Modeling of cold astrochemical processes through matrix isolation: extremely hot chemistry at extremely low temperatures

Vladimir Feldman

Department of Chemistry, Lomonosov Moscow State University, Moscow 119991 Russia
feldman@rad.chem.msu.ru

The chemical evolution of molecules in space is induced by solar and galactic radiation, which make it possible to initiate the reactions in cold astrochemical media, including diffuse interstellar molecular clouds, cometary and planetary ices. Matrix isolation is a useful tool to simulate possible reaction channels for the key relevant molecules and to elucidate the mechanism of molecular assembling occurring under the conditions of completely frozen diffusion mobility. This lecture gives an overview of recent results of the matrix isolation studies on the radiation-induced transformations of astrochemically important molecules and their complexes obtained in our laboratory.

The experimental approach was based on X-ray irradiation of deposited solid-noble gas films doped with small amounts of target compounds at 6 K followed by monitoring of product formation by a combination of FTIR and EPR spectroscopy [1]. In this way we have extensively characterized the mechanism of radiation-induced decomposition of a number of key astrochemical molecules, such as HCOOH [2], CH_3OH [3], CH_3CN [4], CH_3CHO [5] and simple aromatics [6]. An important finding is that physical properties of inert matrix have strong effect on the degradation efficiency and pathways because of primary significance of the excess energy relaxation. To a certain extent, the observed chemistry may look quite "hot" in conventional terms, even though the medium temperature is quite low. In addition, the data obtained in model studies make a challenge for astronomical search of some intermediate species, not yet reported in space [7].

Another direction is concerned with the radiation chemistry of isolated intermolecular complexes. In fact, this approach implies a concept of "building blocks", which may provide an important insight into the mechanism of cold astrochemical synthesis. In this way, we have directly observed elementary steps of the low-temperature reactions, which may be responsible for formation of intermediates and molecules detected in interstellar media, including both prebiotic species and polycyclic aromatic hydrocarbons (PAHs) [8 - 11]. Also, the photoinduced and tunneling dynamics of intermediates was explored [12]. Some new intriguing results and implications are discussed.

The work was supported in part by the Russian Science Foundation (project no. 21-13-00195).

References

1. V.I. Feldman et al., *Rad. Phys. Chem.* **2016**, 124, 7.
2. S.V. Ryazantsev, V.I. Feldman, *Phys. Chem. Chem. Phys.* **2015**, 17, 30648.
3. E.V. Saenko, V.I. Feldman, *Phys. Chem. Chem. Phys.* **2016**, 18, 32503.
4. S.V. Kameneva, A.D. Volosatova, V.I. Feldman, *Rad. Phys. Chem.* **2017**, 141, 363.
5. P.V. Zasimov, E.V. Sanochkina, V.I. Feldman, *Phys. Chem. Chem. Phys.* **2022**, 24, 419.
6. M.A. Lukianova, E.V. Sanochkina, V.I. Feldman, *J. Phys. Chem. A* **2019**, 123, 5199.
7. A.D. Volosatova, S.V. Kameneva, V.I. Feldman, *Phys. Chem. Chem. Phys.* **2019**, 21, 13014.
8. P.V.Zasimov, S.V. Ryazantsev, D.A. Tyurin, V.I. Feldman, *MNRAS* **2021**, 506, 3499.
9. P.V.Zasimov, S.V. Ryazantsev, D.A. Tyurin, V.I. Feldman, *J. Am. Chem. Soc.* **2022**, accepted
10. A.D. Volosatova, M.A. Lukianova, P.V. Zasimov, V.I. Feldman, *Phys. Chem. Chem. Phys.*, **2021**, 23, 18449
11. M.A. Lukianova, V.I. Feldman, *Rad. Phys. Chem.* **2022**, 191, 109847.
12. S.V. Ryazantsev, V.I. Feldman, L. Khriachtchev, *J. Am. Chem. Soc.* **2017**, 139, 9551