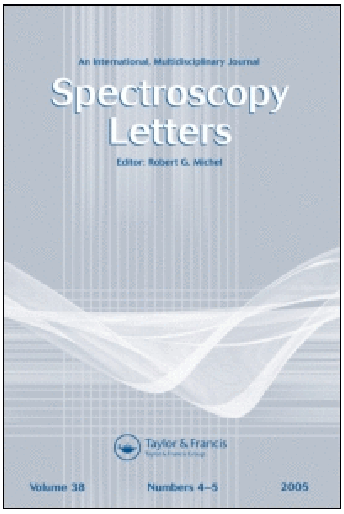

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JUDD-OFELT ANALYSIS OF PHOTOACOUSTIC SPECTRA OF POWDERED NEODYMIUM COMPOUNDS

Key words: Photoacoustic spectroscopy, Neodymium compounds, Nephelauxetic effect, Oscillator strengths, Judd-Ofelt analysis

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ABSTRACT

Photoacoustic (PA) spectra of powdered neodymium oxide: Nd_2O_3 (A type), neodymium hydrated chloride: $NdCl_3{\cdot}6H_2O$ and neodymium fluoride: NdF_3 are reported. PA band shifts as compared to their positions in aqueous Nd(III) ion have been used to calculate the nephelauxetic parameters of their compounds. The variation of these parameters and correlation with the nature of metal-ligand bonding have been discussed. A novel method is introduced to determine relative values of Judd-Ofelt parameters and oscillator strengths of powdered samples using PA spectroscopy. It is found that a linear correlation exists between relative values of τ_2 and relative oscillator strengths of hypersensitive transitions of the title compounds. It can be hoped that the new method of PA technique may serve for the Judd-Ofelt quantitative analysis of powdered rare earth compounds.

INTRODUCTION

The photoacoustic effect was first observed about a century ago by A.G. Bell.[1] Its applications to gaseous analysis have been numerous. A useful laboratory instrument suitable for the investigation of spectral properties of thermally thick samples was, however, only devised during the 1970's.[2] Soon afterwards, Rosencwaig and Gersho provided the theoretical background for understanding the basic principles of photoacoustic effect.[3] Since then, photoacoustic spectroscopy has been widely used to investigate the chemical and physical properties of many samples.[4,5] PA spectroscopy enables spectra to be obtained on any type of solids (whether they be crystalline, powder or gel), which were previously difficult or impossible to measure by ordinary transmission and reflection methods. The method can make determinations of thickness.[6] thermal conductivity,[7] quantum yield and deexcitation pathway of the analyzed substances.[8] However, the measurement of absolute absorption coefficient remains a difficult problem for PA spectroscopy, and is limited to liquid or single crystal samples.[9]

Rare earth compounds have received more and more attention because of their important roles in studies of laser materials, NMR shift reagents and biological systems. Absorption and fluorescence spectroscopies have been widely used in studies of optical properties of rare earth compounds.[10] However, absorption spectroscopy has limits for use in solid state samples because of nontransparent or scattering properties of the samples. Thus an alternative technique must be found in absorption determination of solid state compounds. PA spectroscopy is very suitable to the study of rare earth compounds according to our recent work.[11-14] In this work, PA spectra of powdered neodymium oxide: Nd_2O_3 (A type), neodymium hydrated chloride: $NdCl_3 \cdot 6H_2O$ and neodymium fluoride: NdF_3 are reported. A novel method is introduced to determine relative Judd-Ofelt parameters[15] by calculating PA intensity. Nephelauxetic parameters of neodymium compounds were calculated based on their PA spectra. The variation of these parameters and correlation with the nature of metal-ligand bonding have been discussed and relative magnitudes of τ_2 are used to interpret the oscillator strengths of hypersensitive bands.

THEORETICAL PART

Oscillator strengths of rare earth f-f transitions reflect the perturbing of ligand fields on transition intensity of center lanthanide ions.[16] As we know, the experimental oscillator strength (P) can be calculated from equation(1) for a certain transition j of the sample,

$$P_j = 4.318\times 10^{-9}\cdot\frac{9n}{(n^2+2)^2}\int_j \varepsilon(\nu)d\nu \qquad (1)$$

Where n, $\varepsilon(\nu)$ are the refractive index, the mole extinction coefficient at wave number ν of sample.

In Rosencwaig and Gersho theory[3], for thermally thick samples, the PA signal Q is,

$$Q = \frac{-i\beta\mu_s}{2a_g}\left(\frac{\mu_s}{k_s}\right)Y \qquad (2)$$

where β, μ_s and k_s are the optical absorption coefficient, the thermal diffusion length and the thermal conductivity of the sample respectively. a_g is the thermal diffusion coefficient of the gas, and Y is a constant factor.

From equations (1) and (2), a relation is built up between PA intensity I^{PA} and oscillator strength P through **equation** (3) for a certain transition j of the sample,

$$I_j^{PA} = \int_j Q d\nu = -\frac{i\mu_s Y}{2a_g}\left(\frac{\mu_s}{k_s}\right)\int_j \beta(\nu)d\nu = \frac{i\sqrt{2}\alpha_g^{1/2}Y}{\rho_s c_s\omega^{3/2}}\int_j \beta(\nu)d\nu$$

$$= \frac{i\sqrt{2}\alpha_g^{1/2}XcY}{4.318\times 10^{-9}\rho_s c_s\omega^{3/2}}P_j = AP_j \qquad (3)$$

where c, ρ_s, c_s and α_g are the molar concentration, the density, the specific heat of the sample and the thermal diffusivity of the gas respectively, and ω denotes the chopping frequency of the incident light. The factor X makes allowance for the refractive index of sample, $X=(n^2+2)^2/9n$ and A is a constant factor determined by the sample and experimental condition.

In Judd-Ofelt theory[15], τ_λ $(\lambda=2,4,6)$ are functions of the refractive index of the medium, the radial wave-function of the initial and final states and the parameters describing the perturbing mechanism. From equation (3), relative τ_λ of sample 1 and 2 can be obtained as equation (4) by comparing τ_λ' of the sample which is determined by a least-squares procedure,

$$\tau_{\lambda r} = \frac{\tau_{\lambda 1}}{\tau_{\lambda 2}} = \frac{\tau_{\lambda 1}' c_2 X_2 \rho_{s1} c_{s1}}{\tau_{\lambda 2}' c_1 X_1 \rho_{s2} c_{s2}} \qquad (4)$$

where $\tau_\lambda' = A\tau_\lambda$, thus, a new method for determining relative Judd-Ofelt parameters using only PA signal is proposed.

EXPERIMENTAL

Reagents and Samples

Nd_2O_3(99.99%) was obtained from JMC Company. As a precaution the oxide was heated at 800°C for 24 hours to remove carbonates and absorbed H_2O. The phase of Nd_2O_3 was found to be A type by x-ray powder patterns.

Hydrated $NdCl_3.6H_2O$ was prepared from 99.99% pure Nd_2O_3 by solution in a 10% excess of hot 0.1N HCl, excess H_2O and acid were removed on a water bath; the crystals were washed with small amounts of alcohol and dried at room temperature in a desiccator over $CaCl_2$ for weeks.

Neodymium fluoride NdF_3 (99.99%) was obtained from JMC Company.

Instrumentation

PA spectra were measured on a single-beam spectrometer constructed in our laboratory.[17] Excitation source was a 500w xenon lamp. The optical system was a CT-30F monochromator and a variable speed mechanical chopper at a frequency of 12Hz used to modulate the light source intensity. The acoustic signal was monitored with the sample placed in an indigenous photoacoustic cell fitted with an ERM 10 electron microphone. The output signal from the microphone was amplified by a preamplifier and then fed to a lock-in-amplifier with a reference signal imputed from the chopper. The final signal was normalized for changes in lamp intensity using a carbon-black reference. PA spectra of all the title complexes were recorded at room temperature in the region of 12000~33333cm^{-1}.

Absorption spectra in the range of 12500~33333cm^{-1} were recorded in aqueous solution by the Shimadzu UV 240 UV-Vis spectrophotometer.

RESULTS AND DISCUSSION

PA Spectra and Nephelauxetic Effect

For the shielding effect of the 5s, 5p atomic shell, absorption spectra of rare earth ions corresponding to the intraconfigurational f-f transitions are characterized by narrow, usually well-resolved bands in visible and infrared ranges. Photoacoustic spectra of powdered Nd_2O_3(A type), $NdCl_3{\cdot}6H_2O$, and NdF_3 in the range 12500-33333cm^{-1} are shown in FIG. 1.

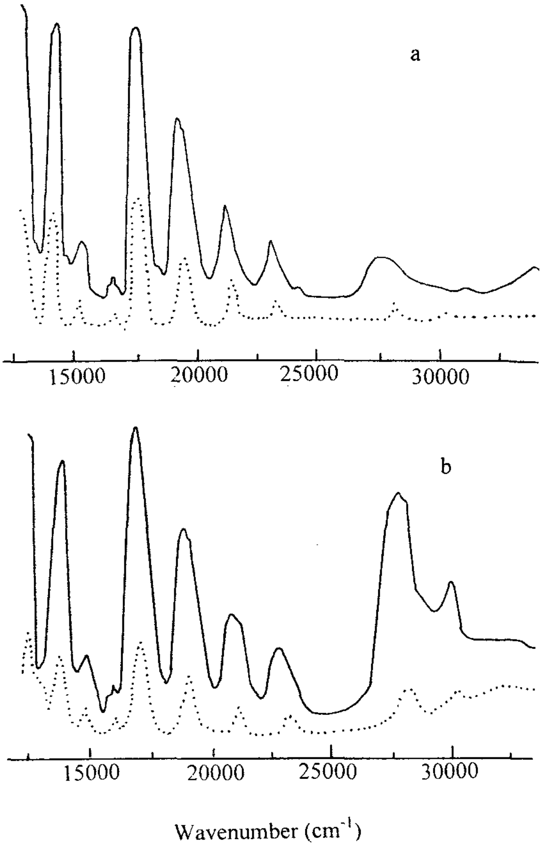

FIG. 1 PA and EAS spectra of Nd(III) compounds a: — PA of $NdCl_3.6H_2O$; ... EAS of $NdCl_3\cdot 6H_2O$ b: — PA of Nd_2O_3 (A type); ... PA of NdF_3

Photoacoustic signal is obtained by detecting the heat generated through the nonradiative relaxation released by the sample after absorbing the modulated incident light. The absorption of different J energy levels of Nd^{3+} is clearly shown in their PA spectra. All PA spectra absorption were assigned based on the lanthanide spectra as summarized by Dieke[18] in TABLE 1.

PA spectrum does not necessarily coincide with the absorption spectrum. Though the absorption spectrum of $NdCl_3\cdot 6H_2O$ reveals some similar absorption bands, it could not detect

TABLE 1 Photoacoustic Band Assignments of Neodymium Compounds (cm^{-1}) (Ground State: ${}^4I_{9/2}$)

	NdF_3	$NdCl_3.6H_2O$	Nd_2O_3 (A type)
${}^4F_{5/2}$	12690	12531	12270
${}^4F_{7/2}$+	13624	13405	13245
${}^4S_{3/2}$		13551	13423
${}^4F_{9/2}$	14837	14663	14472
${}^2H_{11/2}$	16016	15823	15674
${}^4G_{5/2}$+	17331	17094	16639
${}^2G_{7/2}$			16887
${}^4G_{7/2}$	19231	18939	18519
${}^4G_{9/2}$	19469	19268	19011
${}^2D_{3/2}+{}^2G_{9/2}$	21322	20790	20492
${}^4G_{11/2}$	21878	21322	21030
${}^2P_{1/2}$	23485	22989	22523

as many fine structures of Nd^{3+} ion as the PA spectrum does. For example, the energy level ${}^2H_{11/2}$ of Nd(III) ion has absorption at 15820 cm^{-1} in the PA spectrum. Fine structure are clearly observed,

though it can not be detected in the absorption spectrum. The apparent splitting is due to the internal stark effect caused by the surrounding local electric field. In the crystal, the Nd^{3+} ions in the high energy levels decay through their own low-lying levels to the ground state. In the aqueous solution, the ions undergo rapid radiationless relaxation because of the transfer of electronic excitation energy to high frequency vibrations such as the OH group in the solvent.

In ligand fields, 4f electrons may partly participate in the formation of metal-ligand bands. The shielding effect is not so complete. The "degree of covalency" has been estimated from nephelauxetic effect using nephelauxetic ratio β, bonding parameter $b^{1/2}$, and Sinha parameter δ.[19]

Calculated values of those parameters based on PA assignments are listed in TABLE 2. Nd_2O_3(A type) has the largest nephelauxetic effect($1-\beta$), bonding parameter($b^{1/2}$) and convalency parameter(δ). It is because of the reducing character of oxide (O^{2-}) and results in the strong interaction between Nd^{3+} and O^{2-} ions. For Nd_2O_3 (A type), $\delta>1.5$, which is a direct indicator of strong covalent bonding of the compound. For $NdCl_3{\cdot}6H_2O$, $1.5>\delta>0$, which is an indicator of weak covalent bonding of the compound. Where as NdF_3, $\delta<0$, **indicates an** ionic bonding of the compound. In the title compounds, O^{2-} has the largest electron donating

TABLE 2 Calculated Values of Various Covalency Parameters of Nd(III) Compounds

	NdF_3	$NdCl_3.6H_2O$	Nd_2O_3 (A type)
β	100.6%	98.92%	97.27%
$b^{1/2}$	–	0.0735	0.117
δ	-0.596	1.092	2.807

ability, while F^- has the least. As electron donating ability of the ligand increases, the "degree of covalency" in the metal-ligand bonds increases correspondingly.

Judd-Ofelt Analysis of PA Spectra

In Rosencwaig and Gersho theory[3], the authors assumed $\eta = 1$, representing coefficient which absorbed light is converted to heat by nonradiative deexcitation processes. The fluorescence properties of neodymium compounds are very weak, the proposed method can be tested in PA spectra of **title** compounds. Calculated values of τ_λ' and $\tau_{\lambda r}$ are collected in TABLE 3. The optical and thermal parameters used in Equation (4) are form references[20].All $\tau_{\lambda r}$ are obtained by comparing τ_λ' of neodymium compounds with that of NdF_3. The variation of $\tau_{\lambda r}$ may reflect the different perturbing of ligand fields. As can be seen in TABLE 3, τ_{2r} parameter varies quite widely, while τ_{4r} and τ_{6r} are less affected for neodymium compounds. The results confirm that τ_2 parameter in the compound is the most sensitive to environment.

Relative oscillator strengths P_r of hypersensitive transitions $^4G_{5/2}+^2G_{7/2}$ which can be obtained from Equation (3) are also collected in TABLE 3. The value of P_r determined by PA spectroscopy is consistent with that obtained by Krupke[21]. By plotting $\tau_{\lambda r}$ vs. P_r in FIG. 2, it can be pointed out that a linear correlation exists between τ_{2r} and P_r. Here, the result again confirms Judd's statement that hypersensitivity is intimately associated with the τ_2 parameters. As can be seen in TABLE 2, nephelauxetic effect increases for NdF_3, $NdCl_3{\cdot}6H_2O$, and Nd_2O_3, and oscillator strengths of hypersensitive transitions $^4G_{5/2}+^2G_{7/2}$ increase for NdF_3, $NdCl_3{\cdot}6H_2O$, and Nd_2O_3. As the "degree of covalence" increases, the oscillator strength of the hypersensitive transition exhibits a corresponding increase. Therefore, the fact supports that the τ_2 parameter is affected predominately by the covalency in the metal-ligand bonding,

TABLE 3 Values of Judd-Ofelt Parameters for Neodymium Compounds

	τ_2'	τ_4'	τ_6'	τ_{2r}	τ_{4r}	τ_{6r}	P_r
NdF_3	2.64×10^{-4}	2.67×10^{-3}	2.92×10^{-3}	1	1	1	1
$NdCl_3.6H_2O$	5.36×10^{-4}	2.96×10^{-3}	1.65×10^{-3}	3.18	1.74	0.89	2.55
Nd_2O_3	1.25×10^{-3}	2.34×10^{-3}	1.63×10^{-3}	9.20	1.70	1.08	7.86

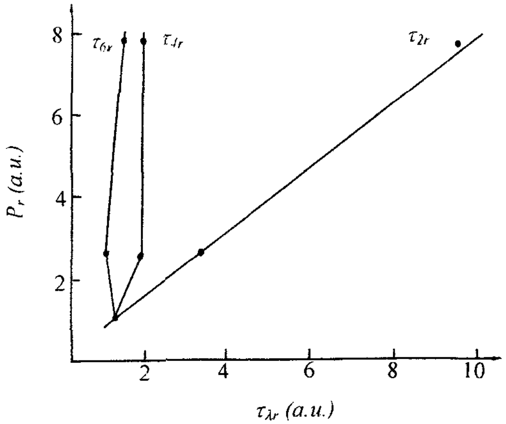

FIG.2 Plot of relative values of $\tau_{\lambda r}$ vs. P_r of hypersensitive transition of $^4G_{5/2}$+$^2G_{7/2}$ for neodymium compounds

while τ_4 and τ_6 reflect the symmetry of the lanthanide environment[22]. It can be hoped that the new method of PA technique may serve for the Judd-Ofelt quantitative analysis of powdered rare earth compounds.

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