

Photoacoustic spectra of rare-earth 1-tyrosine hydrazide, 8-hydroxyquinoline and ammonium metavanadate

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Abstract. The photoacoustic spectra of 1-tyrosine hydrazide, 8-hydroxyquinoline and ammonium metavanadate complexes containing Pr, Nd, Er and Ho have been recorded in the 400–800 nm region using a single beam photoacoustic spectrometer. The main spectral features in the photoacoustic spectra are found to be due to triply ionized rare-earth atoms and the assignments reveal a red shift in their spectral features as compared to their positions in the free ions. These shifts have been used to calculate the nephelauxetic parameters for these complexes. The photoacoustic branching ratios have also been determined and compared with absorption branching ratios for some of these complexes.

Keywords. Photoacoustic spectra; rare-earth complexes; nephelauxetic parameters; photoacoustic branching ratios.

1. Introduction

Chemical compounds containing rare-earth ions form an extremely interesting group of molecules because of their interesting electronic properties. Rare-earth compounds exhibit very sharp lines due to the $f-f$ transitions of the triply ionized ions of the rare earths in the visible and near infrared regions, very similar to the $d-d$ transitions of transition metals. The wavelengths of the spectral lines of the rare earth ions change slightly from one lattice to the other due to interaction with the surrounding charges of the lattice. These small spectral changes sometimes lead to a major difference in the radiation characteristics of the molecule. Interest in the study of these molecules has increased many-fold due to the discovery of strong lasing action involving rare earth ions in some of the compounds. The present work is part of the attempt being made to investigate the non-radiative processes of rare earths ions in solid and liquid matrices (Carnall 1962, 1963; Streck *et al* 1987). Non-radiative transitions in organic compounds containing rare earth ions play a useful role in energy transfer from the excited states of the ion and are of great importance in biological processes. In the present paper we report the results of our studies on the photoacoustic spectra of Pr, Nd, Ho and Er doped 1-tyrosine hydrazide, 8-hydroxyquinoline and ammonium metavanadate.

2. Experimental

The method of preparation of rare earth 1-tyrosine hydrazide and 8-hydroxyquinoline complex was the same as described by Rao and Khan (1987). In brief, a hot methanolic

solution of tyrosine hydrazide (3.75 m mol) or 8-hydroxyquinoline (3.75 m mol) and the rare earth chloride (1.25 m mol) were mixed and vigorously stirred for about 10 minutes. The mixture was then kept aside for a while to settle, and the complex thus formed as a precipitate in the form of macrocrystalline solid collected in the bottom of the tube. These crystals were filtered and washed with a mixture of acetonitrile and methanol and dried under vacuum.

The preparation of rare earth vanadate complexes was carried out by following the procedure given by Antio-Fidancev *et al* (1985). A mixture of rare earth oxide and ammonium metavanadate was maintained at 300°C for 3 h followed by maintaining it at 700°C for 2 h and finally at 1000°C for 15 h. The compound thus formed was in the form of fine powder.

The compositions of these organic compounds and inorganic complexes were checked by recording their absorption spectra and comparing them with those reported earlier.

2.1 Recording of photoacoustic spectra

The photoacoustic (PA) spectra of complexes in powder form were recorded in the range 400–800 nm using a single beam photoacoustic spectrometer fabricated in our laboratory (see Rai *et al* 1986). The powdered sample was placed in a 1 cm diameter cylindrical chamber of the photoacoustic cell which also houses a sensitive electret microphone. Light from a 600 W tungsten halogen lamp dispersed by a 0.25 m Jarrell Ash grating monochromator with 2 mm slit width (7 nm bandwidth) and chopped at 22.5 Hz was allowed to fall on the sample. The signal thus obtained was amplified and fed to an EG and G lock in amplifier (Model 186A) whose output was recorded using a time constant of 30 s. The photoacoustic spectra of the samples were normalized using the photoacoustic signal from carbon black recorded under identical experimental conditions. The PA spectra of pure 1-tyrosine hydrazide, 8-hydroxyquinoline and ammonium metavanadate were also recorded for comparison with those of their rare-earth complexes.

2.2 Study of the PA spectra

The PA spectra of pure 1-tyrosine hydrazide as well as 8-hydroxyquinoline are dominated by strong and broad peaks in the region 400–440 nm. The PA signal on the longer wavelength side decreases monotonically and smoothly (see figure 1). Pure ammonium metavanadate has a negligibly small photoacoustic signal and its spectrum could not be recorded.

The photoacoustic spectra of the 12 complexes exhibit a large number of peaks in the 400–800 nm region. These peaks are due to triply ionized rare-earth atoms shifted slightly from their free ion positions due to the lattice field of the complex. In the case of the two organic lattices the shifts in peak are similar though the intensity of the peaks which result due to different strengths of non-radiative processes in the two lattices sometimes differ appreciably. The spectra for all the 12 complexes are shown in figures 2–5.

The photoacoustic peaks due to rare-earth ions in the vanadate complexes exhibit a red shift as compared to the corresponding rare-earth 1-tyrosine hydrazide or 8-hydroxyquinoline complexes although there is little difference in their half-widths

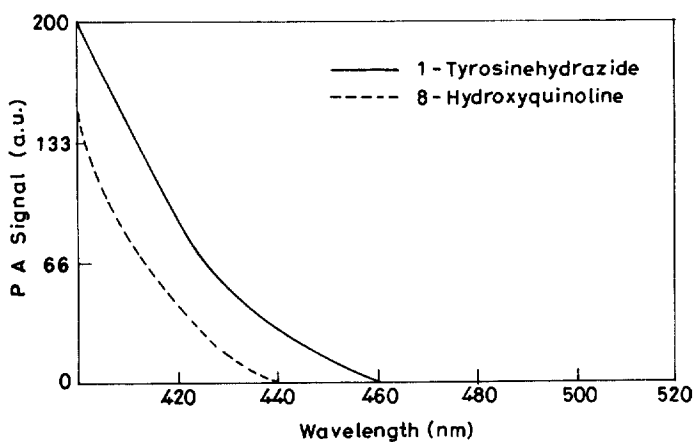


Figure 1. PA spectra of 1-tyrosine hydrazide and 8-hydroxyquinoline ligands.

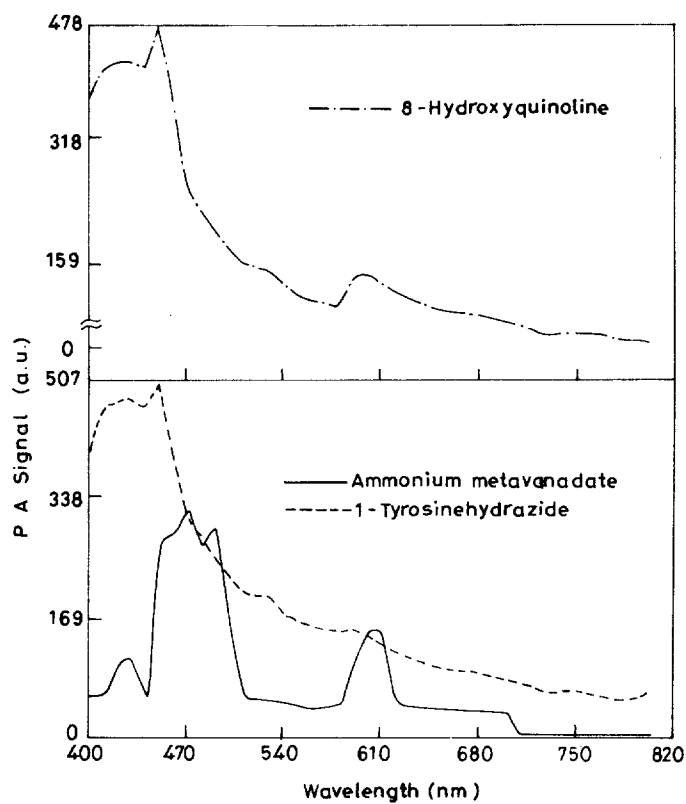


Figure 2. PA spectra of Pr^{3+} complexes.

and shapes. The wavelengths of these peaks, and their transition assignments are given in tables 1–4.

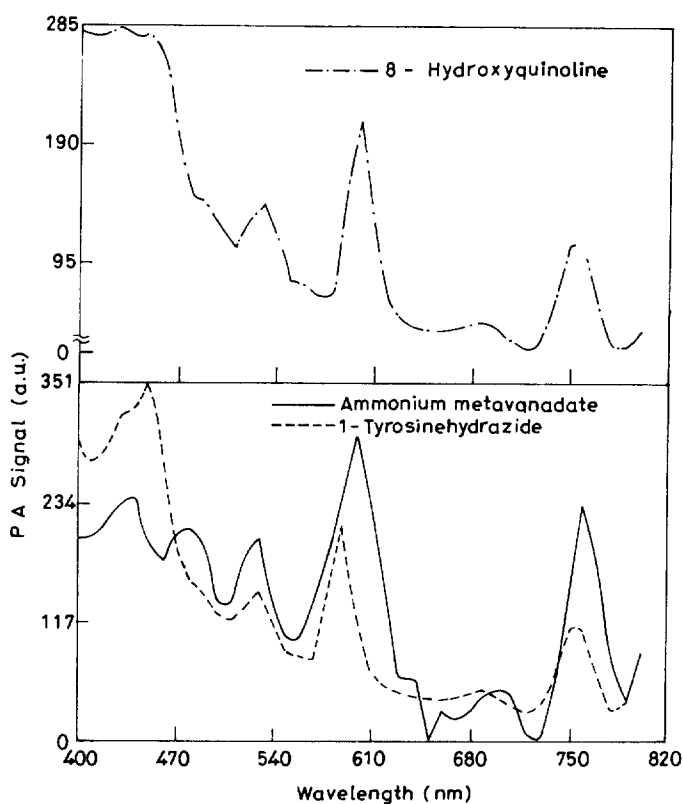


Figure 3. PA spectra of Nd^{3+} complexes.

3. Results and discussion

The photoacoustic spectra of the rare-earth complexes have been analysed in terms of the optical transition in triply ionized rare earth atoms. These transitions are actually forbidden by the Laporte rule as they occur amongst the energy levels of the same configuration but they appear as a result of the effects of the ligand on the complex. The assignments of the peaks in the spectrum have been made on the basis of the earlier absorption, fluorescence and PA spectra of the respective ions either in the free state or in other compounds (Deike 1968; Schoonover *et al* 1984; Streck *et al* 1987; Lakshman and Suresh Kumar 1988).

3.1 PA spectra of Pr^{3+} complexes

The ground state of Pr^{3+} is 3H_4 . There are five excited energy states viz., 1D_2 , 3P_0 , 3P_1 , 3P_2 and 1I_6 to participate in the PA spectra in the region of 400–800 nm. We observe four peaks in Pr^{3+} metavanadate, and three each in 1-tyrosine hydrazide and 8-hydroxyquinoline (see figure 2). The separation between 1I_6 and 3P_1 levels is only 200 cm^{-1} and they are not expected to be resolved in our spectra. However in the organic lattices only three peaks are resolved due to strong overlapping of the Pr^{3+} peaks with those of the pure 1-tyrosine hydrazide or 8-hydroxyquinoline.

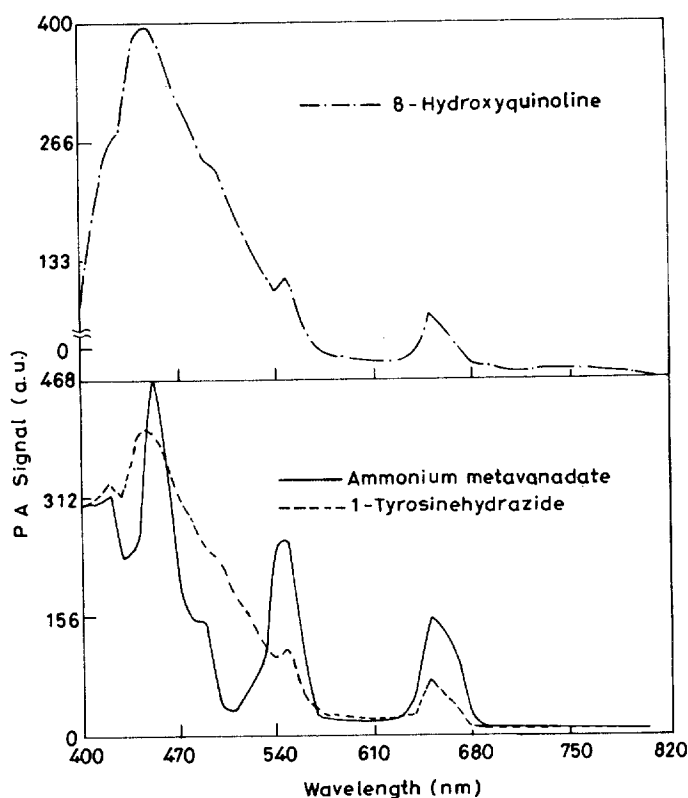


Figure 4. PA spectra of Ho^{3+} complexes.

3.2 PA spectra of Nd^{3+} complexes

The spectra of Nd^{3+} is not known in the gaseous phase and we have used data from its spectrum in aqueous solution for our assignment. Nd^{3+} has excited energy states ${}^2D_{5/2}$, ${}^2P_{1/2}$, ${}^4G_{11/2}$, ${}^2G_{9/2}$ (2D , 2P) $_{3/2}$, ${}^2K_{15/2}$, ${}^4G_{9/2}$, ${}^4G_{7/2}$, ${}^2G_{7/2}$, ${}^4G_{5/2}$, ${}^2H_{11/2}$, ${}^4F_{9/2}$, ${}^2S_{1/2}$ and ${}^4F_{7/2}$ which are expected to give photoacoustic signals in the region 400–800 nm. The levels ${}^2P_{1/2}$, ${}^4G_{11/2}$, ${}^2G_{9/2}$, ${}^4G_{5/2}$ and ${}^4F_{7/2}$ are non-radiative in nature and a strong PA signal arises from them. Some of the levels are grouped closely together, viz. ${}^4G_{5/2}$ and ${}^2G_{7/2}$, ${}^4G_{7/2}$ and ${}^4G_{9/2}$, ${}^2K_{15/2}$, (2D , 2P) $_{3/2}$, ${}^4G_{11/2}$ and ${}^2P_{1/2}$ and ${}^2D_{5/2}$ so that they give single peaks at our experimental resolution and on the basis one expects only seven peaks in Nd^{3+} complexes in the region 400–800 nm. In our recorded spectrum (see figure 3) we observe all the seven peaks in Nd^{3+} metavanadate but only five peaks in Nd^{3+} 1-tyrosine hydrazide and six peaks in the 8-hydroxyquinoline. The assignment of the peaks could be made by comparing these spectra with the spectra of Nd^{3+} in other complexes. The peak due to ${}^4G_{11/2}$, ${}^2K_{15/2}$, (2D , 2P) $_{3/2}$ \leftarrow ${}^4I_{5/2}$ however does not appear in the organic complexes probably due to its overlapping with the broad peak observed in the 440 nm region in these complexes. The peak due to ${}^2G_{7/2}$, ${}^4G_{5/2}$ \leftarrow ${}^4I_{9/2}$ appears to have maximum intensity in all the three complexes.

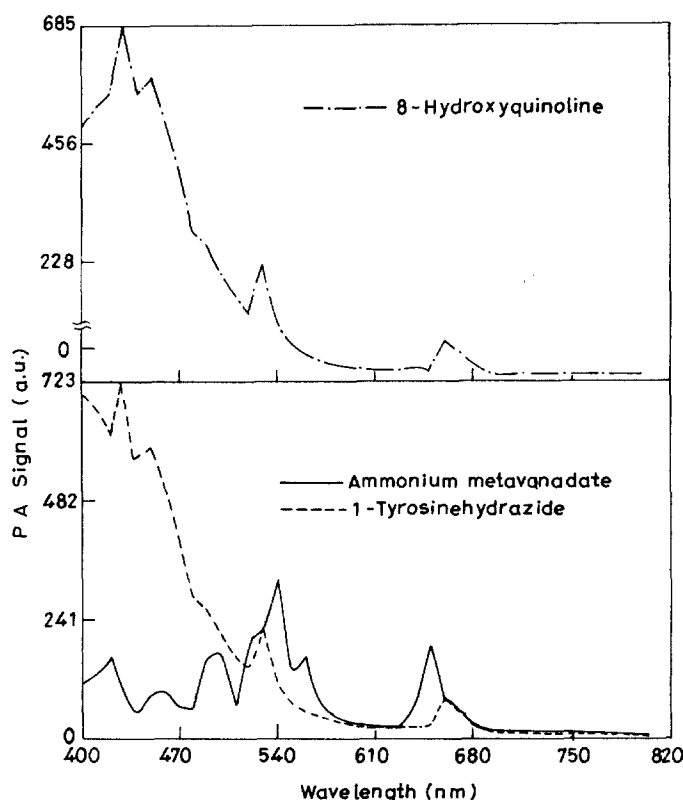


Figure 5. PA spectra of Er^{3+} complexes.

3.3 PA spectra of Ho^{3+} complexes

Like Nd^{3+} , the gaseous spectra of Ho^{3+} is also not known and we have used solution spectra of Ho^{3+} for comparative study. The ground state of Ho^{3+} is 5I_8 . There are excited energy levels viz., 5I_4 , 5F_5 , 5S_2 , 5F_4 , 5F_3 , 5F_2 , 3K_8 , 5G_6 , 5F_1 , $(^5G, ^3G)_5$ with 5F_4 as the non-radiative one which is expected to contribute a strong PA signal. The levels 5S_2 and 5F_4 are superposed exactly and they contribute only one peak. Similarly 5F_3 , 5F_2 and 3K_8 are very close to each other giving rise again to only one signal. Thus there are five peaks expected in the region of our observation. All the five peaks of Ho^{3+} appear in the vanadate complex but only four each in hydroxyquinoline and 1-tyrosine hydrazide could be observed. The peak due to 5F_3 , 5F_2 , $^3K_8 \leftarrow ^5I_8$ appear with very weak intensity in vanadate and it could not be observed in organic lattices. Nearly all the peaks in the present organic lattices are weaker as compared to those seen in the inorganic lattice.

3.4 PA spectra of Er^{3+} complexes

The ground state of Er^{3+} is $^4I_{15/2}$ and its excited levels $^2G_{9/2}$, $^4F_{9/2}$, $^4S_{3/2}$, $(^2H, ^4G)_{11/2}$, $^4F_{7/2}$, $^4F_{3/2}$, $^4F_{5/2}$, $^2H_{9/2}$, $^4F_{9/2}$ are expected to contribute PA signals in the region of our study. Of these levels, except for the level $^2H_{11/2}$, all others are radiative in nature and therefore only weak PA signals are expected from them. The separation between the $^4F_{3/2}$ and $^4F_{5/2}$ levels is very small ($\sim 272 \text{ cm}^{-1}$) and the two transitions

will not be resolved in our spectrum and will result in only one line. In the case of $(^2H, ^4G)_{11/2}$ and $^4S_{3/2}$, the levels are separated by 700 cm^{-1} and they are expected to be just resolved. Thus one expects six peaks to appear in Er^{3+} complexes.

One can see in figure 4 that our recorded spectra show all the six peaks in Er^{3+} metavanadate and only four peaks each in Er^{3+} 1-tyrosine hydrazide and Er^{3+} 8-hydroxyquinoline. The assignment of the peaks could be made by comparing the present spectra with the spectra of other erbium complexes. In the organic lattice the peaks involving $(^2H, ^4G)_{11/2}$ and $^4S_{3/2}$ are not resolved and they appear as one broad feature due to superposition. The peak due to $^4F_{7/2} \leftarrow ^4I_{15/2}$ does not appear in organic lattices but it has very weak intensity in the vanadate complex.

The spectral characteristics of triply ionized rare-earth atoms are known in some cases from gas phase studies or studies in aqueous solution (Carnall *et al* 1968; Yatsimirskii and Davidenko 1979). As mentioned earlier, a comparison of the peak wavelengths of the rare-earth elements as free ions and in the complexes indicate that the latter are red-shifted. The red shift in the case of the inorganic lattice is greater as compared to that in the organic lattice. In the ligand field the whole $4f^n$ energy structure turns out to be shortened as compared to that in the free ion which causes this effect. This red shift has been termed the nephelauxetic effect by Schaffer (1958) and has been discussed in detail by Jorgensen (1956, 1966). The nephelauxetic effect is defined quantitatively by a parameter β which is equal to the ratio of electron repulsion parameters in the complex and in the free ion. In general it is defined as the ratio of Slater's integrals F_K or the Racoh parameter E^K such that

$$\beta = \frac{(F_K)_c}{(F_K)_f} = \frac{(E^K)_c}{(E^K)_f}.$$

In the case of lanthanide complexes, generally the value of β is very nearly unity for $f-f$ transitions and one can take β as the ratio of frequency of transition of the particular band in the complex to its frequency in the free ion (Jorgenson 1966),

$$\beta = \nu_c/\nu_f.$$

There are many rare-earth ions for which the free ion spectra are not known and in such cases one defines an equivalent parameter β' as:

$$\beta' = (\nu^K)_c/(\nu^K)_{\text{aq}}.$$

In our measurements the free ion data is known for Pr^{3+} and Er^{3+} (Yatsimirskii and Davidenko 1979), however for Nd^{3+} and Ho^{3+} only the aquo-ion data is known, and hence in the first two cases the β values and in the latter two the β' values can be calculated as given in tables 1-4.

Relative intensities of peaks in the FA spectrum are different from that in the corresponding absorption spectra due to the fact that the former depend upon the absorption cross-section of the ions as well as on the probability of non-radiative transition. In order to characterize the change in the intensity of the PA transition, Strek *et al* (1987) have defined the branching vector Y_K^{PA} which corresponds to the ratio of the integrated intensity of one of the peaks in the spectrum to the total intensity of all the peaks i.e.

$$Y_K^{\text{PA}} = I_K^{\text{PA}} / \sum_{K=1}^n I_K^{\text{PA}}.$$

Table 1. Spectral data for Pr 1-tyrosine hydrazide, 8-hydroxyquinoline and ammonium metavanadate.

Complex	Assignment	PA branching ratio	Absorption branching	Energy of the peak in free ion (cm ⁻¹)	Energy of the peak in complexes (cm ⁻¹)	β
1-Tyrosine hydrazide	$^3P_2 \leftarrow ^3H_4$	0.65	0.70	23 160	23 249	1.004
	$^1I_6, ^3P_1 \leftarrow ^3H_4$	—	—	22 007	22 215	1.009
	$^1D_2 \leftarrow ^3H_4$	0.35	0.30	17 334	16 944	0.978
8-Hydroxy quinoline	$^3P_2 \leftarrow ^3H_4$	0.60		23 160	23 249	1.004
	$^1I_6, ^3P_1 \leftarrow ^3H_4$			22 007	22 215	1.009
	$^1D_2 \leftarrow ^3H_4$	0.40		17 334	16 662	0.961
Ammonium meta-vanadate	$^3P_2 \leftarrow ^3H_4$	0.12		23 160	23 249	1.004
	$^1I_6, ^3P_1 \leftarrow ^3H_4$	0.59		22 007	21 270	0.967
	$^3P_0 \leftarrow ^3H_4$			21 390	20 402	0.954
	$^1D_2 \leftarrow ^3H_4$	0.29		17 334	16 662	0.961

Table 2. Spectral data of Nd 1-tyrosine hydrazide, 8-hydroxyquinoline and ammonium metavanadate.

Complex	Assignment	PA branching ratio	Absorption branching	Energy of the peak in aq. ion (cm ⁻¹)	Energy of the peak in complexes (cm ⁻¹)	β'
1-Tyrosine hydrazide	$^4G_{11/2} \leftarrow ^4I_{9/2}$	0.38	0.62	21 650	22 215	1.026
	$^2G_{9/2} \leftarrow ^4I_{9/2}$	0.19	0.17	21 300	18 862	0.886
	$^4G_{5/2} \leftarrow ^4I_{9/2}$	0.19	0.10	17 300	16 949	0.980
	$^4F_{9/2} \leftarrow ^4I_{9/2}$	0.14	0.05	14 700	14 488	0.986
	$^4F_{7/2} \leftarrow ^4I_{9/2}$	0.11	0.07	13 500	13 329	0.987
8-Hydroxy quinoline	$^2P_{1/2} \leftarrow ^4I_{9/2}$	0.40		23 250	22 718	0.977
	$^4G_{11/2} \leftarrow ^4I_{9/2}$			21 650	22 215	1.026
	$^2G_{9/2} \leftarrow ^4I_{9/2}$	0.18		21 300	18 862	0.886
	$^4G_{5/2} \leftarrow ^4I_{9/2}$	0.20		17 300	16 662	0.693
	$^4F_{9/2} \leftarrow ^4I_{9/2}$	0.14		14 700	14 488	0.986
Ammonium meta-vanadate	$^2P_{1/2} \leftarrow ^4I_{9/2}$	0.33		23 250	22 720	0.977
	$^4G_{11/2} \leftarrow ^4I_{9/2}$			21 650	20 827	0.982
	$^2G_{9/2} \leftarrow ^4I_{9/2}$	0.25		21 300	18 862	0.886
	$^4G_{5/2} \leftarrow ^4I_{9/2}$	0.26		17 300	16 662	0.963
	$^2H_{11/2} \leftarrow ^4I_{9/2}$			15 870	15 620	0.984
	$^4F_{9/2} \leftarrow ^4I_{9/2}$	0.03		14 700	14 281	0.971
	$^4F_{7/2} \leftarrow ^4I_{9/2}$	0.13		13 500	13 154	0.974

The branching ratios thus obtained for the various peaks in the PA spectra in different compounds are given in tables 1–4. The absorption branching ratio for Pr³⁺ and Nd³⁺ 1-tyrosine hydrazide have been calculated by Rao and Khan (1987) and these are also included for comparison. $^3P_0 \leftarrow ^3H_4$ of Pr³⁺; $^4F_{3/2} \leftarrow ^4I_{9/2}$, $^4I_{11/2}$, $^4I_{13/2}$

Table 3. Spectral data of Ho 1-tyrosine hydrazide, 8-hydroxyquinoline and ammonium metavanadate.

Complex	Assignment	PA branching ratio	Energy of the peak in aq. ion (cm ⁻¹)	Energy of the peak in complexes (cm ⁻¹)	β'
1-Tyrosine hydrazide	$^5G_5 \leftarrow ^5I_8$	0.75	23 950	23 802	0.994
	$^5F_1 \leftarrow ^5I_8$			22 720	
	$^5F_4 \leftarrow ^5I_8$	0.20	18 500	18 176	0.982
	$^5F_5 \leftarrow ^5I_8$	0.05	15 500	15 380	0.992
8-Hydroxy quinoline	$^5G_5 \leftarrow ^5I_8$	0.74	23 950	23 802	0.994
	$^5F_1 \leftarrow ^5I_8$			22 215	
	$^5F_4 \leftarrow ^5I_8$	0.20	18 500	18 176	0.982
	$^5F_5 \leftarrow ^5I_8$	0.06	15 500	15 262	0.992
Ammonium meta-vanadate	$^5G_5 \leftarrow ^5I_8$	0.34	23 950	23 802	0.994
	$^5F_1 \leftarrow ^5I_8$	0.31		22 215	
	$^5F_2 \leftarrow ^5I_8$		18 176	20 402	1.222
	$^5F_4 \leftarrow ^5I_8$	0.19	18 500	18 176	0.982
	$^5F_5 \leftarrow ^5I_8$	0.16	15 500	15 380	0.992

Table 4. Spectral range of Er 1-tyrosine hydrazide, 8-hydroxyquinoline and ammonium metavanadate.

Complex	Assignment	PA branching ratio	Energy of the peak in free ion (cm ⁻¹)	Energy of the peak in complexes (cm ⁻¹)	β
1-Tyrosine hydrazide	$^2G_{9/2} \leftarrow ^4I_{15/2}$	0.37	24 475	23 249	0.950
	$^4F_{5/2} \leftarrow ^4I_{15/2}$	0.43	22 182	22 215	1.001
	$^2H_{11/2} \leftarrow ^4I_{15/2}$	0.14	19 011	18 862	0.992
	$^4F_{9/2} \leftarrow ^4I_{15/2}$	0.06	15 183	15 147	0.998
8-Hydroxy quinoline	$^2G_{9/2} \leftarrow ^4I_{15/2}$	0.38	24 475	23 802	0.973
	$^4F_{5/2} \leftarrow ^4I_{15/2}$	0.42	22 182	22 215	1.001
	$^2H_{11/2} \leftarrow ^4I_{15/2}$	0.14	19 011	18 862	0.992
	$^4F_{9/2} \leftarrow ^4I_{15/2}$	0.06	15 183	15 147	0.998
Ammonium meta-vanadate	$^2G_{9/2} \leftarrow ^4I_{15/2}$	0.24	24 475	23 802	0.976
	$^4F_{5/2} \leftarrow ^4I_{15/2}$		22 182	21 733	0.980
	$^4F_{7/2} \leftarrow ^4I_{15/2}$	0.42	20 494	19 994	0.976
	$^2H_{11/2} \leftarrow ^4I_{15/2}$		19 011	18 513	0.973
	$^4S_{3/2} \leftarrow ^4I_{15/2}$	0.11	18 300	17 852	0.976
	$^4F_{9/2} \leftarrow ^4I_{15/2}$	0.23	15 183	15 380	1.012

transitions of Nd³⁺; and $^4S_{3/2} \leftarrow ^4I_{9/2}$, $^4I_{11/2}$, $^4I_{13/2}$ transitions in Er³⁺ lead to laser action in the visible region and data on the absorption and PA branching ratios defined here may be useful in understanding the mechanism of laser-action since PA signals would cause some loss in laser intensity.

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