Theoretical studies of sulfur bearing molecular systems of astrochemical interest

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Motivation: Sulfur deficit

Sulfur is an abundant element in the universe. With a relative abundance with respect to hydrogen of 1.5×10^{-5} (cosmic abundance) it has attracted interest in the astrophysics community[1]. In diffuse clouds, only few molecules have been so far detected $(\mathrm{SO}, \mathrm{SO}_2, \mathrm{OCS}, \mathrm{H}_2\mathrm{S}$, etc.), with relative abundance similar to the corresponding cosmic abundance[1] . On the contrary, in dense clouds, with a much lower temperature ($\sim 10\mathrm{K}$) the abundance ratio of sulfur, measured in gas phase, is about a factor 1000 times lower than the cosmic abundance[1]. One possibility to rationalize this problem is that sulfur is deposited in interstellar ices. These ices sublimate in hot cores or strong shocks appearing in the star formation, so that sulfur is expected to be back in gas phase. However, observations in hot cores of gas phase molecules report a relative abundance at least 10 times lower than the corresponding for cosmic abundance[2].

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[1] D. Rehder, Chemistry in space (Wiley, 2010), D.A. Neufeld, *et al.*, Astron. & Astrophys. 449, A577 (2015)

[2] A. Tieftrunk,*et al.*, Astron. & Astrophys. 289, 579 (1994)

Motivation: Sulfur deficit

A solution to this sulfur deficit enigma is either that sulfur remain in solid grains (hidden to observations due to other more intense signals) or in gas phase forming molecules not yet detected or assigned.
Sulfur incorporates to ices preferentially as $\mathrm{H_2S}$, but is difficult to observe it [because its bands coincide with those from methanol, which are more intense]. Recent estimations establish an upper limit of 1% of $\mathrm{H_2S}$ with respect to $\mathrm{H_2O}$, providing a relative abundance 10 times lower than the cosmic abundance. Newly reported experiments have demonstrated that irradiated ices with $\mathrm{H_2S}$ produce $\mathrm{H_2S_2}$ or $\mathrm{S_2H}$, which photo-dissociate in $\mathrm{S_2}$ and $\mathrm{S_3}$[3] . The latter molecules have not been detected in space, $\mathrm{S_2H}$ does, but in a lower amount than in the laboratory[4]. For this reason it is supposed that this last molecule is either photo-dissociated or react in gas phase with some other species. **Thus, accurate data for the $\mathbf{S_2H}$ destruction pathways in gas phase are required**

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[3] A.Jiménez-Escobar,*et al.*,Astron. & Astrophys., 536,A91 (2011)

[4] R. Martín-Domenech, *et al.* Astron. & Astrophys. 585, A112 (2016)

Motivation: Sulfur-Silicon molecules

Other S-bearing molecule of interest is SiS. This molecule is detected in high abundance in the envelopes of carbon/oxygen-rich stars, together with SiO. The difference between these two molecules is that SiO is also detected with high abundance in shocks of the ISM associated with newly formed stars or with supernova ejects while SiS has only been detected so far in the ISM in Orion and L1157, both submitted to high velocity shocks. It is then important to understand the differences between SiS and SiO, in particular, why SiS is not detected in environments where SiO is observed, since in evolved stars both species are formed under tyhermodynamical equilibirum near the photosphere of the star. **It is then important to study the reactions that depleting SiS**.

Motivation

Simulation models, as Meudon PDR[5], are used to estimate elemental abundances. Kinetic and thermodynamic models are required considering accurate rate constants for all the considered collision processes are needed[6].

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[5] Le Petit *et al.* 2006, http://ism.obspm.fr.

[6] KIDA,KInetics Database for Astrochemistry http://kida.obs.u-bordeaux1.fr/

Motivation: Kinetic models

Reaction	Rate Reaction
$\cdots$	$\cdots$
$O(^1S) + O_2(a^1) \rightarrow O + O + O$	3.2×10^{-11}
$O(^1S) + NO \rightarrow O + NO$	2.9×10^{-10}
$O(^1S) + NO \rightarrow O(^1D) + NO$	5.1×10^{-10}
$O(^1S) + O_3 \rightarrow O_2 + O_2$	2.9×10^{-10}
$O(^1S) + O_3 \rightarrow O_2 + O + O(^1D)$	2.9×10^{-10}
$O(^1S) + N_2O \rightarrow O + N_2O$	6.3×10^{-12}
$O(^1S) + N_2O \rightarrow O(^1D) + N_2O$	3.1×10^{-12}
$N + NO \rightarrow O + N_2$	$1.8 \times 10^{-11} \times (\mathrm{Tgas}/300.0)^{0.5}$
$N + O_2 \rightarrow O + NO$	$3.2 \times 10^{-12} \times (\mathrm{Tgas}/300.0) \times \cdots$
$N + NO_2 \rightarrow O + O + N_2$	9.1×10^{-13}
$N + NO_2 \rightarrow O + N_2O$	3.0×10^{-12}
$N + NO_2 \rightarrow N_2 + O_2$	7.0×10^{-13}
$N + NO_2 \rightarrow NO + NO$	2.3×10^{-12}
$O + N_2 \rightarrow N + NO$	$3.0 \times 10^{-10} \times \exp(-38370.0/\mathrm{Tgas})$
$O + NO \rightarrow N + O_2$	$7.5 \times 10^{-12} \times (\mathrm{Tgas}/300.0) \cdots$
$\cdots$	$\cdots$

Motivation

As pointed out elsewhere, a full theoretical description of reactive collision (within the Born-Oppenheimer approximation) requires the knowledge of the potential energy surface (PES) for the molecular system[7]. Once the PES is accurately represented it can be used for molecular dynamics studies, describing then the reaction probabilities and molecular energy transfer during a collision.

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[7] M. Brouard and C. Vallance, editors, Tutorials in Molecular Dynamics (RSC publishing, 2010). M. Y. Ballester, A theoretical Study on the $\mathrm{HSO_2}$ molecular system, Ph.D. thesis, Universidade de Coimbra, http://hdl.handle.net/10316/7489 (2008). Y. Z. Song, *et al.*, Mol. Phys. 116, 129 (2018).

PES, concepts

From quantum mechanics, a molecular system is decribed by the Schrödinger equation. In the case of stationary fields it assumes the form

$$\hat{H}\Psi = E\Psi \tag{1}$$

being $\hat{H}$ the Hamilton operator, Ψ the system wave function and E the energy of the system. $\hat{H}$ is then given by:

$$\hat{H}(\mathbf{r},\mathbf{R}) = \hat{T}_{\mathrm{N}}(\mathbf{R}) + \hat{H}_{\mathrm{e}}(\mathbf{r},\mathbf{R}) \tag{2}$$

where $\hat{T}_{\mathrm{N}}$ stands for the nuclear kinetic energy operator, $\hat{H}_{\mathrm{e}}$ is the electronic Hamiltonian.

PES, concepts

In the frame of the Born Born-Oppenheimer approximation (BOA). The nuclei problem is reduced to:

$$[\hat{T}_{\mathrm{N}} + V_n(\mathbf{R})]\chi_n(\mathbf{R}) = E\chi_n(\mathbf{R}) \tag{3}$$

where $V_n(\mathbf{R})$, stands for the energy resulting from the electronic problem. Within BOA, nuclei move on the potential energy function for a given electronic state.

PES, analytic representation

A global PES for an ABC triatomic system can be represented through a many-body expansion (MBE) scheme which is written as the following analytic functional form[8]

$$V_{\mathrm{ABC}}(\mathbf{R}) = \sum_{A} V^{(1)}_{\mathrm{A}} + \sum_{\mathrm{AB}} V^{(2)}_{\mathrm{AB}}(R_{\mathrm{AB}}) + V^{(3)}_{\mathrm{ABC}}(R_{\mathrm{AB}}, R_{\mathrm{AC}}, R_{\mathrm{BC}}), \qquad (4)$$

where $V^{(1)}_{\mathrm{A}}$ represents the atomic energy in their corresponding electronic states, $V^{(2)}_{\mathrm{AB}}$ the diatomic term and $V^{(3)}_{\mathrm{ABC}}$ the triatomic term.

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[8] J.N. Murrell, S. Carter, S.C. Farantos, P. Huxley and A.J.C. Varandas, *Molecular Potential Energy Functions* (Wiley, Chichester, 1984)

PES, analytic representation

The analytic expression of the diatomic terms ($V_{\mathrm{AB}}^{(2)}$) can also be written as a sum of the short and long-range energy contributions, which is then expressed as:

$$V_{\mathrm{AB}}^{(2)}(R_{\mathrm{AB}}) = V_{\mathrm{short}}^{(2)}(R_{\mathrm{AB}}) + V_{\mathrm{long}}^{(2)}(R_{\mathrm{AB}}), \tag{5}$$

where

$$V_{\mathrm{short}}^{(2)}(R_{\mathrm{AB}}) = \frac{a_0}{R_{\mathrm{AB}}} e^{-\beta_1^{(2)} R_{\mathrm{AB}}}, \tag{6}$$

and

$$V_{\mathrm{long}}^{(2)}(R_{\mathrm{AB}}) = \sum_{i=1}^{n} a_i \left(R_{\mathrm{AB}}\, e^{-\beta_2^{(2)} R_{\mathrm{AB}}} \right)^i, \tag{7}$$

where R_{AB} represents the diatomic internuclear distances. The parameters a_0, a_i, β_1 and β_2 are obtained by fitting *ab initio* points.

PES, analytic representation

The three-body term ($V^{(3)}_{\mathrm{ABC}}$) is written as the Mth-order polynomial

$$V^{(3)}_{\mathrm{ABC}}(\bar{R}) = \begin{cases} \sum_{j,k,l=0}^{M} C_{jkl}\, \rho^{i}_{\mathrm{AB}} \rho^{j}_{\mathrm{AC}} \rho^{k}_{\mathrm{BC}} & (k = l) \\ \sum_{j,k,l=0}^{M} C_{jkl}\, \rho^{i}_{\mathrm{AB}} (\rho^{j}_{\mathrm{AC}} \rho^{k}_{\mathrm{BC}} + \rho^{j}_{\mathrm{BC}} \rho^{k}_{\mathrm{AC}}) & (k \neq l), \end{cases} \tag{8}$$

where $\bar{R} = (R_{\mathrm{AB}}, R_{\mathrm{BC}}, R_{\mathrm{AC}})$, $\rho_{\mathrm{AB}} = R_{\mathrm{AB}}\, e^{-\beta^{(3)}_{\mathrm{AB}} R_{\mathrm{AB}}}$, which also holds for the expressions of ρ_{AC} and ρ_{BC}. The coefficients C_{jkl} and $\beta^{(3)}_{\mathrm{AB}}$ are the linear and nonlinear parameters to be determined in the fitting.

Quasi-classical trajectories

The main idea behind QCT is to solve classical equations for the motion of atomic nuclei on the potential energy resulting from the electronic problem. Initial conditions are such that the classical values of energies and momenta are in accordance with the corresponding quantum values. Of course, once the time evolution follows classical laws, the mentioned values will no longer kept the correct physical meaning. Yet, averaged results from a considerable large number of so calculated trajectories are expected to produce consistent quantities.

QCT

For a given set of translational (E_{tr}), and ro-vibrational energy of the reactants, the reactive/inelastic cross section for a given channel is calculated as:

$$\sigma_r(E_{tr}; v; j; v', j') = \pi b_{max}^2 \frac{N_r}{N_T}(E_{tr}; v; j; v', j') \tag{9}$$

being $\mathrm{N_r}$ the number of reactive/inelastic trajectories for a given channel from a total of N_T.

QCT

Then, if assuming a Maxwell-Boltzmann distribution over the translational energy the initial state specific rate coefficient is obtained as:

$$k(T; v, j, v', j') = g_e(T) \left(\frac{2}{k_B T}\right)^{3/2} \left(\frac{1}{\pi\mu}\right)^{1/2} \int_0^{\infty} E_{tr}\sigma_r(E_{tr}; v; j; v', j') \times \exp\left(\frac{-E_{tr}}{k_B T}\right) dE_{tr} \tag{10}$$

Where T is the temperature, μ is the reduced mass of the reactants, $\mathrm{k_B}$ is the Boltzmann constant, and $g_e(T)$ is a factor accounting for the electronic degeneracy

H_2S^+ PES and dynamics[9]

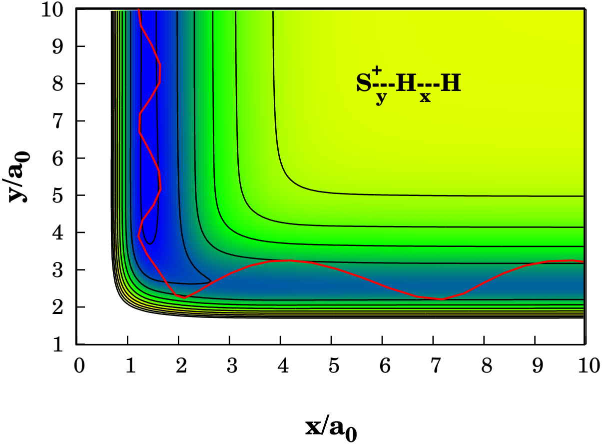

Figure: Contours plot for the $H_2 + S^+ \rightarrow H + HS^+$ reaction PES.

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[9] Y. Z. Song, *et al.*, Mol. Phys. 116, 129 (2018)

H_2S^+ PES and dynamics[10]

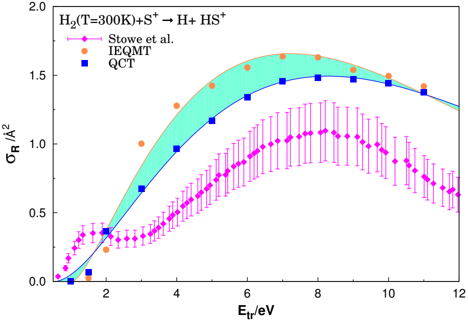

Figure: Calculated and experimental cross-section for $\mathrm{H_2 + S^+ \rightarrow H + HS^+}$ reaction

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[10] Y. Z. Song, *et al.*, Mol. Phys. 116, 129 (2018)

SiSH PES[11]

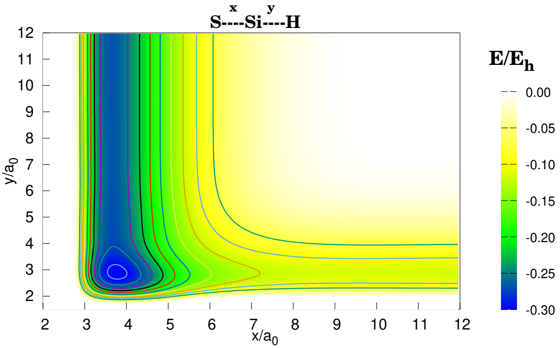

Figure: Contours plot for the $S + SiH \rightarrow H + SSi$ reaction PES

$SO + OH \rightarrow H + SO_2$ at low temperatures[12]

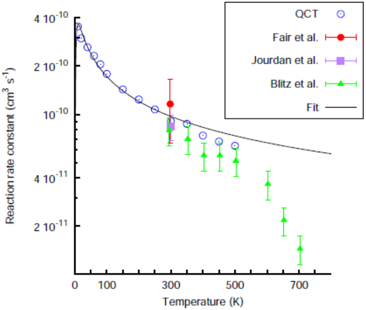

Figure: Rate constant for the $\mathrm{SO} + \mathrm{OH} \rightarrow \mathrm{H} + \mathrm{SO_2}$ reaction

The updated rate constant is 4 times larger than previous values used in simulations. Better accordance of the Astronomical observations was obtained

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[12] A. Fuente, *et al.* Astron. & Astrophys. 624, A105 (2019)

Forthcoming Steps

- Accurately represent interatomic potentials: Validate with experimental evidences (molecular structure, spectroscopic data)
- Calculate rate constants: Good agreement with experimental values. Reliable predictions at the low temperature domain
- Include updated results in the kinetic and termodynamic models
- Rationalize observations

Challenges

- High level electronic structure calculations are expensive.
- Analytically representing a PES requires dealing with functions of more than 3 dimensions.
- The use of machine learning (*e.g.* Neural) needs a huge number of *ab initio* points and needs to circumvent gradient problems
- Models for the calculated cross sections may eventually fail. New models are required.
- Quantum dynamics calculations, involving sulfur atoms are still too expensive

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