Cosmic Ray-Driven Radiation Chemistry *in* Astrochemical Models

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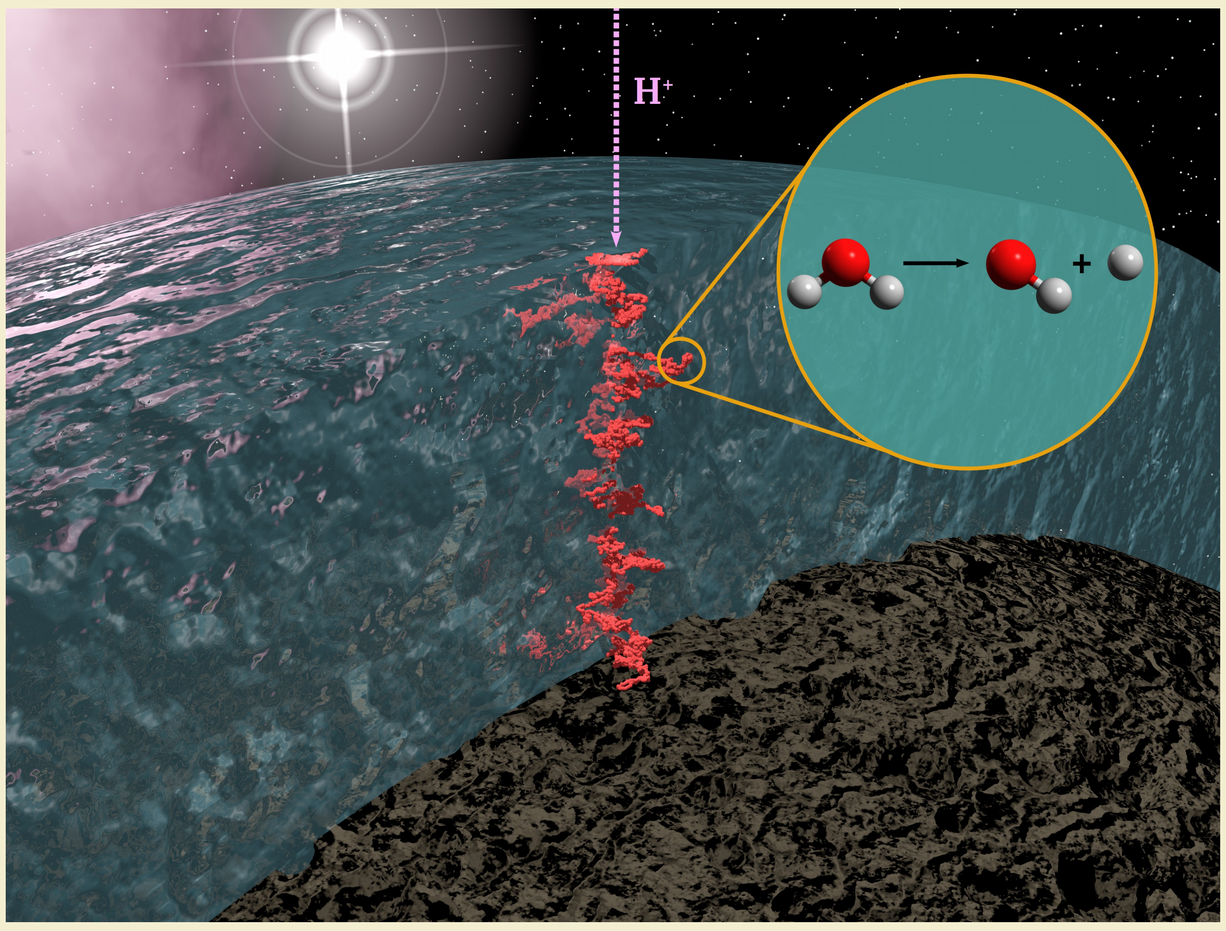
Abstract

Cosmic rays are widely known to have significant physiochemical impact on interstellar sources. In addition, laboratory astrophysics experiments have indicated that cosmic ray interactions with dust grain ice mantles could lead to astrochemically relevant species, including complex organic and prebiotic molecules [1].

In spite of the growing body of experimental work on interstellar radiation chemistry, incorporating cosmic ray-driven reactions and processes into astrochemical models has proven challenging, in part because of a lack of relevant data for many species now included in chemical networks. Recently [2], we have developed a general method of estimating radiochemical yields (G-values), rate coefficients, and decomposition pathways for species that have not been studied in detail in the laboratory in this context. Here, we will describe the derivation and application of our method, as well as point to much needed areas for future development in astrochemical radiation chemistry modeling.



Above) *Pictured here is an illustration of what the bombardment of an interstellar dust grain might look like. In red is a simulated track of the cosmic ray and "secondary electrons" that are formed when the cosmic ray collides with molecules in the ice. This track was generated using the CIRIS program - the first microscopic model that can simulate both the physical and chemical changes that occur in an irradiated solid.* [1]

Suprathermal Species

Example Network

A → A⁺ + e⁻ → B* + C*

A + B* → Products

$$\Rightarrow \quad \frac{dn(B^*)}{dt} = k_{ion\,2}\,n(A) - \nu_0^B\,n(B^*) - k_{ST}\,n(A)\,n(B^*)$$

The Fate of Suprathermal Species in Our Network

Formation of B*

Possibility 1: Quenching

$$\nu_0^B = \left(\frac{2\,N_{site}\,E_b^B}{\pi^2\,m_B}\right)^{\frac{1}{2}}$$

Possibility 2: Reaction

$$k_{ST} = f_{br}\left[\frac{\nu_0^A + \nu_0^B}{N_{site}\,n_{dust}}\right]$$

Theory

Adding Radiation Chemistry to Astrochemical Models: As Easy As 1, 2, 3

1) Elementary Processes

$aA \rightsquigarrow aA^+ + e$

$aA \rightsquigarrow aA^+ + e \rightarrow bB^* + cC^*$

$aA \rightsquigarrow aA^* \rightarrow bB + cC$

$aA \rightsquigarrow aA^*$

2) Radiation-Chemical Yields

$$G_{\rm ion1}(-A) = a\,P_{\rm e}\left(\frac{100}{W}\right)M_{\rm ion}^{\rm (A)}$$

$$G_{\rm ion2}(-A) = a\,(1-P_{\rm e})\left(\frac{100}{W}\right)M_{\rm ion}^{\rm (A)}$$

$$G_{\rm exc1}(-A) = a\,P_{\rm dis}\left(\frac{100}{W}\right)M_{\rm exc}^{\rm (A)}$$

$$G_{\rm exc2}(-A) = a\,(1-P_{\rm dis})\left(\frac{100}{W}\right)M_{\rm exc}^{\rm (A)}$$

3) Rate Coefficients

$$k_{\rm ion1} = \left(\frac{G_{\rm ion1}}{100}\right)S_{\rm e}\,\phi_{\rm ism}$$

$$k_{\rm ion2} = \left(\frac{G_{\rm ion2}}{100}\right)S_{\rm e}\,\phi_{\rm ism}$$

$$k_{\rm exc1} = \left(\frac{G_{\rm exc1}}{100}\right)S_{\rm e}\,\phi_{\rm ism}$$

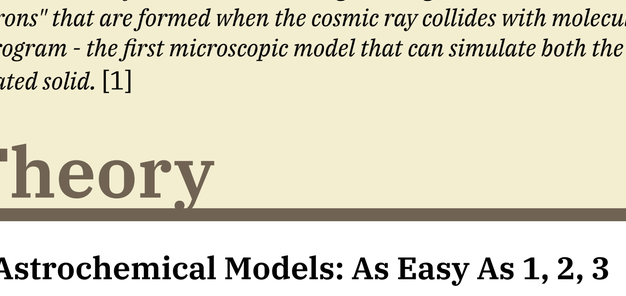
$$k_{\rm exc2} = \left(\frac{G_{\rm exc2}}{100}\right)S_{\rm e}\,\phi_{\rm ism}$$

Above) *Our method of incorporating cosmic ray-driven radiation chemistry into astrochemical models for any arbitrary species, A, starts with assuming the elementary processes shown in the red box (far left). From these, we calculate radiation-chemical yields, G-values, using the formulæ in the green (middle) box. Finally, from these, we can calculate rate coefficients assuming appropriate values for the flux (φ_{ISM}) and the electronic stopping cross section (S_e). We set the electron escape probability, P_e, to zero, and the dissociation probability, P_{dis} to 0.5.* [2]

Input Parameters

1) E_{ion}
   - *The ionization energy (work function)*
   - *Can be obtained from NIST*
2) W_{exc}
   - *The average ionization energy*
   - *Can be estimated from UV-Vis spectra*
3) W_s
   - *The average sub-excitation energy*
   - *Can be calculated as a function of E_{ion} and W_{exc}*

Breakdown of Mean Energy per Ion-Pair



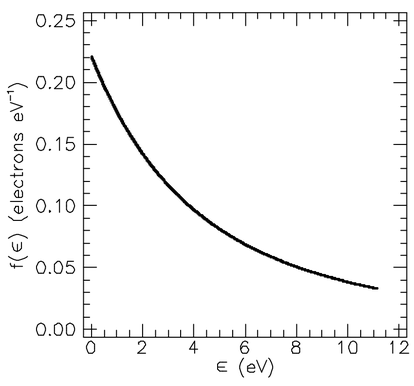
$$W = E_{ion} + W_s + \xi W_{exc} \qquad (1)$$

$$M_{ion}^{(A)} = 1 \qquad (2)$$

$$M_{exc}^{(A)} = \xi = \frac{W - (E_{ion} + W_s)}{W_{exc}} \qquad (3)$$

Left) *As shown in Eq. (1), we assume that the mean energy per ion-pair is the sum of the ionization energy as well as the energy lost in some number (ξ) of excitative collisions, in addition to sub-excitation electrons. Thus, as shown in Eq. (2), axiomatically, we set the number of ionizing collisions per W to unity, while the number of excitative collisions (ξ) is calculated using Eq. (3).* **Above)** *The breakdown of the energy contributions to the mean energy per ion-pair of water.*

Calculating the Average Sub-excitation Electron Energy, W_s



$$W_s = \frac{\int_0^{W_{exc}} f(\epsilon)\,\epsilon\,d\epsilon}{\int_0^{W_{exc}} \epsilon\,d\epsilon} \qquad (4)$$

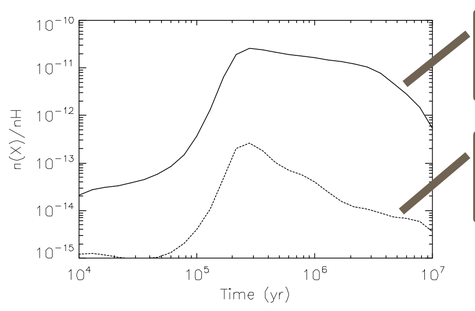
$$f(\epsilon) = \left(\frac{1}{\left[1+\left(\frac{\epsilon}{E_{ion}}\right)\right]^3}\right)\left(\frac{\left[1+\left(\frac{W_{exc}}{E_{ion}}\right)\right]^2}{W_{exc}\left[1+\left(\frac{W_{exc}}{2\,E_{ion}}\right)\right]}\right) \qquad (5)$$

Above Right) *The average sub-excitation electron energy, calculated using Eq. (4) above, is a function of the ionization energy (E_{ion}) and the average excitation energy (W_s).* **Above Left)** *Shown here is the sub-excitation energy distribution for water, calculated using Eq. (5).*

Results in Cold Core Models

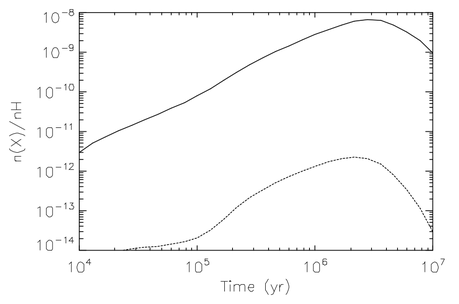
Methyl Formate ($HCOOCH_3$)

(a) Gas Phase

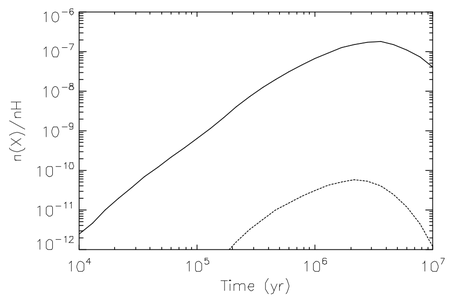


Abundances of methyl formate in the gas (a), ice surface (b), and ice bulk (c) calculated both with (solid line) and without (dotted line) cosmic ray-driven solid-phase radiation chemistry. [3]

(b) Ice Surface



(c) Ice Bulk



Formation of Suprathermal Precursors

$H_2CO \rightarrow H_2CO^+ + e^- \rightarrow HCO^* + H^*$

$CH_3OH \rightarrow CH_3OH^+ + e^- \rightarrow CH3O^* + H^*$

Formation of Methyl Formate

$HCO^* + CH_3O \rightarrow HCOOCH_3$

$HCO + CH_3O^* \rightarrow HCOOCH_3$

Ethanol (CH_3CH_2OH)

Gas Phase

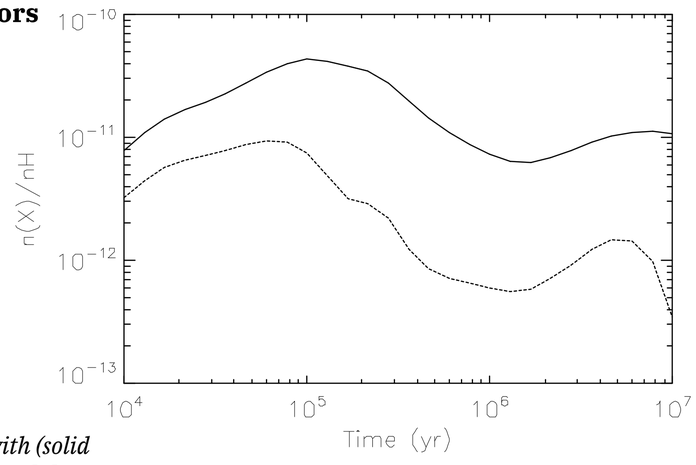
Formation of Suprathermal Precursors

$CH_4 \rightarrow CH_4^+ + e^- \rightarrow CH_2^* + H_2$

Formation of Ethanol

$CH_2^* + CH_3OH \rightarrow CH_3CH_2OH$

Here, ethanol forms via a (typically endothermic) insertion reaction at 10 K. [4]



Right) *Gas-phase abundances of ethanol both with (solid line) and without (dotted line) radiation chemistry.* [3]

References

[1] **Shingledecker, C. N.**, Gal, R. L. & Herbst, E. A new model of the chemistry of ionizing radiation in solids: CIRIS. Phys. Chem. Chem. Phys. 19, 11043–11056 (2017).

[2] **Shingledecker, C. N.** & Herbst, E. A general method for the inclusion of radiation chemistry in astrochemical models. Phys. Chem. Chem. Phys. 20, 5359–5367 (2018).

[3] **Shingledecker, C. N.**, Tennis, J. D., Le Gal, R., & Herbst, E. On Cosmic Ray-Driven Grain Chemistry in Cold Core Models. The Astrophysical Journal (2018).

[4] Bergantini, A., Góbi, S., Abplanalp, M. J. & Kaiser, R. I. A Mechanistical Study on the Formation of Dimethyl Ether (CH 3 OCH 3) and Ethanol (CH 3 CH 2 OH) in Methanol-containing Ices and Implications for the Chemistry of Star-forming Regions. ApJ 852, 70 (2018).

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