Title	表面増強ラマン分光スペクトルにおけるランタノイド-クエン酸複合体の実験的および理論的研究
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Citation	
Issue Date	2025-09
Type	Thesis or Dissertation
Text version	ETD
URL	http://hdl.handle.net/10119/20087
Rights	
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Abstract

The works of this thesis present a series of studies focusing on the surface-enhanced Raman spectroscopy (SERS) measurement, spectral analysis, and density functional theory (DFT)-based SERS simulation of lanthanide (Ln)–citrate complexes. Due to their unique 4f electronic configurations, Ln^{3+} ions exhibit exceptional physical properties, such as luminescence and magnetism. Thus, they are important in functional material field. However, their chemical properties remain extremely similar, making their identification and classification challenging. This difficulty highlights the need for advanced spectroscopic techniques, which forms the core motivation of this thesis.

To address this issue, a stable SERS measurement method was first developed using citrate capped silver nanoparticles (citrate@AgNPs), enabling the detection of Ln-citrate complexes at concentrations as low as 10^{-4} M. Simultaneously, we optimized a DFT-based approach for simulating SERS spectra and assigning vibrational modes. Using this integrated method, we systematically studied the SERS spectral features of seven representative Ln-citrate complexes (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd) and proposed possible mechanisms for the observed spectral variations. To our knowledge, this is the first systematic SERS investigation of Ln-molecular complexes.

In the initial study, La-citrate and Gd–citrate complexes were measured and compared. Although both exhibited similar SERS peak positions, The relative intensities of peaks around 1065, 1315 and 1495 cm^{-1} were differed significantly. DFT simulations revealed that these SERS signals from vibrational modes localized in the coordination region. The intensity ratio of the peaks around 1065 and 1315 cm^{-1}

(I_{1065}/I_{1315}) was found to be approximately 1 for La^{3+} and around 0.55 for Gd^{3+}, providing a qualitative means of distinguishing the two ions.

Further, the SERS spectra of all seven Ln-citrate complexes (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd) were collected under 488, 532, and 660 nm excitations. All showed three prominent peaks near 1065, 1315, and 1485 cm^{-1}. The intensity ratios I_{1065}/I_{1315} and I_{1485}/I_{1315} varied systematically with the Ln^{3+} species, but remained nearly constant across excitation wavelengths. DFT results indicated that as the number of unpaired 4f electrons increases, the attraction between Ln^{3+} and oxygen strengthens, reducing the dipole moment and vibrational symmetry of the C–O bonds. These insights provide a theoretical foundation for understanding the indirectly influence of 4f electronic configurations on SERS spectral behavior.

In the appendix, we describe preliminary results from a complementary spin-based study using nitrogen-vacancy (NV) centers in diamond to measure the T_1 relaxation times of La-citrate and Gd-citrate complexes. Significant T_1 shortening was observed in Gd^{3+}-coated regions due to magnetic fluctuations from its seven unpaired 4f electrons, while La^{3+}-coated regions showed minimal change, consistent with its non-magnetic $4f^0$ configuration. This provides experimental validation of their distinct spin properties.

Final, these findings in above works contribute a novel approach for some Ln^{3+} identification based on vibrational and spin characteristics and also laying the groundwork for future Ln-selective detection and studies of SERS variations response to Ln^{3+}.

Keywords: Surface-enhanced Raman scattering, lanthanide, Raman, DFT, Rare earth