

Deposition products predicted from conceptual DFT: The hydrolysis reactions of MoF₆, WF₆, and UF₆

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Multi-step gas-phase reactions terminating in deposition represent a challenge for predictive *ab initio* theory. Upon applying the conventional methods for characterizing elementary steps, it is unclear at which step termination by deposition occurs. As an illustrative example, the hexafluoride vapors of uranium (UF₆), tungsten (WF₆), and molybdenum (MoF₆) each hydrolyze to deposit compounds with differing fluorine-to-oxygen ratios. While the corresponding reaction mechanisms are analogous,^{1,2} as evidenced by the close resemblance of anharmonic vibrational simulations and measured infrared spectra,^{3,4} UF₆ hydrolysis undergoes a comparatively premature deposition, yielding uranyl fluoride (UO₂F₂ (s)) rather than the trioxide produced by the WF₆ and MoF₆ hydrolyses. Here we utilize a theoretical framework known as conceptual density functional theory (CDFT) to predict the intermediate which deposits in each reaction. An analogous framework is proposed based on equation-of-motion coupled-cluster (EOMCC) methods for electronically excited, ionized, and electron-attached states. Such methods have great utility in the development of automated workflows targeting reaction network exploration, molecular clustering towards deposition, and particle nucleation kinetics.

¹ J. J. Lutz, J. N. Byrd, et al., "A theoretical investigation of the hydrolysis of uranium hexafluoride: the initiation mechanism and vibrational spectroscopy," *Phys. Chem. Chem. Phys.* **24**, 9634 (2022).

² J. J. Lutz, D. S. Jensen, and J. A. Hubbard, "Deposition products predicted from conceptual DFT: The hydrolysis reactions of MoF₆, WF₆, and UF₆," *J. Chem. Phys.* **159**, 184305 (2023).

³ L. E. McNamara, A. Waldron, et al. "Investigating the hydrolysis of cryogenically layered molybdenum hexafluoride through a disordered hydrogen-bonded network" *Phys. Chem. Chem. Phys.*, **25**, 2990 (2023).

⁴ L. E. McNamara, J. T. Kelley, et al., "Online monitoring the hydrolysis of uranium hexafluoride for intermediates by cryogenic layering and FTIR" *Front. Nucl. Eng.*, **2**, 1300544 (2023).

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