

A New Mechanism of Raman Enhancement and its Application

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Abstract: Strong electronic Raman bands corresponding to the transition between $^4I_{9/2}$ and $^4I_{11/2}$ manifolds of Nd^{3+} , caused by a Raman-enhancement effect, are observed in the FT-Raman spectrum of Nd_2O_3 . Neither resonance enhancement (RR) nor surface enhancement (SERS) accounts for the Raman enhancement observed here. We propose a new mechanism of Raman enhancement called the “feed-back” mechanism. A YAG laser excites the final state of the Raman transition ($^4I_{11/2}$ of Nd^{3+}) to the $^4F_{3/2}$ state and causes a significant de-

crease in the population of Nd^{3+} at the $^4I_{11/2}$ state. This causes the population ratio of Nd^{3+} at $^4I_{9/2}$ and $^4I_{11/2}$ to deviate from the value required by Boltzmann’s law. To restore equilibrium, Raman scattering is enhanced so that more Nd^{3+} ions are brought from the $^4I_{9/2}$ state to the $^4I_{11/2}$ state. This hypothesis gets

support from the temperature-variable FT-Raman spectroscopic results. Additionally, obvious differences between the Stokes and anti-Stokes Raman spectrum of Nd^{3+} provide further evidence to support the feed-back mechanism. The Raman-enhancement effect confers on the electronic Raman bands a special ability to reflect the variation of coordinated structure around metal ions. The structural variations in polymer–metal ion composites and biomineralization systems have been investigated by using the electronic Raman bands.

Keywords: analytical methods · enhancement · feed-back mechanism · lanthanides · Raman spectroscopy · structural probe

Introduction

Raman spectroscopy is a powerful method for characterizing molecular structure and has extensive applications.^[1–4] The Raman-enhancement effect is important in improving the sensitivity of Raman spectroscopy. For instance, Raman enhancement makes it possible to detect single molecules by the Raman method.^[5, 6] Although Raman enhancement has been extensively utilized, only resonance Raman^[7] (RR) and surface enhanced Raman^[8–10] (SERS) have been reported.

Until recently, aggregate enhancement Raman scattering (AERS) was proposed.^[11] The work in this paper has led us to find a new mechanism of Raman enhancement.

Experimental Section

All the FT-Raman spectra were recorded on a Nicolet Raman 950 FT-Raman spectrometer with a YAG laser (Nd: YVO₄, 1064 nm). A CaF₂ beam-splitter and a germanium detector were utilized. The resolution of the FT-Raman spectra was 4 cm⁻¹, and 5000 scans were coadded. For comparison, Raman spectra of Nd_2O_3 were also collected on a Renishaw Raman-imaging system 1000 (Renishaw plc, UK) equipped with a He–Ne laser from Spectra physics (Model 127–25RP, $\lambda_0 = 632.8$ nm) and a Peltier-cooled CCD detector. A 50× objective mounted on an Olympus BH-2 microscope was used to focus the laser beam onto a spot approximately 1 μ m in diameter and to collect back-scattering signals of the samples. FTIR and FTNIR spectra were measured on a Nicolet Magna 750 spectrometer at a resolution of 4 cm⁻¹ and 128 scans were coadded. A KBr beam-splitter and an MCT detector were used in the FTIR spectroscopic measurement. For the FTNIR experiment, a CaF₂ beam-splitter and a PbSe detector were utilized.

Doxycholic acid was purchased from Sigma Company and other chemical reagents were AR grade. Lanthanide oxides with a purity of 99.99% were used in this work. First, the lanthanide oxides were dissolved in concentrated HCl to prepare lanthanide chloride. Then, lanthanide complexes were synthesized by dissolving the lanthanide chloride and ligand in ethanol. NaOH was added to remove H⁺ and prompt the formation of the lanthanide complexes. NdCl₃–polyvinylpyrrolidone (PVP) composites were prepared by mixing different amount of NdCl₃ and PVP in

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water, and the composites were obtained after removing water. Nylon 6 and neodymium chloride with different weight ratios were dissolved in HCl, and the composites were acquired after the solvent had been vaporized. Neodymium phosphate was synthesized by adding NdCl_3 to an aqueous solution of Na_3PO_4 (pH \sim 11–12), Na_2HPO_4 (pH \sim 8–9), and NaH_2PO_4 (pH \sim 4–5). Bovine serum albumin (BSA) was dissolved in an aqueous solution of sodium phosphate before being mixed with neodymium salts to prepare the neodymium phosphate–BSA composite. Neodymium deoxycholate and its BSA composite were prepared in a similar way.

Results and Discussion

An unexpected finding during this work was that unusually strong Raman bands from Nd_2O_3 powder were recorded on a Nicolet Raman 950 FT-Raman spectrometer by using a near infrared YAG laser (1064 nm, 300 mW), as shown in Figure 1.

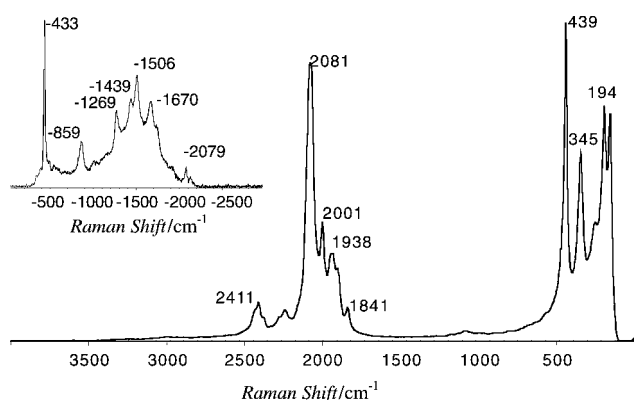


Figure 1. FT-Raman and, inset, anti-Stokes Raman spectra of Nd_2O_3 . Electronic Raman bands corresponding to the transition between $^4I_{9/2}$ and $^4I_{11/2}$ of neodymium ions are observed at about 2000 cm^{-1} in both Stokes and anti-Stokes Raman spectra.

The bands cannot be attributed to the normal vibrations of ligands. Further experiments demonstrated that similar bands are also observed in various complexes containing Nd^{3+} (Figure 2), whereas such bands are absent in the complexes without neodymium ions. Consequently, the above results demonstrate that the bands are related to Nd^{3+} ions.

A good linear relationship between the intensity of the Raman band of neodymium oxide at 2081 cm^{-1} and the laser power (Figure 3) precludes the possibility that the bands stem from multiphoton excitation. The observation of broad bands around 2000 cm^{-1} in the Raman spectra of a solution of neodymium nitrate (20%) in acetone and in an aqueous solution with neodymium chloride (30%) rules out the possibility that the bands stem from luminescence caused by thermal shock (Figure 4).

According to the electronic energy levels of neodymium,^[12] the bands are assigned to the electronic transition between $^4I_{9/2}$ and $^4I_{11/2}$ manifolds of Nd^{3+} . The observation of weak bands around 2081 cm^{-1} in the anti-Stokes Raman spectrum supports the above assignment. (insert, Figure 1).

The electronic Raman bands corresponding to the $f-f$ transition of lanthanide were first observed by Hough and Singh.^[13] Konigstein and others^[14–20] in their systematic

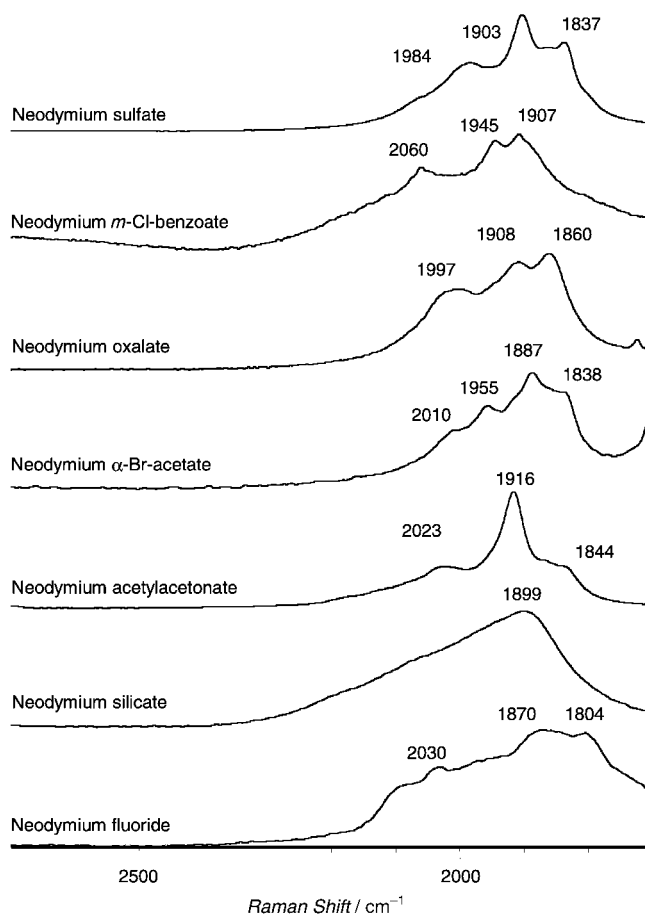


Figure 2. FT-Raman spectra of a variety of neodymium complexes

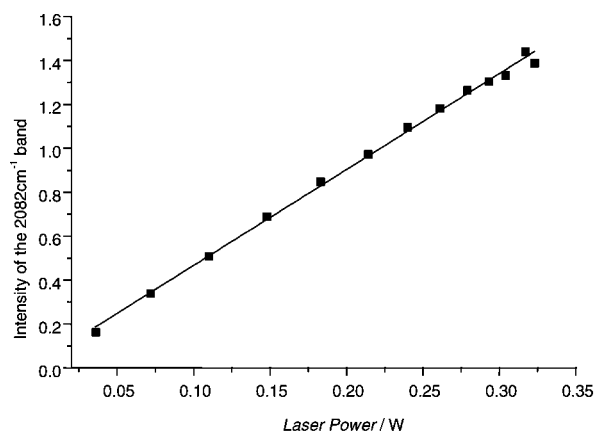


Figure 3. The correlation between the intensity of the 2081 cm^{-1} band of neodymium oxide and the laser power.

studies demonstrated that the electronic Raman bands for lanthanides are often rather weak and are difficult to observe, unless the cryogenic technique or a resonance Raman enhancement is used. This is indeed true in our experiment; for example, the above electronic Raman bands disappeared when the Raman spectra of Nd_2O_3 were recorded with He–Ne laser at 632 nm (Figure 5). In addition, although the energy gap between 3H_4 and 3H_5 manifolds for Pr^{3+} is also around 2000 cm^{-1} , no electronic Raman bands appear in the FT-Raman spectrum (Figure 6). The above results show that

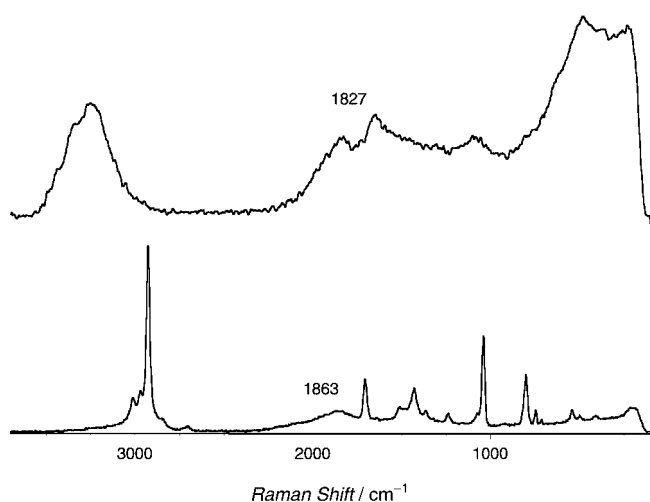


Figure 4. FT-Raman spectra of (top) an aqueous solution of neodymium chloride (30%) and (bottom) a solution of neodymium nitrate in acetone (20%).

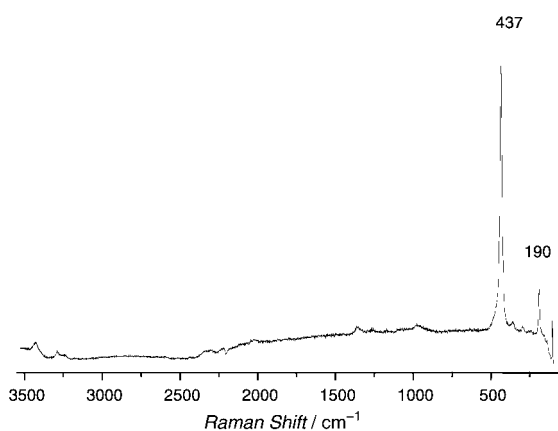


Figure 5. Raman spectrum of neodymium oxide obtained by using a He-Ne laser (632 nm). No electronic Raman transition bands between ${}^4I_{9/2}$ and ${}^4I_{11/2}$ can be observed.

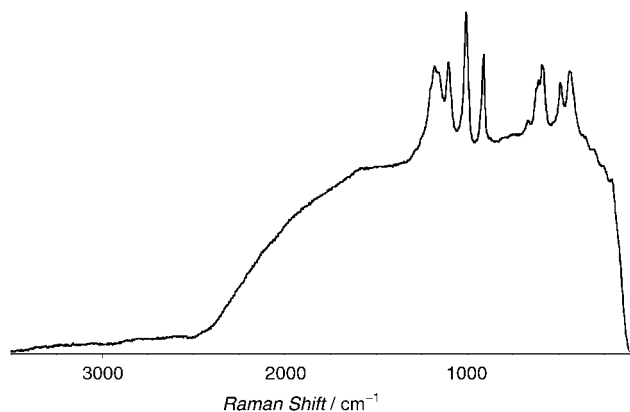


Figure 6. FT-Raman spectrum of praseodymium sulfate obtained with a 1064 nm laser, no 3H_4 – 3H_5 transition was observed around 2000 cm^{-1} .

the observation of the electronic Raman spectrum of Nd^{III} under routine conditions is quite unusual, and some Raman enhancing effect must be involved.

The next task was to estimate the time of Raman enhancement. The electronic Raman band around 2000 cm^{-1} in Figure 5 is too weak; so we selected a small perturbation that

was around 2030 cm^{-1} and a little larger than the noise level as the electronic Raman bands under conventional conditions. Since the Raman spectra shown in Figures 1 and 5 were recorded by using different Raman spectrometers, it is difficult to calculate the time of Raman enhancement by using the intensities of the 2000 cm^{-1} band directly from these Figures. However, the 439 cm^{-1} band in the FT-Raman spectrum and the 433 cm^{-1} band in the Raman spectrum, which were recorded by using a 632 nm laser, are from the same vibrational mode. The intensity ratio of the bands is shown in Equation (1):

$$I_{439(1064)}/I_{433(632)} = (632/1064)^4 \approx 8 \quad (1)$$

With the help of the 439 cm^{-1} band, the factor of enhancement was estimated according to Equation (2):

$$T = I_{2081(1064)}/I_{2030(632)} = \frac{(I_{2081(1064)}/I_{439(1064)}) (I_{439(1064)}/I_{433(632)})}{(I_{2030(632)}/I_{433(632)})} \approx 640 \quad (2)$$

Resonance Raman enhancement cannot account for the Raman-enhancement phenomenon observed in Figure 1. This is due to the fact that the wavelength of the exciting laser must coincide with the absorption band of the sample in the conventional resonance Raman process,^[21] while no band was observed around 1064 nm when the FTNIR spectrum of Nd^{3+} in the ground state was measured (Figure 7). In fact, the YAG

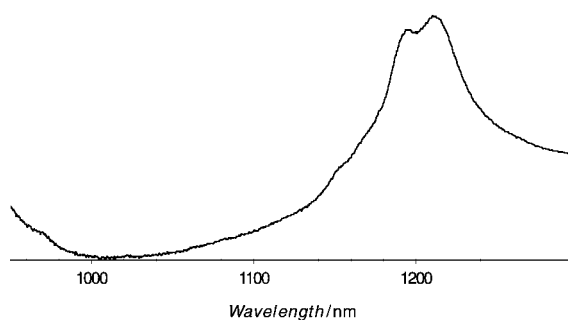


Figure 7. FTNIR spectrum of Nd_2O_3 , no absorbance band occurs around 1064 nm.

laser is related to the transition between ${}^4I_{11/2}$ and ${}^4F_{3/2}$ of neodymium, and the ground state ${}^4I_{9/2}$ is not involved in this transition. On the other hand, according to Albrecht, Peticolas, Collins and their co-workers,^[22–24] resonance Raman enhancement may also be possible if the wavelength of the scattering light can match an energy gap between the ground state and an excited state. However, this is not the case in the Nd^{III} system. Our experiment is not SERS or AERS. We propose a new mechanism as shown in Figure 8.

Figure 8a illustrates the conventional Raman process: Nd^{3+} ions at the ground state (${}^4I_{9/2}$) are excited to a virtual state. Then the Nd^{3+} ions at the virtual state have two ways to go: either they return to the ground state and give rise to Rayleigh scattering or they go to the ${}^4I_{11/2}$ state and give rise to Raman scattering. On the other hand, the relaxation rate from ${}^4I_{11/2}$ to ${}^4I_{9/2}$ is not very fast, because the f – f transition is forbidden. The Raman scattering, being the by-product of the above transfer from ${}^4I_{9/2}$ to ${}^4I_{11/2}$ of Nd^{3+} , cannot be very strong or the

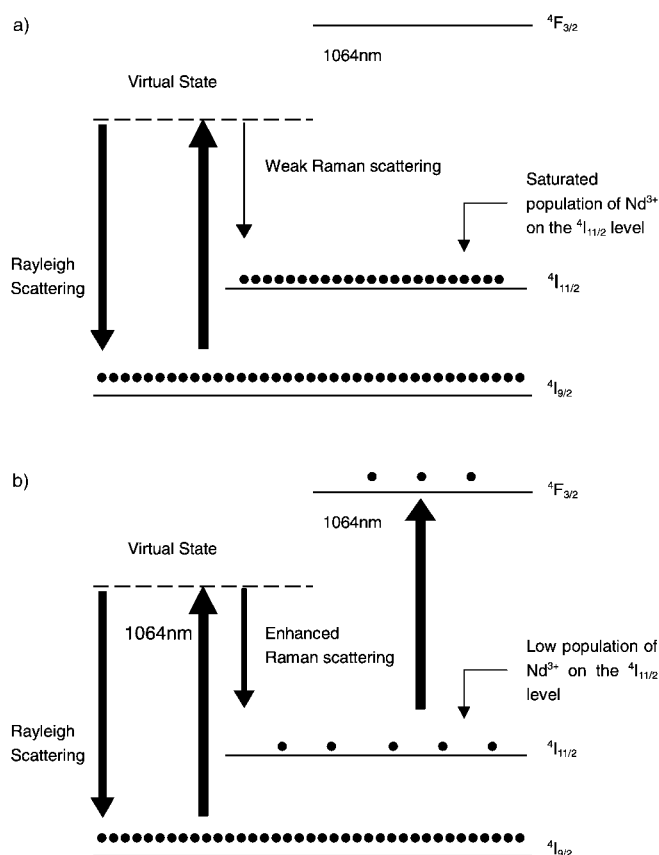


Figure 8. Schematic diagram of the feedback Raman-enhancement mechanism. a) The conventional electronic Raman process of Nd^{3+} , the Raman band cannot be very strong because the population of Nd^{3+} at ${}^4\text{I}_{11/2}$ is saturated, and the Raman process is prohibited by Boltzmann's law. b) Because the energy of the YAG laser coincides with the energy gap between ${}^4\text{I}_{11/2}$ and ${}^4\text{F}_{3/2}$ of Nd^{3+} , a significant amount of Nd^{3+} at the ${}^4\text{I}_{11/2}$ state is lifted to the ${}^4\text{F}_{3/2}$ state. This causes the population ratio of Nd^{3+} between ${}^4\text{I}_{11/2}$ and ${}^4\text{I}_{9/2}$ to deviate from the value allowed by the Boltzmann's law. Raman flux is thus enhanced to push the system back toward equilibrium.

Nd^{3+} will accumulate in the ${}^4\text{I}_{11/2}$ state. This will cause the population ratio between ${}^4\text{I}_{9/2}$ and ${}^4\text{I}_{11/2}$ to deviate from the Boltzmann distribution. From Figure 8b we see that the energy gap between ${}^4\text{F}_{3/2}$ and ${}^4\text{I}_{11/2}$ just coincides with the energy (9398 cm^{-1}) of the YAG laser (1064 nm),^[6] so that Nd^{3+} ions at the ${}^4\text{I}_{11/2}$ state can absorb the YAG laser excitation and be excited to the ${}^4\text{F}_{3/2}$ state. Since the intensity of the laser is very strong, the population of Nd^{3+} at ${}^4\text{I}_{11/2}$ decreases dramatically. Consequently, the population of the Nd^{3+} at ${}^4\text{I}_{11/2}$ will be so low that the population ratio between ${}^4\text{I}_{11/2}$ and ${}^4\text{I}_{9/2}$ becomes much smaller than the value required by the Boltzmann distribution. In order to restore equilibrium, many Nd^{3+} at the ground state have to be transferred to the ${}^4\text{I}_{11/2}$ state. The flux of the Raman process, being an effective route to bring Nd^{3+} from the ground state to the ${}^4\text{I}_{11/2}$ state, will increase, thereby enhancing the Raman scattering. However, once the Nd^{3+} ions are transferred to the ${}^4\text{I}_{11/2}$ state, they will be further excited to the ${}^4\text{F}_{3/2}$ state; this makes the population of Nd^{3+} at the ${}^4\text{I}_{11/2}$ state less than that allowed by Boltzmann's distribution. Thus the flux of Raman process will keep increasing till the rate of Nd^{3+} transferring from the ground state to ${}^4\text{I}_{11/2}$ is equal to the rate of Nd^{3+} at ${}^4\text{I}_{11/2}$ being

excited to the ${}^4\text{F}_{3/2}$ state with the YAG laser. According to the characteristics of this Raman enhancement, we suggest calling this phenomenon a "feed-back Raman-enhancement" mechanism.

To check if this hypothesis was correct or not, we used this mechanism to predict what would happen when recording FT-Raman spectra of Nd complexes at decreasing temperatures. From Figure 9, it can be seen that the population allowed by

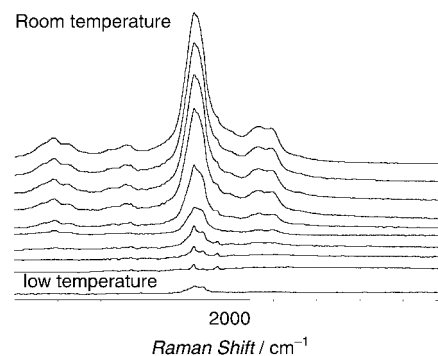


Figure 9. Temperature-variable FT-Raman spectra of Nd_2O_3 , as the temperature drops, the intensities of the electronic Raman bands of Nd^{3+} decrease significantly.

the Boltzmann distribution decreases as the temperature drops. Thus less Nd ions are needed to compensate for the vacant sites of Nd at ${}^4\text{I}_{11/2}$ state, and the flux of Nd^{3+} transferring from the ground state to ${}^4\text{I}_{11/2}$ state will decrease. Consequently, the Raman scattering will decrease significantly as the temperature drops. This conclusion is strikingly different from those reported in references that show that the intensities of the electronic Raman for the f–f transition bands of lanthanides will increase at low temperature because of the decreasing of bandwidth.^[13–17] However, the experimental results in Figure 9 show that the intensities of the band around 2000 cm^{-1} decrease with decreasing of the temperature. Thus, our temperature-variable FT-Raman experiments support the new Raman-enhancement mechanism proposed in this paper.

The central part of the feed-back mechanism is that the final state of Raman scattering (${}^4\text{I}_{11/2}$) can absorb the YAG laser excitation, and go to the ${}^4\text{F}_{3/2}$ state. Thus, the transition from ${}^4\text{I}_{11/2}$ to ${}^4\text{F}_{3/2}$ caused by the YAG laser makes the anti-Stokes Raman process a Resonance Raman process. Because of the resonance Raman-enhancement effect, some bands that do not occur in conventional Raman can be observed. This is the case for the anti-Stokes Raman spectrum of Nd_2O_3 . Significant differences were observed between the Stokes and anti-Stokes Raman spectra. For example, a series of bands appears between 1700 and 1200 cm^{-1} in the anti-Stokes Raman spectrum, while such bands do not occur in the Stokes Raman spectra (insert, Figure 1). Therefore, the anti-Stokes Raman spectrum of Nd_2O_3 , from an alternative aspect, supports the feed-back mechanism proposed in this paper.

Due to the spin–orbital interaction and the influence of the ligand field, the band splits and exhibits complex spectral features. Figure 2 lists a variety of neodymium complexes. A number of bands and peak positions as well as the band shape

differ from sample to sample as the ligand is varied. Another typical example is from our research work on three lanthanide–saccharide complexes. Single-crystal structures show that the coordinated atoms are oxygen and that the coordination number is 9 for the three complexes.^[25–27] However, the subtle variations in the coordinated environment around the neodymium ions manage to produce significant differences in the electronic bands of Nd^{3+} among the three neodymium saccharide complexes (Figure 10). Since the electronic Raman

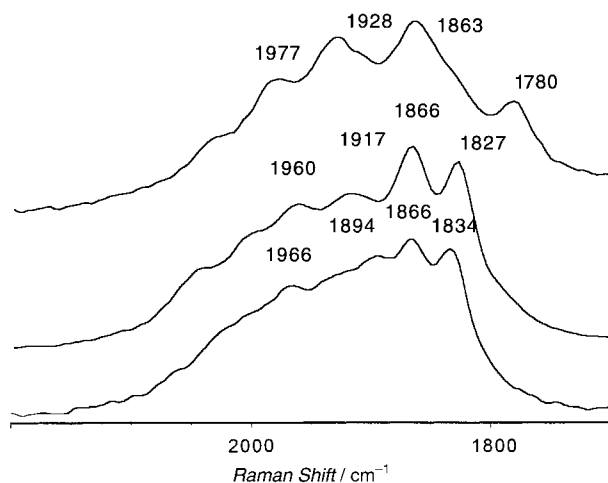


Figure 10. FT-Raman spectra of three neodymium saccharide complexes, top: neodymium–inositol, middle: neodymium–galactitol, bottom: neodymium–ribose. Significant differences can be observed among the electronic Raman bands of the three samples.

bands of Nd^{3+} in FT-Raman spectroscopy are sensitive to the subtle variation of the coordination environment around the Nd^{3+} ions, the bands can be developed as a sensitive probe to characterize the coordination structures of complexes and their variations. Preliminary investigations by using the electronic Raman bands of Nd^{3+} as a structural probe have been performed in our laboratory. Here we provide two examples.

Amide groups possess a considerable ability to coordinate with metal ions.^[28, 29] The interactions between metal ions and the amide groups of polymers such as nylon provide a chance to modify the performance of polymers in various aspects^[30–41] and have been investigated in our laboratory.^[42, 43] The variation of the amide group caused by metal ions can be clearly observed by using FTIR spectroscopic method, since the amide I band splits, becomes broad, and exhibits a red-shift upon coordination with metal ions.^[43–45] On the other hand, transmission electron microscopic investigation shows that microphases enriched by metal ions often form in the polymer–metal salt composite under certain conditions. However, what happens around metal ions when phase separation takes place is still beyond our understanding. The electronic Raman bands provide us with an effective probe to characterize the variation of the coordination environment around metal ions in metal salt–polymer composite. Figure 11a shows the FT-Raman spectra of nylon 6– NdCl_3 systems. Since the electronic Raman of Nd^{3+} is almost the

same as that observed from neodymium chloride, the presence of adsorbed water prevents the coordination between Nd^{3+} and the amide groups of nylon. However, as the weight ratio between neodymium chloride and nylon 6 reaches 1:10, observable variations in the electronic Raman bands suggest that the overwhelming amount of amide groups nylon can compete with water to take part in the coordination of Nd^{3+} . Nylon 6 is a crystalline polymer; the crystallization of the polymer chain and the formation of hydrogen bonds among C=O groups and N–H groups prevents the amide groups from coordinating with the metal ions. For comparison, we used poly(vinyl pyrrolidone) (PVP) to coordinate with Nd^{3+} . The selection of PVP was based on the following considerations: PVP is a noncrystalline polymer and its amide groups cannot be bound in a crystalline region—the amide groups are tertiary and no hydrogen bonds occur among them. With a lack of crystallization and hydrogen bonds among the polymer chain, PVP exhibits a greater trend of coordinating with Nd^{3+} , and the electronic Raman bands of Nd^{3+} are dramatically different from those of neodymium chloride (Figure 11b), even if adsorbed water is present in the system. After removing adsorbed water, remarkable differences occur in the Raman spectra of the nylon– NdCl_3 system in comparison with those of neodymium chloride (Figure 11c); this shows that coordination between Nd^{3+} and the amide groups occurs. The observation of changes in the electronic Raman bands indicates that different amounts of neodymium result in different coordination environments around the neodymium ions, and suggests that phase separation may accompany the variation of the coordination structure around the metal ions. Similar spectroscopic behavior was observed in the PVP– NdCl_3 system after adsorbed water had been removed (Figure 11d).

Another example is the formation of pigment gallstones.^[46–55] Insoluble calcium salts such as calcium bilirubinate, calcium carbonate, calcium phosphate, etc., are the important components of gallstones. Investigations have shown that biopolymers such as proteins, mucin, etc., are also found in gallstones. A hypothesis has thus been proposed that an interaction between biomolecules and Ca^{2+} results in the formation of calcium clusters that act as templates on which insoluble calcium salts are formed. Protein is expected to play a ligand role and co-coordinate to the calcium ion with bilirubinate, carbonate, phosphate, etc., and form mixed complexes.^[56–67] However, the calcium ion is a “silent” ion because its electron shell is closed. It is impossible to monitor the variation of calcium states caused by the variation of the coordination sphere around the calcium ions by using spectroscopic techniques under ambient conditions. Thus, the hypothesis of mixed complexes involving proteins is still beyond experimental verification.

The variation of the electronic Raman bands provides us with an opportunity to see what happens in calcium salt formation in the presence of biomolecules. Nd^{3+} , which has similar chemical properties to those of calcium ions, can be used as a probe to study the variation of coordinated states in calcium salts. First, FT-Raman spectra of neodymium phosphate synthesized in different pH environments were measured. The structural changes around the Nd^{3+} caused by the

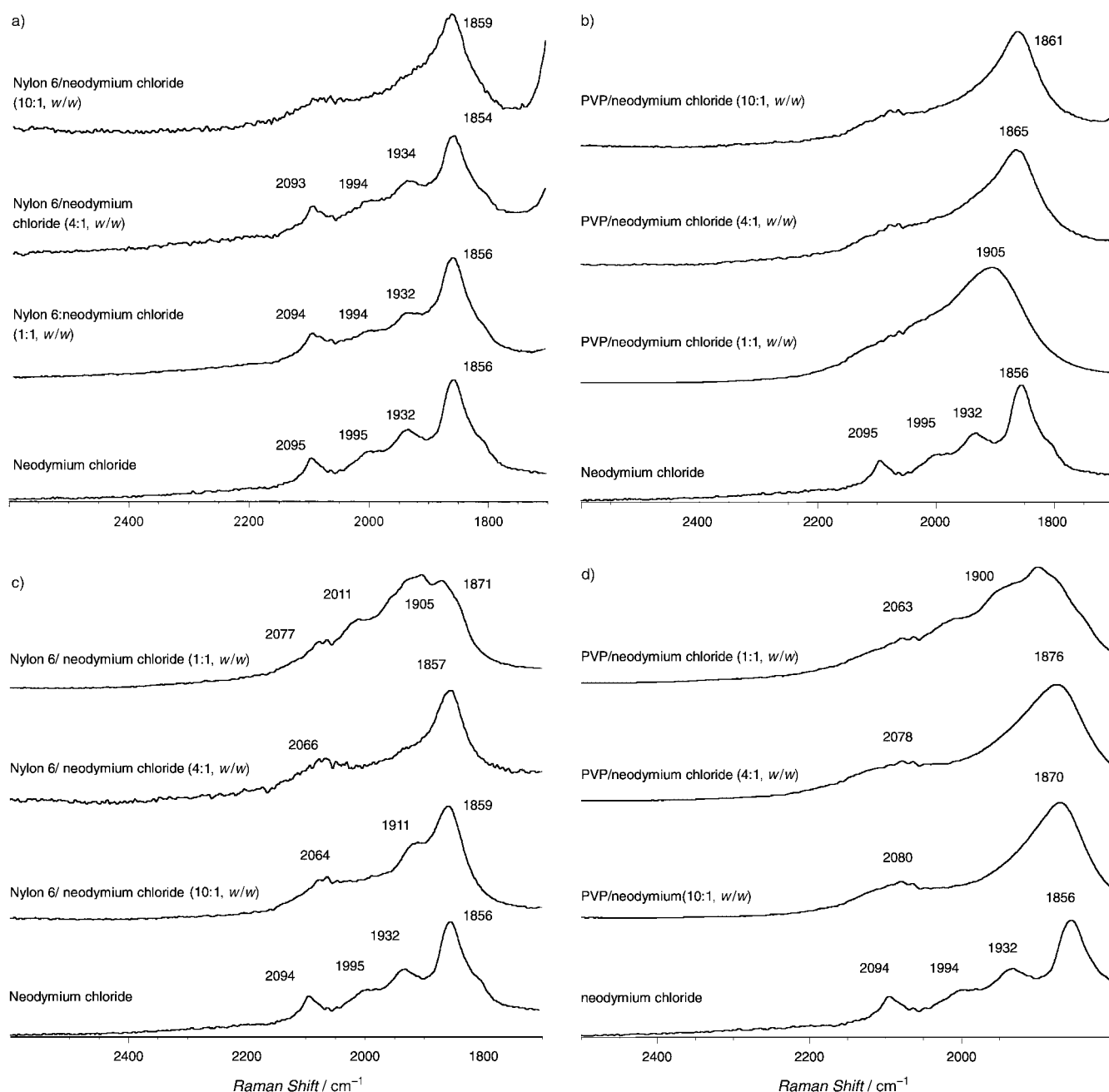


Figure 11. FT-Raman spectra of a) nylon 6/neodymium chloride systems, b) PVP/neodymium chloride systems, c) nylon 6/neodymium chloride systems after removing adsorbed water, d) PVP/neodymium chloride systems after removing adsorbed water. The electronic Raman bands (c) and (d) varied as the amount of Nd^{3+} changed.

coordination of OH^- at high pH value can be clearly seen from the electronic Raman bands (Figure 12a). This result demonstrates that the method is sensitive enough to reveal structural variation in metal ions. We used bovine-serum albumin (BSA) as a model protein to study the influence of protein on the formation of insoluble salts. BSA exhibits a different behavior in the formation of insoluble neodymium salts. As far as neodymium deoxycholate is concerned, protein is involved in the formation of the salt, since a strong amide I band occurred in the FT-Raman spectrum of neodymium salts synthesized with BSA. The binding between BSA and neodymium deoxycholate is strong, since the amide I band did not disappear even if the samples were washed

carefully with distilled water. However, there is no significant variation in the electronic Raman bands between the FT-Raman spectra of neodymium salts synthesized with or without BSA (Figure 12b). Although protein takes part in the precipitate process of the neodymium cholate, it did not coordinate to the metal ions. Protein may link to the neodymium salt by intermolecular interactions. Our study on neodymium phosphate showed that pH is a factor that governs whether protein involves coordination with the metal or not. When neodymium chloride reacts with sodium phosphate, the presence of BSA brings about significant variation in the electronic Raman band of Nd^{3+} ; this suggests that BSA is involved in the coordination with Nd^{3+} (Fig-

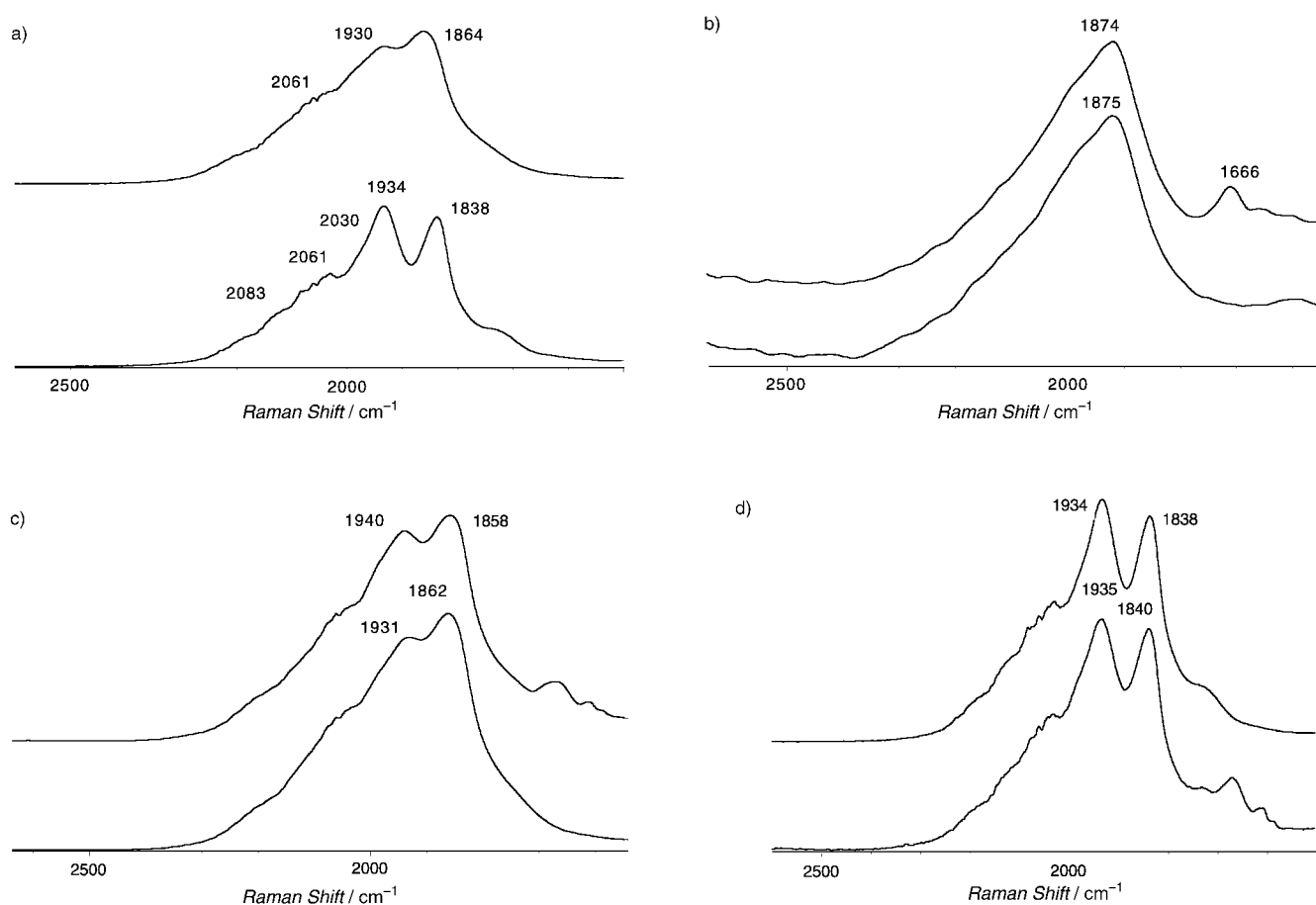


Figure 12. a) FT-Raman spectra of the phosphate salt of neodymium synthesized in different pH environment; by mixing top: NdCl_3 and Na_3PO_4 , bottom: NdCl_3 and Na_2HPO_4 . b) FT-Raman spectra of neodymium deoxycholate precipitated with (top) and without (bottom) BSA. The BSA takes part in the precipitation, since the amide I band can be observed in the sample synthesized with BSA. However, the presence of the BSA does not bring about significant variation in the electronic Raman bands. c) FT-Raman spectra of a phosphate salt of neodymium made by mixing NdCl_3 and Na_3PO_4 , the presence of BSA (top) causes significant variation in the electronic Raman bands. d) FT-Raman spectra of a phosphate salt of neodymium made by mixing NdCl_3 and Na_2HPO_4 , the presence of BSA (bottom) causes insignificant variation in the electronic Raman bands.

ure 12c). As the pH value decreases, the differences between the FT-Raman spectra of neodymium phosphates synthesized with and without BSA become insignificant; this suggests that BSA does not coordinate to metal ions at lower pH (Figure 12d). Considering the fact that about 10% of amino residues of BSA contain carboxyl groups as side chains, the pH-dependent behavior suggests that the coordination of BSA with metal ions is through its carboxyl group. At a high pH, the carboxyl groups change into carboxylate groups and have a greater chance of coordinating with metal ions.

The $f-f$ transitions of lanthanides have been used as probes to investigate molecular structure at various levels.^[68] For example, high-resolution and cryogenic fluorescence spectra of Eu^{3+} are powerful tools for characterizing different coordination sites and the symmetry around the coordination sphere.^[69–71] The 4f orbitals of lanthanide are masked by 5s and 5p orbitals, and coordination of ligands to lanthanide ions can cause only subtle variations in the $f-f$ transition bands. Consequently, a high-resolution spectroscopic technique is necessary to reveal the spectral behavior of these bands. Compared with the Eu^{3+} probe, the electronic Raman bands of Nd^{3+} described here can reveal fine spectral structure at room temperature. Thus, the bands are convenient and

sensitive fingerprints that can differentiate between various coordination states (coordinate site and the symmetry around the coordination sphere) of lanthanide complexes.

The abundant electronic levels of lanthanides provide appealing opportunities to develop a variety of new functional materials, and extensive investigations on lanthanides have been going on for several decades.^[72–84] The $\text{Nd}^{3+}/\text{YAG}$ laser system may have a bright future in helping to develop new functional materials. From the energy point of view, the YAG laser–neodymium complex is an open system and far from equilibrium state. According to Prigogine's theory,^[85] some complex behavior such as self-organization may occur in these systems. FT-Raman spectroscopy may help us to understand this complex behavior at a molecular level.

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