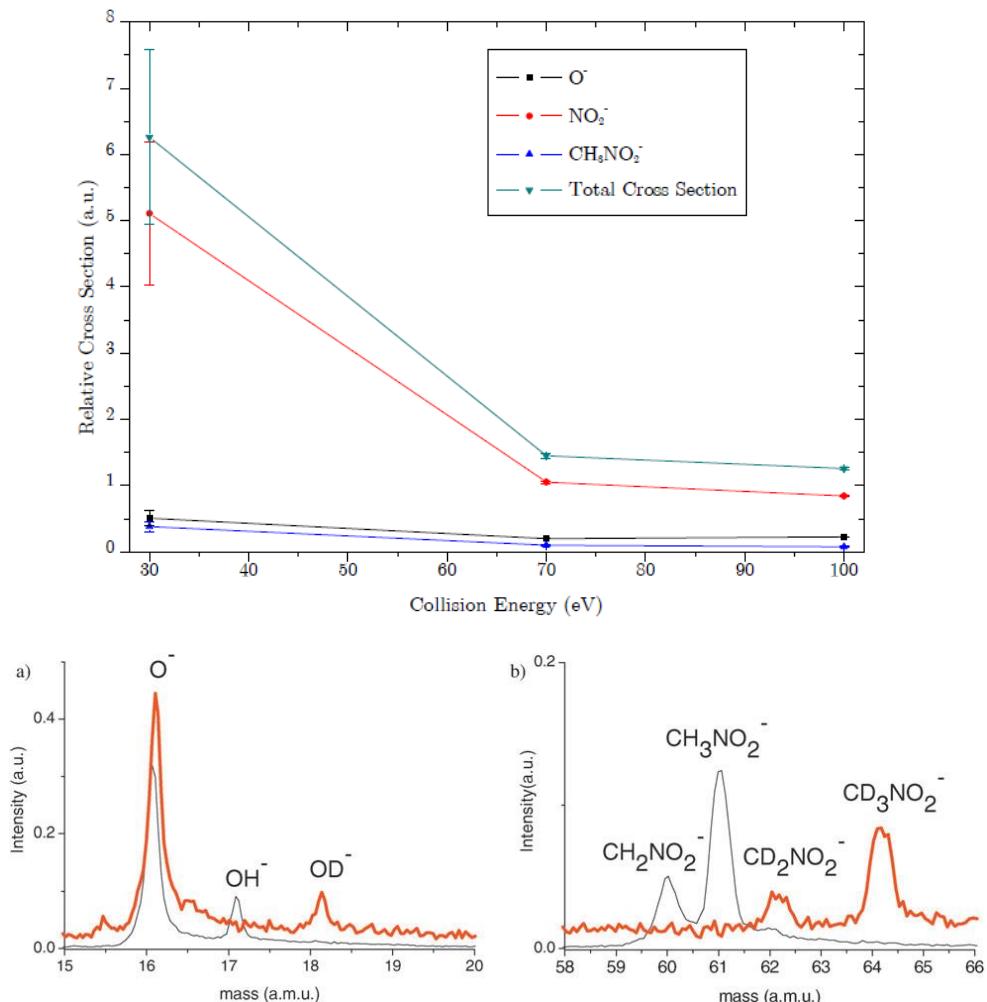
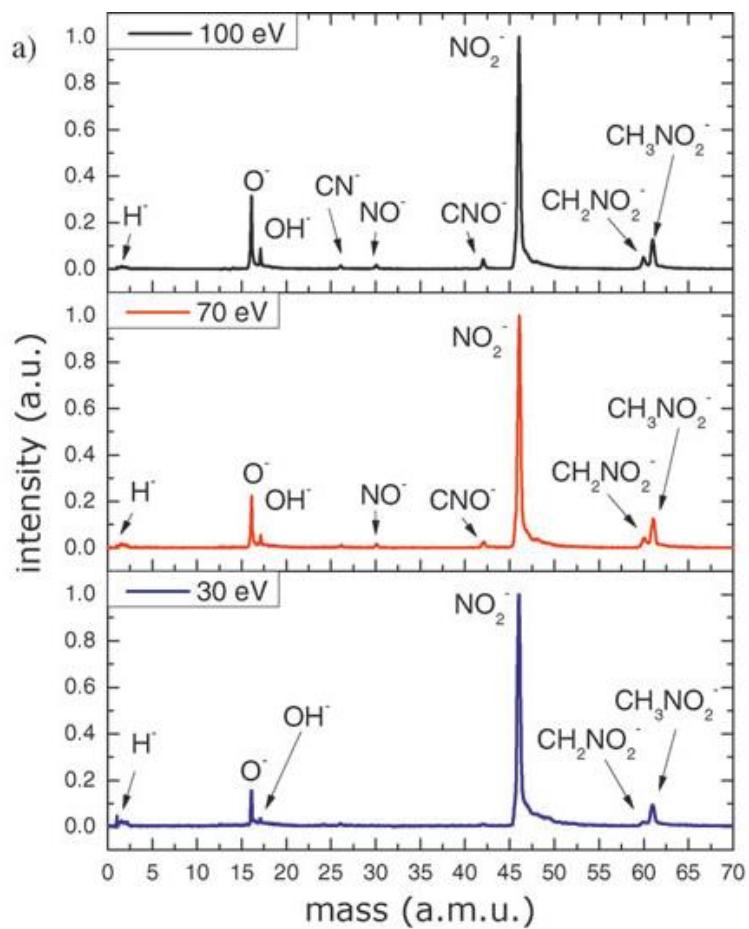
Table 1 Scaled virtual orbital energies (SVOEs) from HF/6-31G* calculations for the optimized neutral equilibrium molecules (see Fig. 1), in eV

Compound	π_1^*	π_2^*	π_3^*	$\sigma^*(N-CH_3)$
3meU	0.40	1.94	5.39	6.06
1meT	0.48	1.91	5.58	5.35



K + CH₃NO₂ and K + CD₃NO₂

uncertainty ≈ 20%



Conclusions

- site- and bond-selective mechanism in purines;
- the electron donor can greatly affect the chemical pathways of the reaction (e.g. CH_3NO_2);
- compared to an isolated TNI formed by free electron capture, the anion in the vicinity of a K^+ favours dissociation rather than autodetachment;
- K^+ may delay autodetachment, allowing for intramolecular electron transfer
- Branching ratios (uncertainties up to 20%) and the collision dynamics;
- Provide K^+ energy loss profiles.