Réactivité bimoléculaire

Riccardo Spezia
riccardo.spezia@univ-evry.fr

CNRS – Université d'Evry-Val-d'Essonne

23/01/2017 Label Chimie Théorique

Outline

Collisions

- Elastic scattering: $A + B \rightarrow A + B$
  No rovibrational energy exchange during collision
- Inelastic scattering: $A + B \rightarrow A^* + B^*$
  The molecule(s) is (are) rovibrationally excited. This can lead to dissociation of excited species (see unimolecular dissociation theory and experiments)
- Reactive scattering: $A + B \rightarrow C + D$ This is a chemical reaction : new species are formed !

Potential at long distance I

Classical electrostatic interactions.

- Strong interaction: if one partner has a charge (ion) or a permanent dipole. This gives rise to the **Induction Energy**.
  Long-range attraction to an ion of charge q ($E = q/R^2$):

$$V_{induction}(R) = -\frac{1}{2}\alpha E^2 = -\frac{\alpha q^2}{2R^4} \tag{1}$$

  Long-range attraction to a permanent dipole μ ($E = \mu/R^3$):

$$V_{induction}(R) = -\frac{\alpha \mu^2}{2R^6} \equiv -\frac{C_{ind}}{R^6} \tag{2}$$

Potential at long distance II

For an ion interacting with a molecule with a permanent dipole there is an extra $\mu \cdot \mathbf{E}$ term, such that

$$V(R) = -\mu \cdot \mathbf{E} - \frac{1}{2}\alpha E^2 = -\frac{\mu q \cos\gamma}{R^2} - \frac{\alpha q^2}{2R^4} \tag{3}$$

- If atoms or molecules have no permanent charge or dipole moment. There can be a fluctuating dipole that averages out of zero. It can be associated to transition dipole moment of the atom (or the molecule). We can see it by taking the simple example of an atom with an s and three p states of energy $\epsilon_0 = -\hbar\omega_0$ and $\epsilon_1 = \hbar\omega_0$. The Hamiltonian without the electric field is:

$$\mathcal{H}_0 = \hbar\omega_0 \left(-|s\rangle\langle s| + \sum_\alpha |p_\alpha\rangle\langle p_\alpha| \right) \tag{4}$$

Potential at long distance III

Introducing the field we can express the perturbation Hamiltonian as:

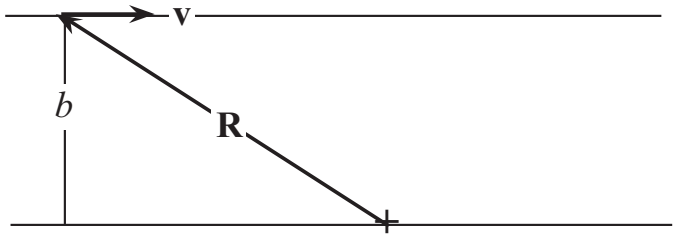
$$\mathcal{H}_E = -\hat{\mu} \cdot \mathbf{E}^0 = \hbar \sum_\alpha \left(|s\rangle\langle p_\alpha + |p_\alpha\rangle\langle s| \right) \xi_\alpha \tag{5}$$

where $\hbar\xi_\alpha = \langle s|\hat{\mu}_\alpha|p\rangle$. The final ground state wave function will be a mixing of s and p states which is the quantum picture of the classical fluctuating dipole.

- This gives rise to the **Dispersion Energy**.
  The resulting long-range attraction is:

$$V_{dispersion} = \frac{1}{2}\left(\alpha_2 E_1^2 + \alpha_1 E_2^2\right) = -\frac{\alpha_2\mu_1^2 + \alpha_1\mu_2^2}{2R^6} \equiv -\frac{C_{disp}}{R^6} \tag{6}$$

The approaching motion



Being R the relative distance of the colliding A + B molecules, the motion of this coordinates looks like the motion of a single particle with mass $\mu = m_A m_B/(m_A + m_B)$, called the reduced mass. b is the impact parameter, which corresponds to a miss-distance. If $b = 0$ the two particles run into one another head-on. In absence of a force, we can use a simple expression for R at any time t:

$$R^2 = v^2 t^2 + b^2 \tag{7}$$

If there is no force **b** is perpendicular to **v** at any time, otherwise **b** must be specified before the collision (and set at a distance large enough such that there is no interaction).

The centrifugal barrier I

To examine the classical trajectory we can use the conservation of energy.

- In absence of the force, the kinetic energy for $R \to \infty$ is:

$$E_T = \mu v^2/2 \tag{8}$$

During the collision it changes the magnitude and the direction of **R**:

$$K = \mu \left(\frac{d\mathbf{R}}{dt} \right)^2 \tag{9}$$

Using the relation 8 we have that $dR^2/dt = 2R(dR/dt) = 2v^2 t$ and the kinetic energy along the lince of centers is found to be $(\mu/2)(dR/dt)^2 = E_T(1 - b^2/R^2)$

The centrifugal barrier II

Without a force the kinetic energy before and during the collision have to be equal

$$E_T = \frac{\mu}{2} v^2 = \frac{\mu}{2} \left(\frac{dR}{dt} \right)^2 + \frac{E_T b^2}{R^2} \tag{10}$$

The second term is the **centrifugal energy**

- In the presence of a force, the conservation of energy reads:

$$E_T = K + V(R) = \frac{1}{2} \mu \left(\frac{dR}{dt} \right)^2 + \frac{E_T b^2}{R^2} + V(R) \tag{11}$$

To focus the attention on $R(t)$ is useful do define an effective potential:

$$V_{eff}(R) = V(R) + \frac{E_T b^2}{R^2} \tag{12}$$

The centrifugal barrier III

The total energy is

$$E_T = \frac{1}{2}\mu\dot{R}^2 + V_{eff}(R) \tag{13}$$

and now is function only of the scalar quantity R. The centrifugal energy acts as a repulsive contribution to V_{eff}, called **centrifugal barrier**.

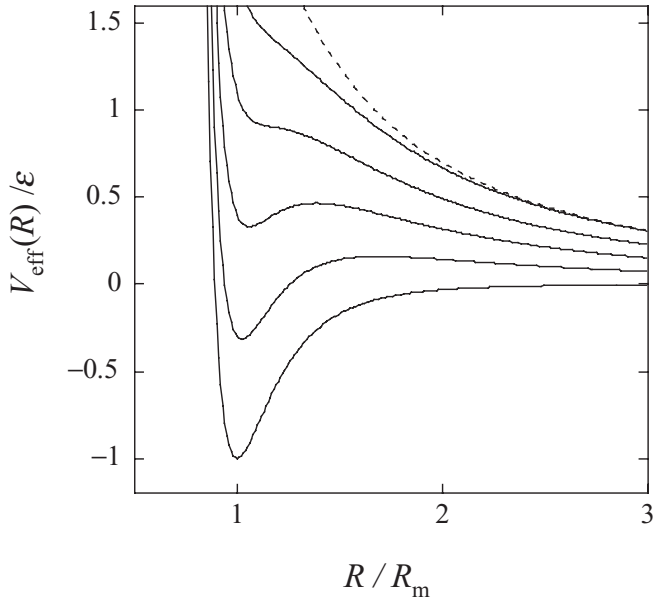


Figure 2.9 A plot of the effective potential for several (increasing) values of the impact parameter. At high b values the well in the potential $V(R)$ is filled in and the effective potential is purely repulsive. The dashed line is the centrifugal barrier alone for the last case.

The center-of-mass system

The description of the motion of two point particles in three-dimensional space requires:
2 (particles) $\times$ 3 (position coordinates) = 6 scalar coordinates.
If there si no external force, it is sufficient to describe the collision in terms of $R(t)$.
Center-of-mass framework: a coordinate system in which the c.m. of the colliding particles is at rest.
The equation

$$\frac{1}{2}\mu R^2 = E_T - V_{eff}(R) = E_T\left(1 - \frac{b^2}{R^2}\right) - V(R) \qquad (14)$$

specifies the scalar velocity with which the particles approach (or recede) in terms of R(t), the collision energy and the impact parameter.

Kinematics in the center-of-mass framework I

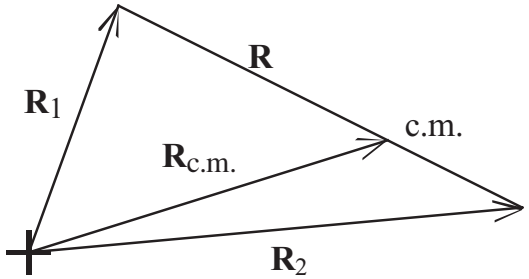


Figure 2.14 Position coordinates of the two colliding particles as well as the position of the center of mass $\mathbf{R}_{c.m.}$ and the relative distance $\mathbf{R}$.

$$\mathbf{v}_1 = d\mathbf{R}_1/dt \quad \mathbf{v}_2 = d\mathbf{R}_2/dt \quad \mathbf{v} \equiv d\mathbf{R}/dt = \mathbf{v}_1 - \mathbf{v}_2 \tag{15}$$

$$\mathbf{R}_{c.m.} \equiv (m_1\mathbf{R}_1 + m_2\mathbf{R}_2)/M \tag{16}$$

$$M = m_1 + m_2 \tag{17}$$

$$\mathbf{R}_i = \mathbf{R}_{c.m.} - (m2/M)\mathbf{R} \tag{18}$$

Kinematics in the center-of-mass framework II

By definition of center of mass at rest: $d\mathbf{R}_{c.m.}/dt = 0$ and so

$$\mathbf{v}_i = \frac{\mathbf{R}_{c.m.} - (m_2/M)\mathbf{R}}{dt} = \left(\frac{d\mathbf{R}_{c.m.}}{dt}\right) - (m_2/M)\mathbf{v} \equiv \mathbf{v}_{c.m.} + \mathbf{u}_i \qquad (19)$$

$$\mathbf{v}_{c.m.} \equiv \frac{d\mathbf{R}_{c.m.}}{dt} = (m_1/M)\mathbf{v}_1 + (m2/M)\mathbf{v}_2 \qquad (20)$$

where $\mathbf{u}_i$ os the velocity of particle i with respect to the center of mass. The kinetic energy in the c.m. system is thus:

$$K = \frac{1}{2}m_1\mathbf{u}_1^2 + \frac{1}{2}m_2\mathbf{u}_2^2 = \frac{1}{2}\mu\mathbf{v}^2 \qquad (21)$$

Since $\mathbf{v} = \mathbf{v}_1 - \mathbf{v}_2 = \mathbf{u}_1 - \mathbf{u}_2$ and $\mu = m_1 m_2/(m_1 + m_2)$

The collision cross section

- Collision cross section, σ. Defined as: $\lambda = (\sigma n_B)^{-1}$.
  λ : mean free path between two collisions ;
  $n_B = P_B/k_B T$ with P_B the target gas pressure.
  Collision rate constant, $k(v) = v\sigma$ where v is the molecule speed.
  Averaging on temperature: $k(T) = \langle k(v) \rangle = \langle v\sigma \rangle \approx \langle v \rangle \sigma$
- Microscopic definition: differential collsion cross section.

$$d\sigma = 2\pi b db \tag{22}$$

$$\sigma = \int 2\pi b db \tag{23}$$

The reaction cross section I

- If $k(v)$ is the chemical reaction rate constant for molecules colliding with a velocity v, then:

$$k(v) = v\sigma_R \tag{24}$$

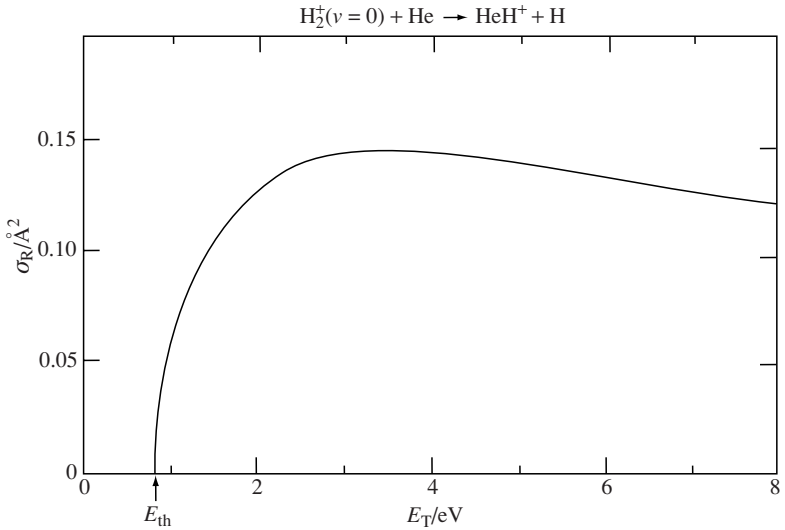


Figure 3.1 Translational energy dependence of the reaction cross-section, $\sigma_R(E_T)$ for the $H_2^+(v = 0) + He \rightarrow HeH^+ + H$ reaction [adapted from T. Turner, O. Dutuit, and Y. T. Lee, *J. Chem Phys.* **81**, 3475 (1984)]. For this ion–molecule reaction the observed threshold energy is equal to the minimal possible value, the endoergicity of the reaction. Exoergic ion–molecule reactions often have no threshold.[3] By exciting the vibrations of the H_2^+ reactant the cross-section for the reaction above can be considerably enhanced.

The reaction cross section II

- Temperature dependence of the reaction rate constant. Average is done by evaluating the integral over a Maxwell-Boltzmann velocity distribution, $f(v)$:

$$
\begin{aligned}
k(T) &= \langle v\sigma_R(v)\rangle && (25)\\
&= \int v\sigma_R f(v)dv && (26)\\
&= (\mu/2\pi k_B T)^{3/2} \int v\sigma_R \exp\left(-\mu v^2/2k_B T\right)4\pi v^2 dv && (27)\\
&= (8k_B T/\pi\mu)^{1/2} \int \frac{E_T}{k_B T}\sigma_R \exp\left(-E_T/k_B T\right)d\left(\frac{E_T}{k_B T}\right) && (28)
\end{aligned}
$$

where we used the relation $E_T = \mu v^2/2$

The reaction cross section III

- Microscopic view. Giving collisions in a range b to $b + db$, the cross-section is defined in terms of the opacity function $P(b)$:

$$d\sigma_R = 2\pi b P(b) db \tag{29}$$

where $2\pi b db$ is the area presented to the colliding reactants when $b \in [b, b + db]$.
$P(b)$: the fraction of all such collisions that lead to reaction.
Not all collisions react, such that the non-reactive cross section is:

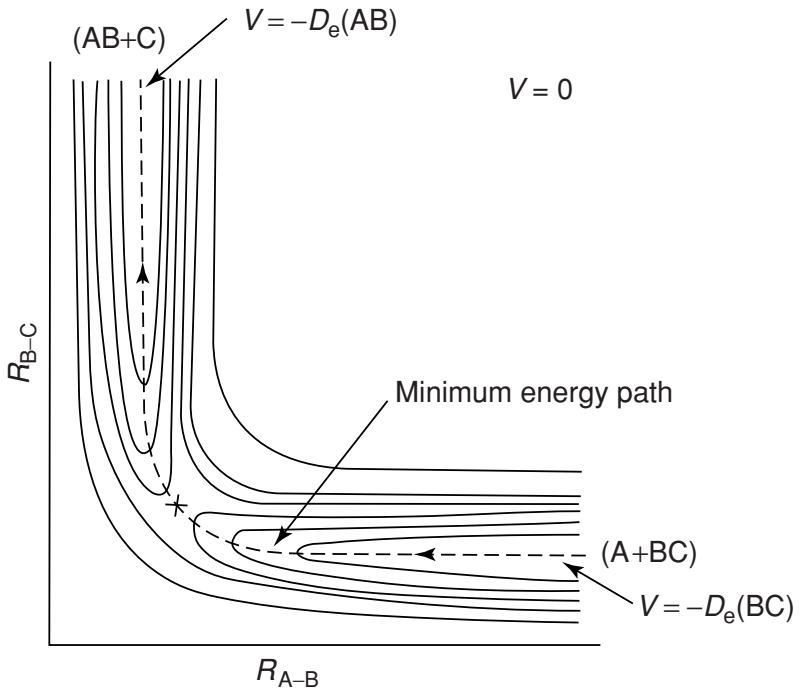
$$d\sigma_{NR} = 2\pi b[1 - P(b)] db \tag{30}$$

The total reaction cross-section is:

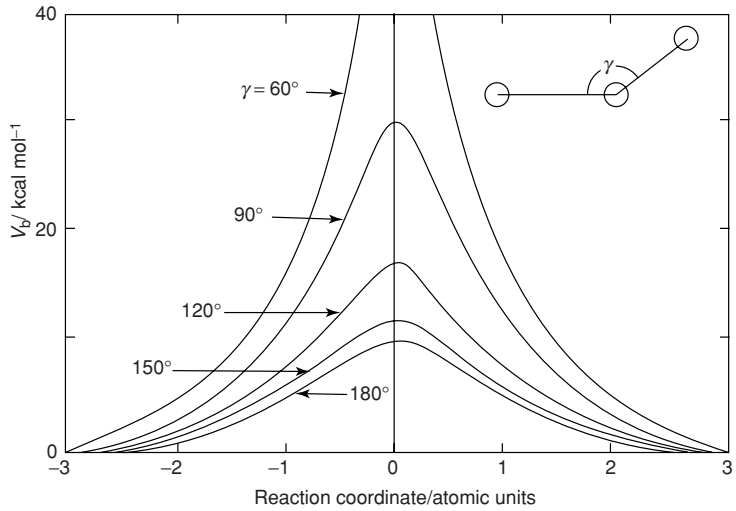
$$\sigma_R = 2\pi \int_0^\infty b P(b) db \tag{31}$$

Motion on the Potential Energy Surface (PES) I

Contour map for collinear collisions

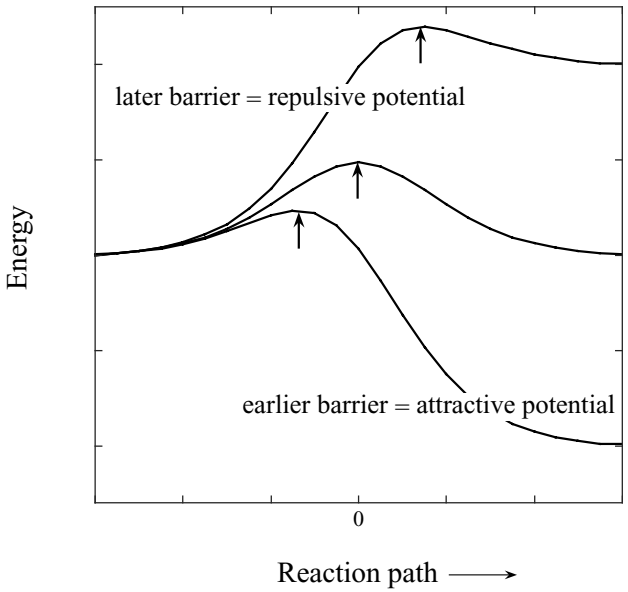


Angular effect

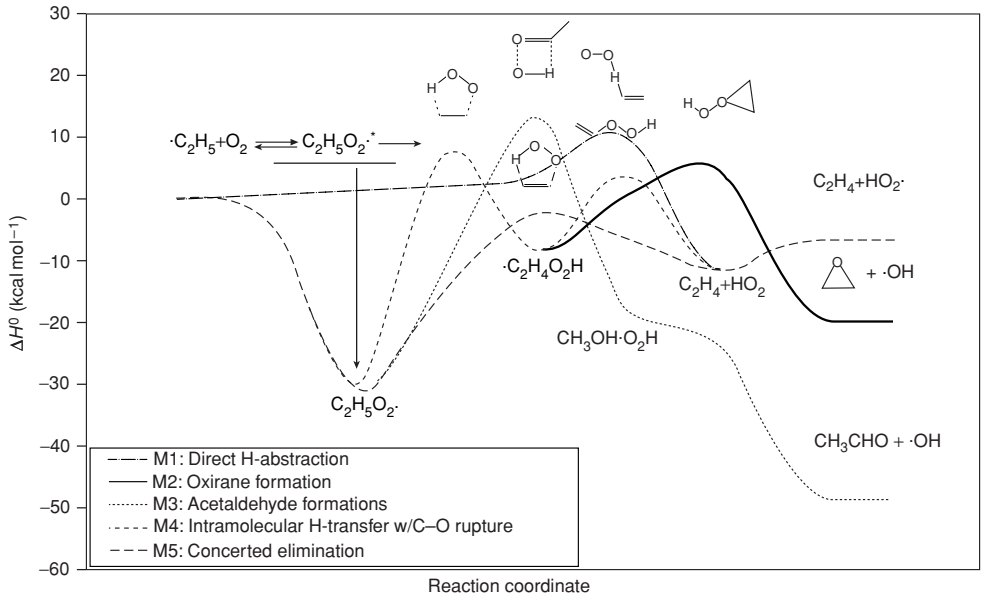


Motion on the Potential Energy Surface (PES) II

The reaction path

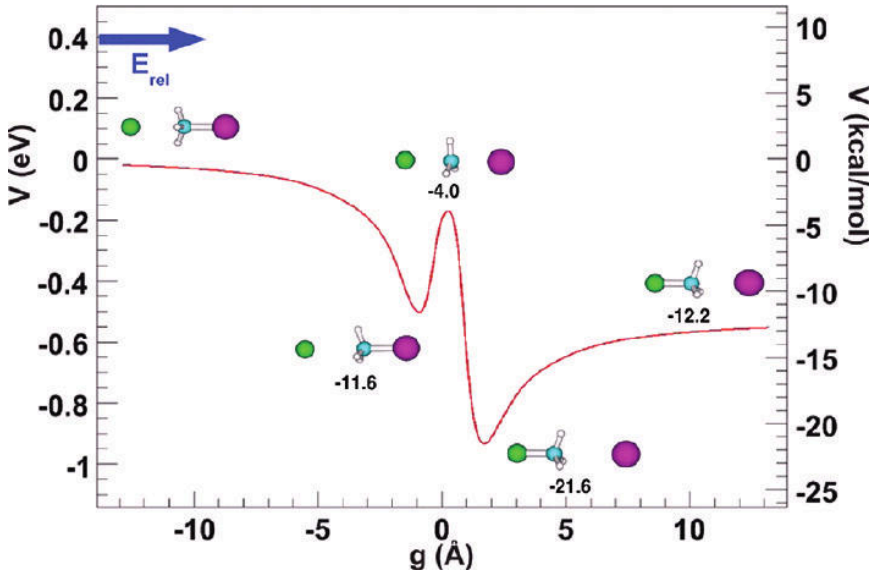


Complex multi-products reaction:



SN_2 reaction: $X^- + CH_3Y \rightarrow XCH_3 + Y^-$

An example of theory and simulations together[1]



The reaction can be schematized as:

$$X^- + CH_3Y \rightleftharpoons X^- - -CH_3Y \rightarrow XCH_3 + Y^- \qquad (32)$$

with three rate constants: k_{cap}, k_{diss} and k_{isom}

[1] Manikandan, Zhang, Hase. J. Phys. Chem. A 2012, 116, 3061.

SN_2 reaction: $X^- + CH_3Y \rightarrow XCH_3 + Y^-$

The total rate constant can be written as

$$\begin{aligned} k_{SN2}(E_{rel}, T) &= k_{cap}(E_{rel}, T) \sum_{l=0}^{l_{max}} P(l) \\ &\times \sum_{j=0}^{\infty} \sum_{j_z=-j}^{j} P(j, j_z) \sum_{n=0}^{\infty} P(n) \\ &\times \sum_{J=|l-j|}^{J=|l+j|} P(j) \frac{k_{isom}(E, J)}{k_{diss}(E, J) + k_{isom}(E, J)} \end{aligned} \tag{33}$$

SN_2 reaction: $X^- + CH_3Y \rightarrow XCH_3 + Y^-$

To obtain $P(I)$ one can use simulations to evaluate the maximum value of b and

$$k_{cap}(E_{rel}, T) = v_{rel}\sigma_{cap}(E_{rel}, T) \quad (34)$$

$$\sigma_{cap} = \int_0^{b_{max}} P_r(b) 2\pi b db \quad (35)$$

RRKM modeling vs simulations

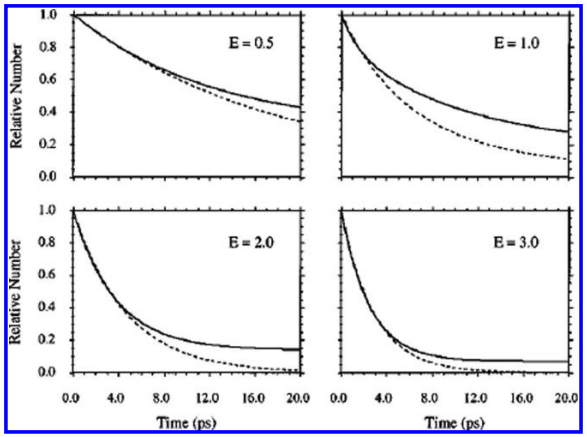


Figure 8. Comparison between trajectory (—) and fitted RRKM (---) values of the relative number of Cl^----CH_3Cl complexes versus time, i.e., $N(t)/N(0)$. The Cl^- + CH_3Cl collision energy E_{rel} is denoted E and is in units of kcal/mol. Adapted from ref 36.

The importance of studying SN2 reactions

J. Am. Chem. Soc. **1988**, *110*, 8355–8359

Evaluation of the Rate Constant for the S_N2 Reaction $CH_3F + H^- \rightarrow CH_4 + F^-$ in the Gas Phase

Angela Merkel,[†] Zdeněk Havlas,*[‡] and Rudolf Zahradník[§]

Contribution from the Central Institute of Physical Chemistry of Academy of Sciences of GDR, 1199 Berlin-Adlershof, Rudower Chaussee 5, German Democratic Republic, Institute of Organic Chemistry and Biochemistry, Czechoslovak Academy of Sciences, Flemingovo nám. 2, 16610 Prague 6, Czechoslovakia, and J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, Dolejškova 3, 18223 Prague 8, Czechoslovakia. *Received February 19, 1988*

Merkel et al.

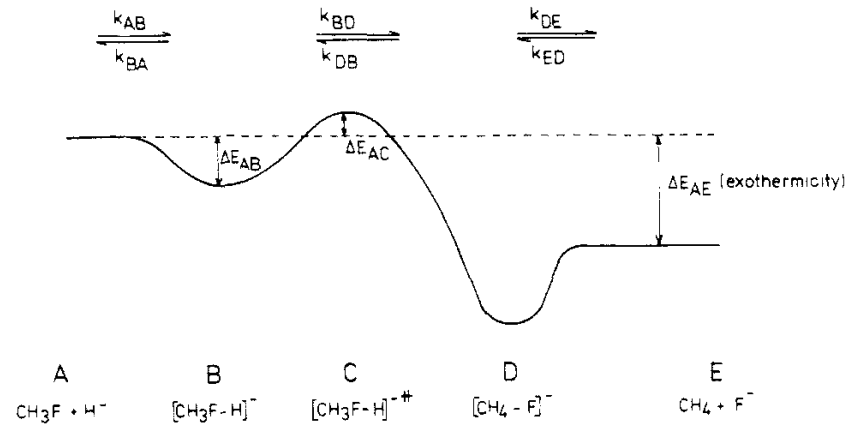


Figure 1. Schematic potential energy profile of the reaction $CH_3F + H^- \rightarrow CH_4 + F^-$.

Molecules in the interstellar medium

- Radioastronomy observed many molecules in the space

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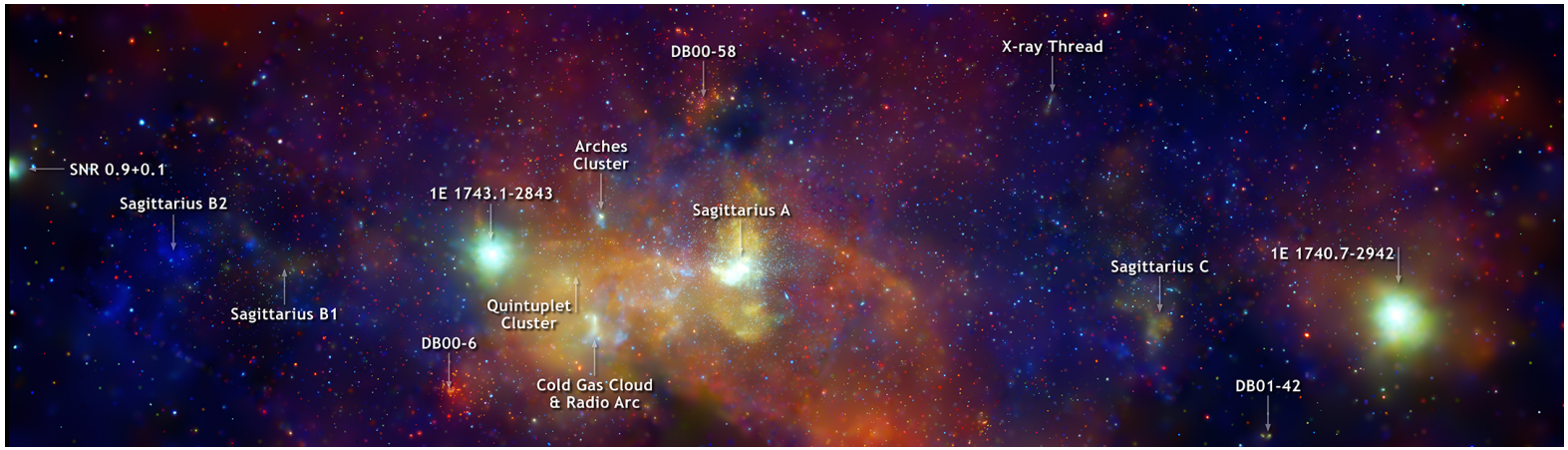
- Molecules with peptide bond (–NHCO–) were observed in the ISM: giant molecular clouds (Orion-KL, **Sgr B2**) and over dozen of molecular clouds in our Galaxy



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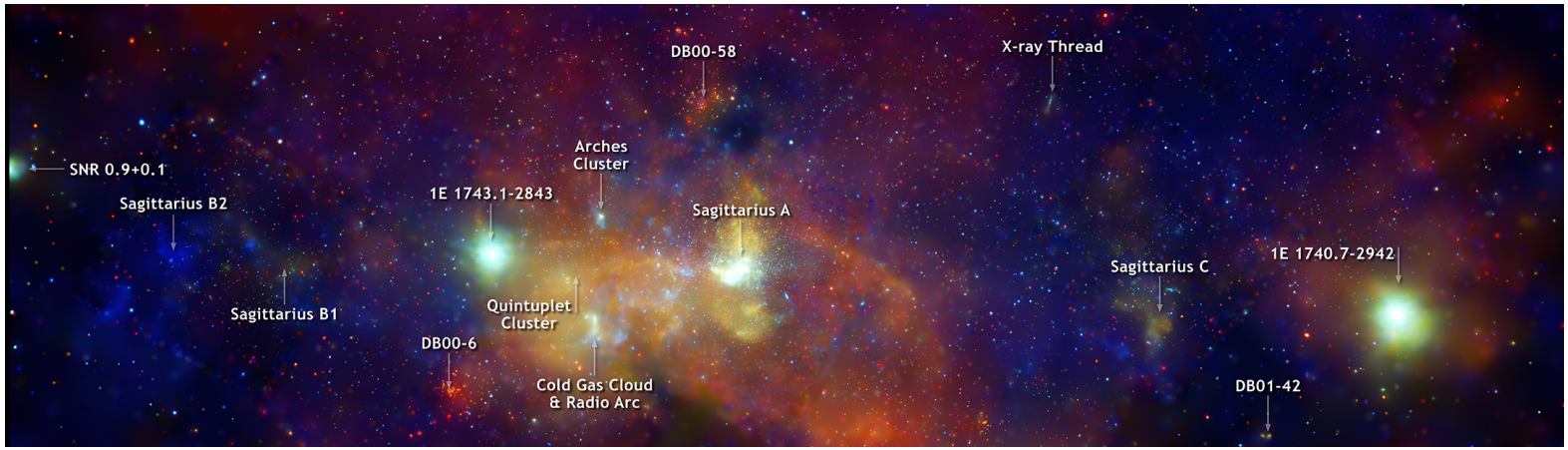

- Extraterrestrial origin of life ...

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- Other solution is : ion-molecule reaction. The ion can have some translation energy and in presence of magnetic field it can be even more accelerated

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  Venus + MSINDO
  Venus + MOPAC (AM1, PM3, PM6, ...)
- Experiments: mass spectrometry as a chemical reactor (e.g. Bohme)

Formamide in the ISM

Rubin, et al. 1971, ApJ, 169, L39

The Astrophysical Journal, 743:60 (12pp), 2011 December 10 doi:10.1088/0004-637X/743/1/60

FORMATION OF PEPTIDE BONDS IN SPACE: A COMPREHENSIVE STUDY
OF FORMAMIDE AND ACETAMIDE IN Sgr B2(N)

D. T. Halfen[1,2,3], V. Ilyushin[4], and L. M. Ziurys[1,2,3]
[1] Departments of Chemistry and Astronomy, University of Arizona, Tucson, AZ 85721, USA; halfendt@as.arizona.edu, lziurys@as.arizona.edu
[2] Arizona Radio Observatory, University of Arizona, Tucson, AZ 85721, USA
[3] Steward Observatory, University of Arizona, Tucson, AZ 85721, USA
[4] Institute of Radio Astronomy of the National Academy of Sciences Ukraine, Chervonopraporna 4, 61002 Kharkov, Ukraine
Received 2011 June 29; accepted 2011 August 25; published 2011 November 22

Observed in giant molecular clouds (Orion-KL, Sgr(B2)) but also in dozen of molecular clouds through space

The high abundances of acetamide and formamide in Sgr B2(N) additionally suggest that there might be other plausible synthetic routes to simple peptide polymers that do not involve amino acids.

Formamide in the ISM

THE ASTROPHYSICAL JOURNAL, 780:181 (7pp), 2014 January 10 doi:10.1088/0004-637X/780/2/181

SOME INSIGHTS INTO FORMAMIDE FORMATION THROUGH GAS-PHASE REACTIONS IN THE INTERSTELLAR MEDIUM

PILAR REDONDO, CARMEN BARRIENTOS, AND ANTONIO LARGO
Computational Chemistry Group, Departamento de Química Física, Facultad de Ciencias, Universidad de Valladolid, E-47011 Valladolid, Spain; predondo@qf.uva.es
Received 2013 October 3; accepted 2013 November 21; published 2013 December 23

- Ion-molecule reaction with the smallest barrier (0.12 eV) is: $NH_2OH_2^+ + H_2CO \rightarrow NH_2CHOH^+ + H_2O$

Formamide in the ISM

THE ASTROPHYSICAL JOURNAL, 780:181 (7pp), 2014 January 10 doi:10.1088/0004-637X/780/2/181

SOME INSIGHTS INTO FORMAMIDE FORMATION THROUGH GAS-PHASE REACTIONS IN THE INTERSTELLAR MEDIUM

PILAR REDONDO, CARMEN BARRIENTOS, AND ANTONIO LARGO
Computational Chemistry Group, Departamento de Química Física, Facultad de Ciencias, Universidad de Valladolid, E-47011 Valladolid, Spain; predondo@qf.uva.es
Received 2013 October 3; accepted 2013 November 21; published 2013 December 23

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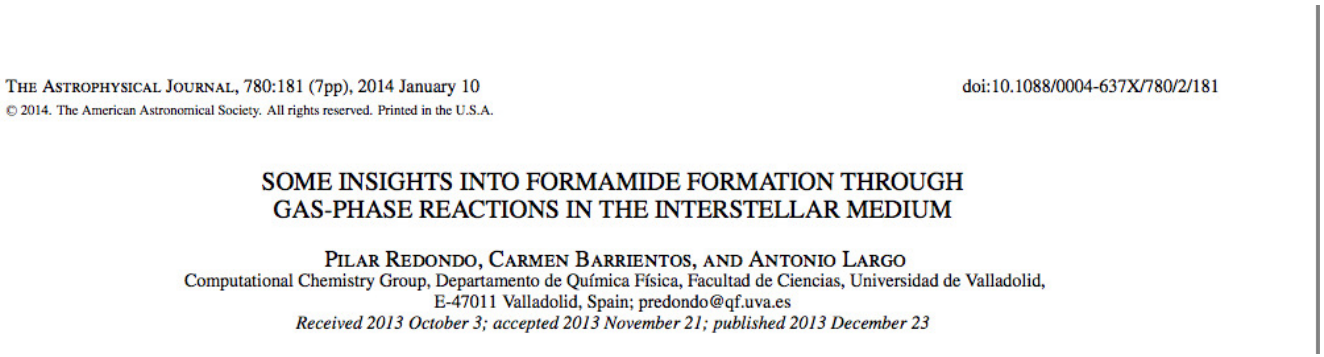
Formamide in the ISM



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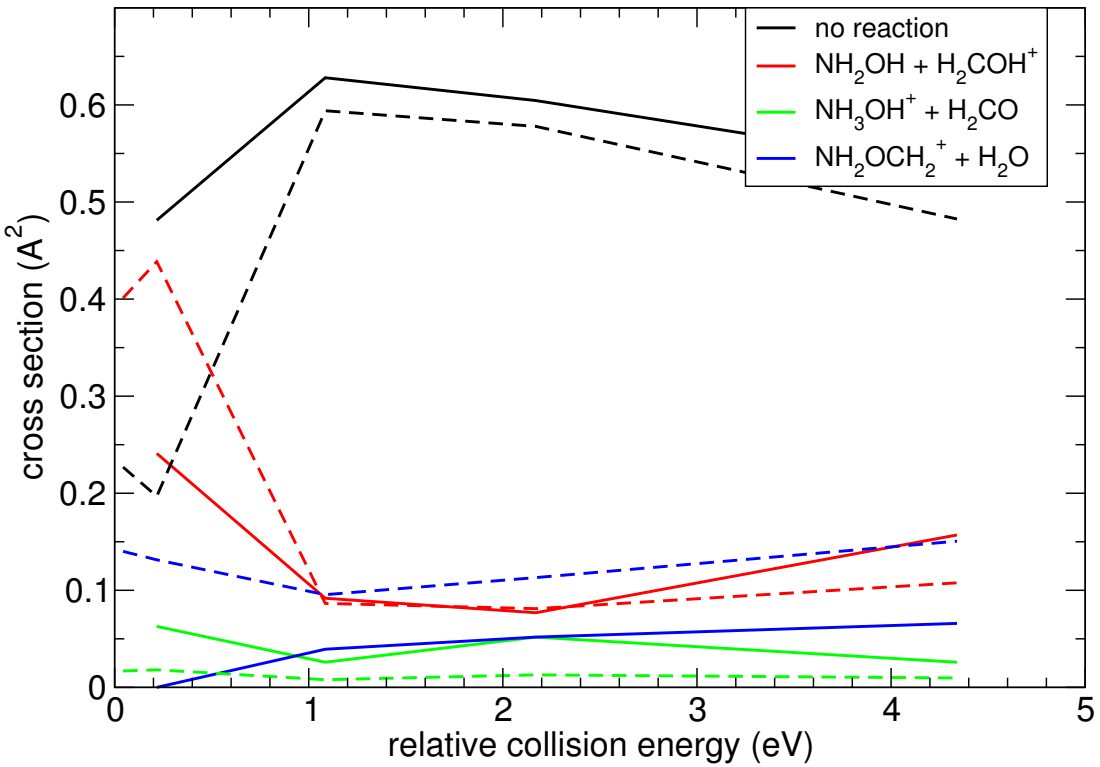
- MP2/6-31G(d,p) and MSINDO Born-Oppenheimer chemical dynamics

Formamide synthesis

Cross section

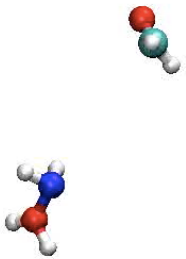
$$NH_2OH_2^+ + H_2CO \rightarrow NH_2OCH_2^+ + H_2O \ (\Delta E = \text{-}0.9 \text{ eV})$$



Formamide synthesis

Mechanism

$$NH_2OH_2^+ + H_2CO \rightarrow NH_2OCH_2^+ + H_2O$$



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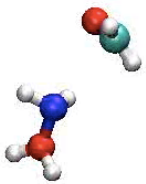

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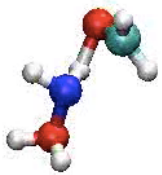

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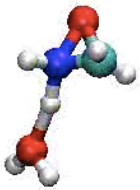

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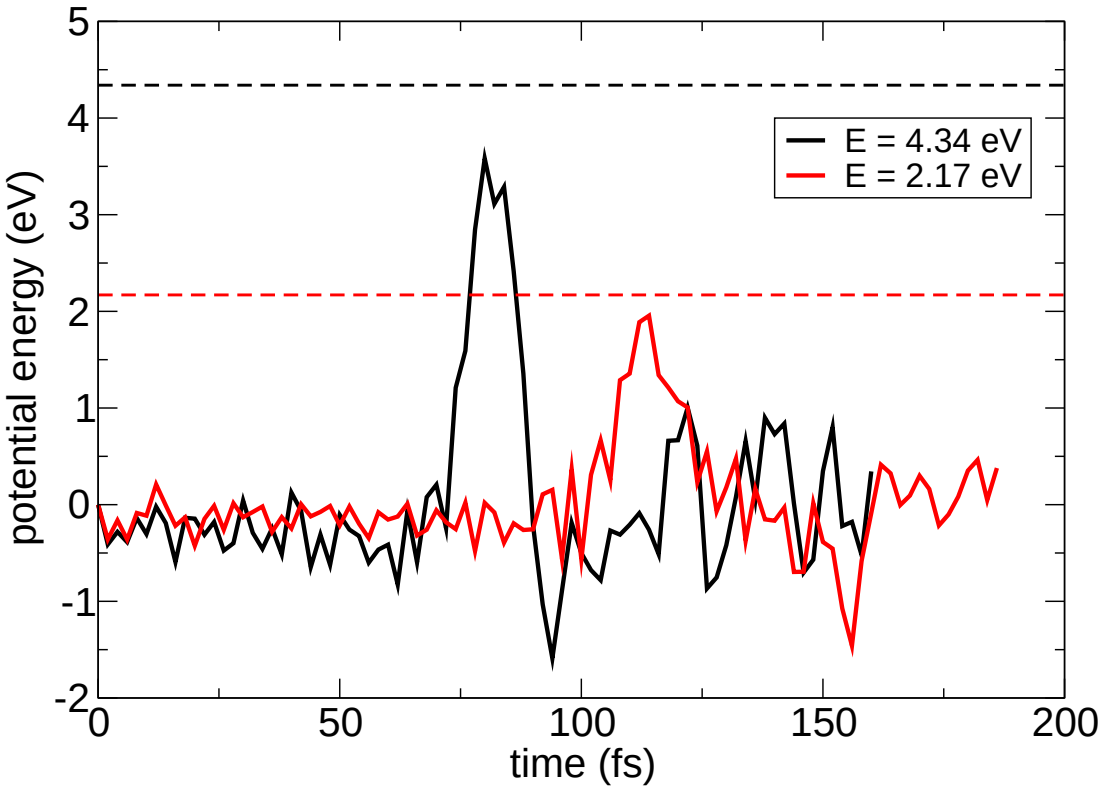
Formamide synthesis

Energetics

$$NH_2OH_2^+ + H_2CO \rightarrow NH_2OCH_2^+ + H_2O$$



Other products

$NH_4^+ + H_2CO$ and $NH_3 + H_2COH^+$

$NH_4^+ + H_2CO \rightarrow NH_2CHOH^+ + H_2$: ΔE = -0.16 eV but not observed

$NH_4^+ + H_2CO \rightarrow NH_3CHO^+ + H_2$: ΔE = -0.7 eV but not observed

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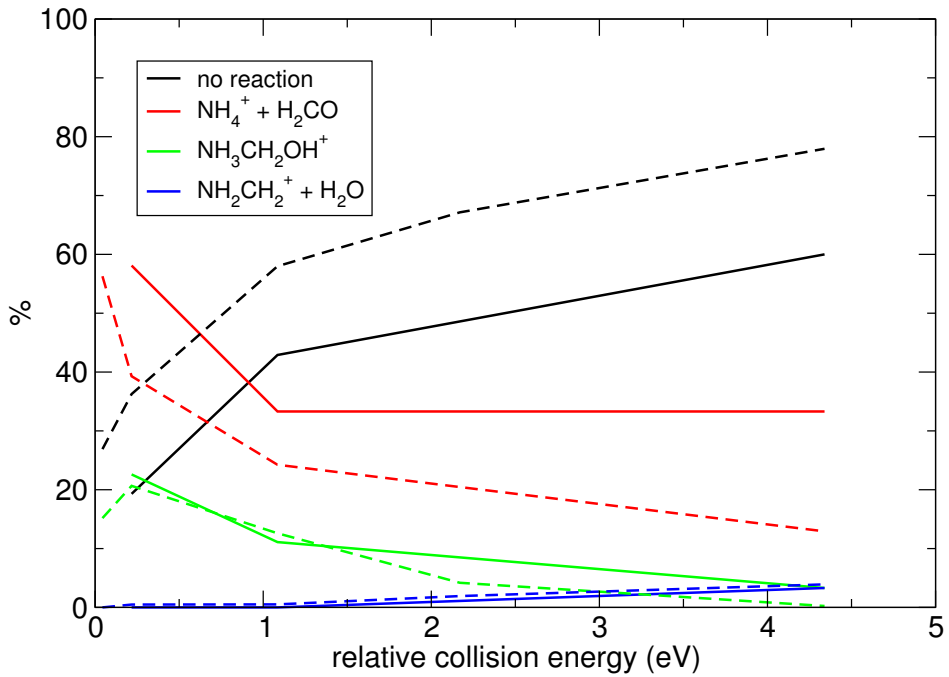
$NH_3 + H_2COH^+ \rightarrow NH_2CH_2^+ + H_2O$: ΔE = -1.6 eV

$NH_3 + H_2COH^+ \rightarrow NH_3CH_2OH^+$: ΔE = -1.6 eV (radiative association)



Other products

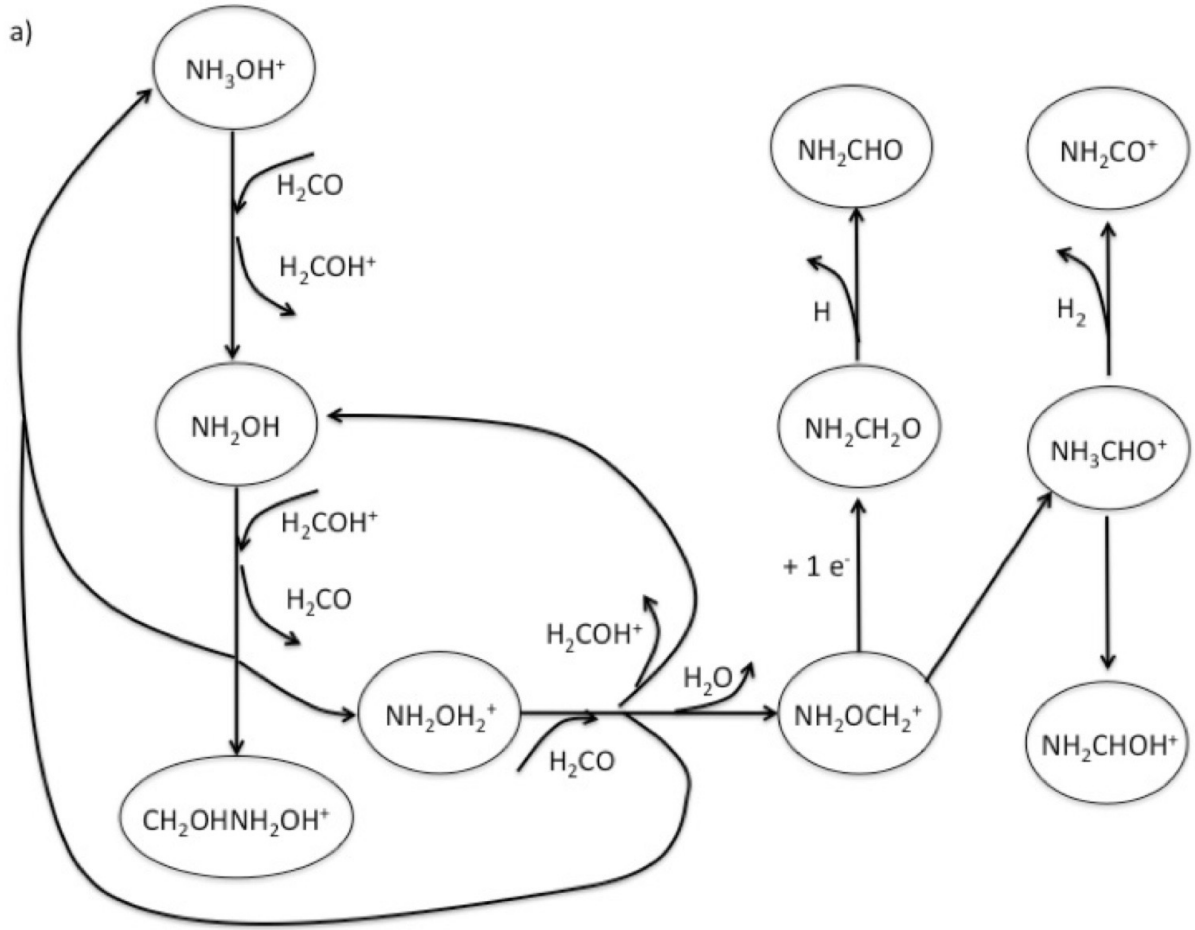
$NH_3 + H_2COH^+$

$NH_3 + H_2COH^+ \rightarrow NH_2CH_2^+ + H_2O$: ΔE = -1.6 eV
$NH_2CH_2^+$ has not yet been observed in the ISM.
But it can further react :

1. Dissociative recombination $NH_2CH_2^+ + e^- \rightarrow NH_2CH + H$
   NH_2CH was observed in 1973
2. Radiative association $NH_2CH_2^+ + CN^- \rightarrow NH_2CH_2CN + h\nu$:
   ΔE = -7.2 eV
   NH_2CH_2CN was observed in 2008. The radiative association can go through vibrational relaxation ($k_r = 29\ s^{-1}$) but also through excited states (S_1 is at about 6 eV).

Formamide synthesis

Summary of reaction mechanisms



NH_2CHO: observed in 1971 ; NH_2CO^+: observed in 2013;

Spezia et al. Astrophy. J. 826, 107 (2016).

Formamide synthesis

The Astrophysical Journal, 826:107 (8pp), 2016 August 1 doi:10.3847/0004-637X/826/2/107

SYNTHESIS OF FORMAMIDE AND RELATED ORGANIC SPECIES IN THE INTERSTELLAR MEDIUM VIA CHEMICAL DYNAMICS SIMULATIONS

Riccardo Spezia[1], Yannick Jeanvoine[1], William L. Hase[2], Kihyung Song[3], and Antonio Largo[4]
[1] CNRS, Laboratoire Analyse et Modélisation pour la Biologie et l'Environnement, UMR 8587, Université d'Evry-Val-d'Essonne, Evry, France; riccardo.spezia@univ-evry.fr
[2] Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, TX 79409, USA
[3] Department of Chemistry, Korea National University of Education, Chungbuk, Korea
[4] Computational Chemistry Group, Departamento de Quimica Fisica, Facultad de Ciencias, Universidad de Valladolid, Valladolid, Spain
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