Density Functional Theory for Nuclear Forensics: Characterizing UO$_2$F$_2$

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BACKGROUND

Uranyl fluoride (UO$_2$F$_2$) is a product of the hydrolysis of uranium hexafluoride (UF$_6$), making the characterization of UO$_2$F$_2$ relevant for nuclear forensics.

Anhydrous UO$_2$F$_2$ has a layered structure, as shown below. Water molecules have been shown to readily sorb between the layers in ambient conditions [1,2,3]. The susceptibility to hydration can make the anhydrous state difficult to study experimentally.

Density functional theory (DFT) was thus used to calculate the structure and vibrational frequencies of the anhydrous state to complement Raman scattering on both the anhydrous and hydrated states [4].

DENSITY FUNCTIONAL THEORY

Fundamentally, DFT involves solving the Kohn-Sham equation for a multi-electron system:

$$E = -\frac{1}{2} \sum \int \psi_i(\mathbf{r}_i)^2 \phi_i(\mathbf{r}_i) d\mathbf{r}_i + \sum \frac{Z_i}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{1}{2} \sum \int \psi_i(\mathbf{r}_i)^2 \nabla \phi_i(\mathbf{r}_i) \cdot \nabla \phi_j(\mathbf{r}_j) d\mathbf{r}_i d\mathbf{r}_j + E_\text{xc}.$$

The exchange-correlation energy functional, $E_{\text{xc}}$, is unknown and must be approximated. The approximated analytical form typically depends on the electron density (Local Density Approximation, LDA), or its gradient (Generalized Gradient Approximation, GGA).

The formally closed-shell electronic structure of UO$_2$F$_2$ is amenable to electronic structure calculations. However, DFT typically fails to accurately describe f-shell electrons and van der Waals interactions.

The Hubbard $+U_{\text{eff}}$ correction can be applied to better account for self-interaction and thus localization of the f-shell electrons. Van der Waals interactions are introduced by using specific van der Waals density functionals.

Vibrational frequencies can be calculated using density functional perturbation theory (DFPT) to solve the harmonic equations of motion, 

$$\det \left[ \frac{\partial^2 E(\mathbf{R})}{\partial \mathbf{R}_i \partial \mathbf{R}_j} - \omega^2 \right] = 0.$$

VIBRATIONAL FREQUENCIES

Vibrational frequencies were calculated via DFPT using a variety of functionals and $U_{\text{eff}}$ values. Predicted frequencies of the O-U-O and F-U-F stretches were found to be in excellent agreement with Raman scattering results when the vdW functional and Hubbard correction were used.

The geometry of anhydrous UO$_2$F$_2$ was optimized using the LDA, GGA, and vdW functionals with a range of $U_{\text{eff}}$ values. The GGA functional overestimates both the U-O and U-F bond lengths compared to experimental values, while LDA and vdW are overall in better agreement. However, LDA underestimates the interlayer spacing (not shown). In all cases, increasing the Hubbard parameter decreases the U-O bond length and increases the U-F bond length.

EXPERIMENTAL RAMAN SCATTERING

Raman scattering measurements show that the O-U-O stretching frequency is redshifted from 915 cm$^{-1}$ to 867 cm$^{-1}$ in the hydrated state. This shift has been noted previously [4,5], but the phase transition has not been directly observed.

To probe this transition, spectra were collected continuously between 25°C and 200°C. The O-U-O redshift is shown to be irreversible and discrete, occurring at 125°C. Along with previous TGA data, this suggests that loosely bound water molecules are removed continuously between 60-100°C, and then a second population of strongly bound waters is removed in a phase transition.

CONCLUSION AND FUTURE WORK

Excellent agreement between our theoretical and experimental results on the anhydrous structure suggests that DFT will be an invaluable tool to further probe the hydrated state.

Ab initio molecular dynamics will allow for the theoretical calculation of vibrational frequencies at various levels of hydration.

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REFERENCES