Radiation-induced transformations of matrix-isolated intermolecular complexes

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Radiation-induced transformations (induced by UV light or ionizing radiation) of matrix-isolated intermolecular complexes reveals an interesting direction of low-temperature chemistry and spectroscopy studies. Photolysis or radiolysis of complexes of stable molecules in matrices may yield stabilized radical-molecule complexes, that are not easy to prepare and characterize via different experimental approaches. Experimental spectroscopy of radical-molecule complexes brings new challenges for computational chemistry.[1] Reactivity of some radical-molecule complexes is crucial for atmospheric chemistry and astrochemistry and can be investigated in low-temperature noble gas matrices. For example, the matrix-isolated OH···CO complex (prepared by photolysis or radiolysis of the H_2O···CO complex) can be converted into the HOCO radical at temperatures below 35 K,[2,3] while further annealing activates the H + HOCO → HCOOH reaction.[4] Thus, radiation-induced transformations of intermolecular complexes in low-temperature matrices may involve the 'cold' synthesis of organic molecules. This provides the 'single-molecule' approach in the experimental model studies devoted to the chemical evolution of matter in cold space areas.[5] Numerous studies have showed the applicability and advantages of this approach in the field of laboratory astrochemistry.[5–7] As was shown in our recent study,[8] radiolysis of matrix-isolated intermolecular complexes can be also used as non-trivial synthetic strategy to prepare the elusive organic radical cations for its further spectroscopic and photochemical investigation. Thus, this experimental approach can be used in the studies devoted to the physical organic chemistry. To sum up, the studies of radiation-induced transformations of matrix-isolated intermolecular complexes bring new valuable information, which might be of interest and importance in many research fields, such as chemistry and spectroscopy of highly-reactive species, astrochemistry (a.k.a. molecular astrophysics), physical organic chemistry, as well as fundamental photo- and radiation chemistry.

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[1] Ryazantsev, S.V.; Tarroni, R.; Feldman V.I.; Khriachtchev, L. Effect of noncovalent interactions on vibronic transitions: an experimental and theoretical study of the C_2H···CO_2 complex. *ChemPhysChem.* **2017**, *18*, 949–958.

[2] Ryazantsev, S.V.; Duarte, L.; Feldman V.I.; Khriachtchev, L. VUV photochemistry of the H_2O···CO complex in noble-gas matrices: formation of the OH···CO complex and the HOCO radical. *Phys. Chem. Chem. Phys*. **2017**, *19*, 356–365.

[3] Ryazantsev, S.V.; Feldman V.I.; Khriachtchev, L. Conformational switching of HOCO radical: selective vibrational excitation and hydrogen-atom tunneling. *J. Am. Chem. Soc.* **2017**, *139*, 9551–9557.

[4] Ryazantsev, S.V.; Zasimov, P.V.; Feldman, V.I. Radiation-induced synthesis of formic acid in the H_2O–CO system: a matrix isolation study. *Chem. Phys. Lett.* **2020**, *753*, 137540.

[5] Feldman, V. I.; Ryazantsev, S.V.; Kameneva, S.V. Matrix isolation in laboratory astrochemistry: State-of-the-art, implications and perspective. *Rus. Chem. Rev.* **2021**, *90*, 1142–1165.

[6] Zasimov, P.V.; Ryazantsev, S.V.; Tyurin, D.A.; Feldman, V.I. Radiation-induced chemistry in the C_2H_2–H_2O system at cryogenic temperatures: a matrix isolation study. *Mon. Not. R. Astron. Soc.* **2020**, *491*, 5140–5150.

[7] Zasimov, P.V.; Ryazantsev, S.V.; Tyurin, D.A.; Feldman, V.I. C_2H_2···CO complex and its radiation-induced transformations: a building block for cold synthetic astrochemistry. *Mon. Not. R. Astron. Soc.* **2021**, *506*, 3, 3499–3510.

[8] Zasimov, P.V.; Tyurin, D.A.; Ryazantsev, S.V.; Feldman, V.I. Formation and evolution of $H_2C_3O^{+\bullet}$ radical cations: a computational and matrix isolation study *J. Am. Chem. Soc.* **2022**, *144*, 8115–8128.