Electronic Supplementary Information:

Mechanism of phase transfer of uranyl ion: A vibrational sum frequency generation spectroscopy study on solvent extraction in nuclear reprocessing

Ryoji Kusaka* and Masayuki Watanabe

Nuclear Science and Engineering Center, Japan Atomic Energy Agency (JAEA), 2-4 Shirakata, Tokai, Ibaraki 319-1195, Japan

E-mail: kusaka.ryoji@jaea.go.jp

1. Materials and samples

Aqueous solutions dissolving TBP, TBP + uranyl nitrate, and TBP + uranyl nitrate + nitric acid were prepared by using high-purity water (18.2 MΩ cm resistivity, Millipore, Milli-Q), tri-n-butyl phosphate (TBP, >98.0%, Kanto Chemical), nitric acid (1.42) (for Ultratrace Analysis, Wako), and uranyl nitrate. The uranyl nitrate was obtained by evaporating an aqueous solution dissolving uranium metal by the nitric acid. The concentrations of TBP and nitric acid in the samples are 10^{-4} M and 3 M, respectively. The concentration of uranyl nitrate in the samples is 0.1 M or 0.9 M.

2. VSFG spectroscopy

A Ti:Sapphire regenerative amplifier (Spectra Physics, Solstice Ace) was used as the light source (795 nm, 5.7 mJ, 95 fs, 1 kHz). One part of the output was spectrally narrowed by a bandpass filter (CVI, center wavelength: 794.7 nm, bandwidth: 1.5 nm) (ω_1). The other part of the output was converted to a tunable and broadband infrared beam by an optical parametric amplifier with a difference frequency generation unit (Light Conversion, TOPAS-prime) (ω_2). The ω_1 and ω_2 beams were focused by a spherical concave mirror onto the sample surface of an aqueous solution to generate sum frequency light (ω_3) from the sample surface. The incident angle and the polarization direction were ~50° and s for ω_1, and ~60° and p for ω_2.

The *s*-polarized component of ω_3 was isolated by a Glan–Taylor prism, and introduced into a polychromator (Andor, Shamrock, SR-303i-B), and detected using an electron-multiplying charge-coupled device (EMCCD) camera (Andor, newton, DU970P-BVF). VSFG spectra of the samples were normalized by the VSFG signal obtained from a GaAs surface. All VSFG measurements were performed immediately after putting a sample solution on a container made of Teflon. The temperature of the experimental room was 19–22 °C.

We fit the VSFG spectra with a Lorentzian line shape:

$$I_{VSFG} \propto \left|\chi_R^{(2)}\right|^2 = \left|\frac{A_{P=O}}{\omega - \omega_{P=O} + i\Gamma_{P=O}}\right|^2$$

where $\chi_R^{(2)}$ is the second-order resonant nonlinear susceptibility element. $A_{P=O}$, $\omega_{P=O}$, and $\Gamma_{P=O}$ are the amplitude, center frequency, and width of the resonance of P=O stretch, respectively. The spectra are fitted well by a Lorentzian line, meaning that the VSFG spectra have almost no nonresonant background. The parameters obtained from the fitting analysis are presented in Table S1.

Table S1. Fitting Parameters for the VSFG spectra in the P=O stretch region.

Interface	$A_{P=O}$	$\omega_{P=O}$ / cm^{-1}	$\Gamma_{P=O}$ / cm^{-1}
TBP/uranyl (0.9 M), nitric acid (3 M) aq	4.43	1256	42
TBP/uranyl (0.1 M), nitric acid (3 M) aq	4.23	1253	40
TBP/uranyl (0.1 M) aq	4.01	1251	36
TBP/water	4.02	1249	34

3. FTIR spectroscopy

TBP is used without dehydration. The water concentration in the TBP solution dissolving water is 60 µL water / 1 mL TBP. The concentration of uranyl nitrate in the TBP solution dissolving uranyl nitrate is saturated. A drop of the sample solution is put between two CaF_2 windows without any spacers, and the IR spectra were measured using a commercial FTIR spectrometer (JASCO, FT/IR-4600) at 2 cm^{-1} spectral resolution.