Attention may be paid to the fact that both a_L and a_A are lower than in other isodielectric media [14]. [On the other hand, these results agree with data supplied by FERNANDEZ PRINI and PRUE [15] on several electrolytes in pure sulfolane.] Correspondingly a remarkable association to ion pairs may be observed.

Thus, further evidence is given to the supposition that sulfolane shows only a weak capacity to give rise to an ion solvation; hence the association to ion pairs would be enhanced.

The plots of $\log A$ vs. $1/D$ are linear (Fig. 4) within the reliability limits of the calculated A values. (The uncertainty on the first A value is as large as A itself.)

The Walden products appear but little affected by solvent composition, except for a small region close to pure water. Accordingly, with the above mentioned steady decrease of ionic contact distances, the initial increase in the Walden product may be related to a gradual desolvation of ions.

The conclusion may be also drawn from experimental data that, as expected, the sulfolane-water mixtures behave as an ideal conducting medium.

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Spectral Investigations of Some Rare Earth β-Diketonates in the Region 750–250 cm^{-1}

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The infrared absorption spectra of fifteen La^{3+}, Pr^{3+}, Nd^{3+}, and Sm^{3+} β-diketonates have been studied in the spectral region 750–250 cm^{-1}. The existence of three metal-oxygen vibration modes suggests D_3 symmetry for the chelates under study. The stretching force constants, f_{MO}, of the MO bonds have been computed from the observed infrared M–O vibrations using the method of Müller. The value of f_{MO} is nearly constant ($\sim 2.7 \times 10^5$ dynes/cm) in all the chelates suggesting similar bond strengths.

Introduction

Rare earth β-diketonates are becoming important laser materials due to narrow line width of the internal 4 f transitions and weak crystal field interactions [1]. Though Slater-Condon, Racah, Lande, nephelauxetic and intensity parameters for many of these complexes have been reported [2–6], very little information regarding their structure and strength of various bonds are available. The potential energy and hence the force constant provides valuable information about the nature of interatomic forces [7]. With this in view the present investigation of infrared absorption was undertaken.

The present paper reports the infrared spectra of fifteen La^{3+}, Pr^{3+}, Nd^{3+} and Sm^{3+} complexes of acetylacetone (A), benzoylacetone (BA), dibenzoylmethide (DBM) and thenoyltrifluoroacetone (TFA), in the spectral region 750 – 250 cm^{-1}. The metal-oxygen force constants from the infrared active modes of vibration of these complexes have been computed using the method of MÜLLER [8].

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Experimental and Results

The infrared absorption measurements in the region $750-250\ cm^{-1}$ of the complexes under study were carried out on a Perkin-Elmer 521 double beam Infrared spectrophotometer employing KBr pellet technique. The instrument was calibrated by using indene. All the spectra were measured under the condition of high resolution ($3-5\ cm^{-1}$). The results of measurements are given in Figs. 1–4.

Discussion

It is well known [7] that the spectra in the region $4000-750\ cm^{-1}$ are characteristic of the ligand, while those in the region $750-250\ cm^{-1}$ characterize the rare earth ion and reflect the nature of metal-ligand bonding.

Metal-Oxygen Vibrations

A theoretical study of different types of metal complexes shows that the number of infrared active vibration is different for different types of of metal complexes e. g., 4 for tetrahedral (1 : 2 metal/ligand) and 3 for octahedral (1 : 3 metal/ligand)[9] ones. Thus the total number of M–O bands can give the geometry of the complex. The

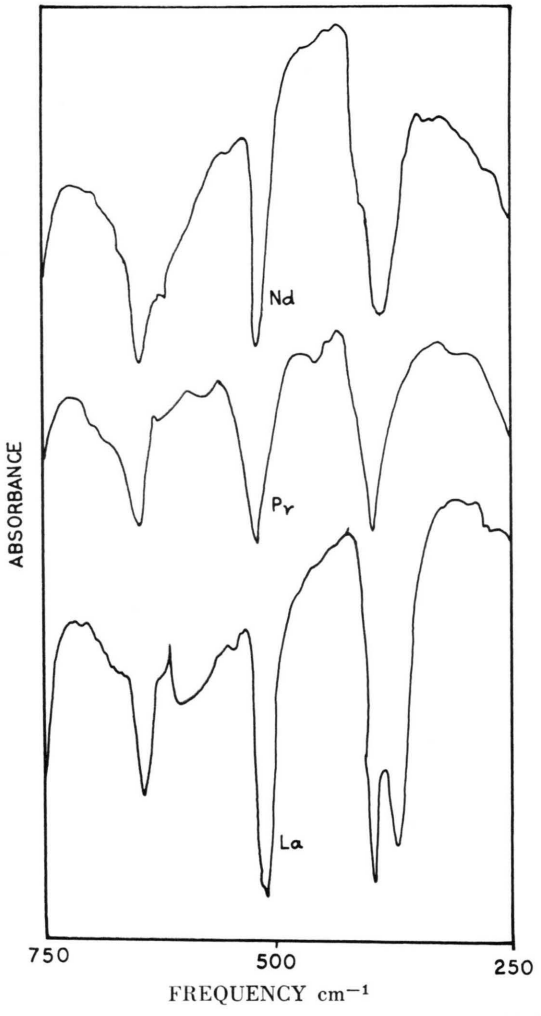

Fig. 1. Infrared absorption spectra of A complexes of La^{3+}, Pr^{3+} and Nd^{3+}.

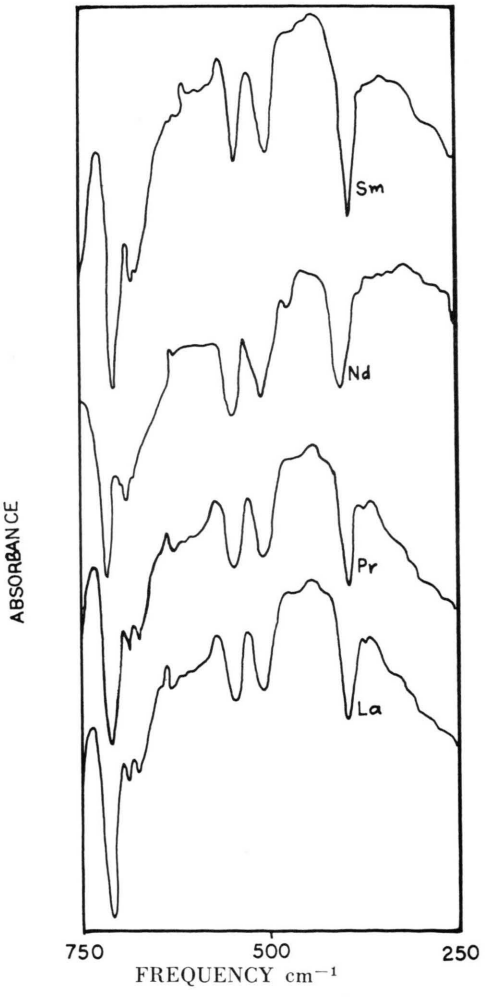

Fig. 2. Infrared absorption spectra of BA complexes of La^{3+}, Pr^{3+}, Nd^{3+} and Sm^{3+}.

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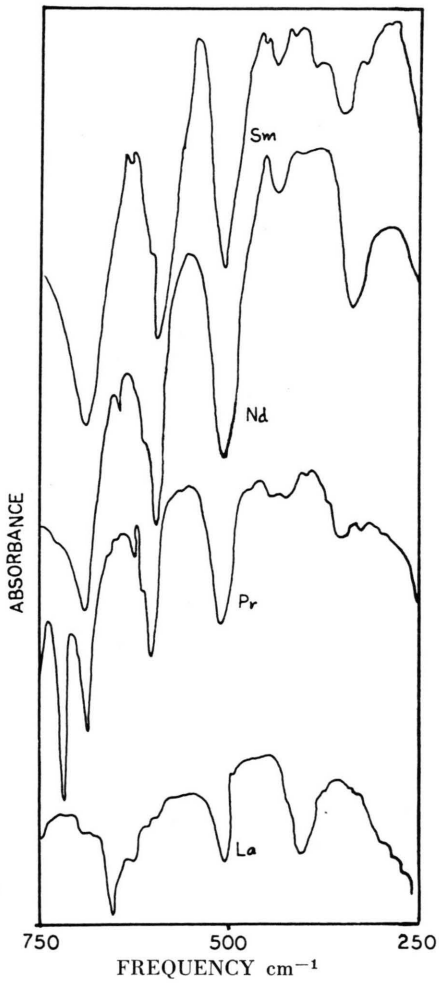

Fig. 3. Infrared absorption spectra of DBM complexes of La^{3+}, Pr^{3+}, Nd^{3+} and Sm^{3+}.

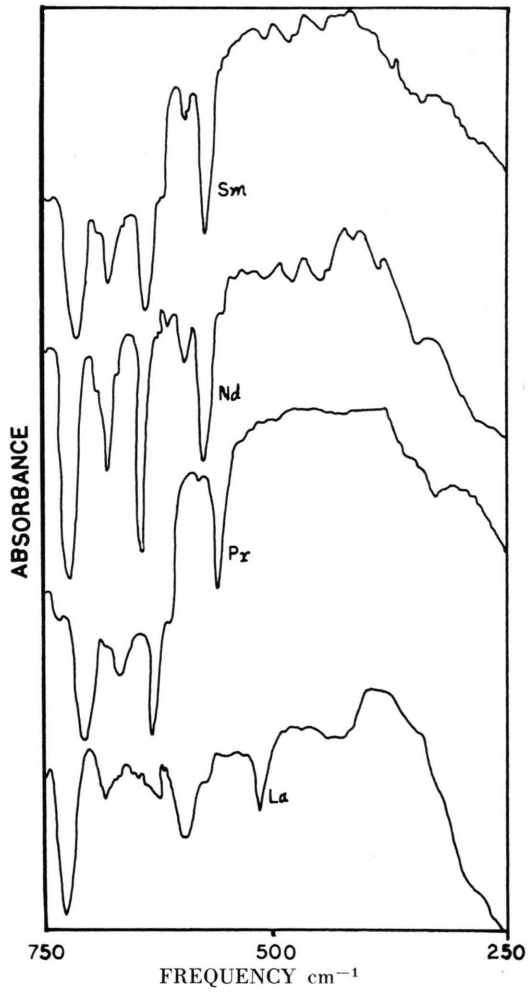

Fig. 4. Infrared absorption spectra of TFA complexes of La^{3+}, Pr^{3+}, Nd^{3+} and Sm^{3+}.

energy and intensity of the bands in the regions $\sim 600-510\ cm^{-1}$, $\sim 490-400\ cm^{-1}$ and $\sim 400-290\ cm^{-1}$ in the spectrum of β-diketones have been found to be very sensitive to complex formation [10–14]. Three metal sensitive bands in each complex have been observed in these regions, although the bending (δ) vibration contain also δ(ring)-character [7]. This suggests [9] an octahedral structure with D_3 symmetry for all the complexes.

Metal-Oxygen Force Constants

Exact structural data of the complexes under study are not known, and therefore exact calculations of force constants are not possible. An attempt will be made to compute the force constants by making simplifying assumptions. Although the compounds are 1 : 3 (metal/ligand) complexes having an octahedral configuration around the central

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metal, a simple 1 : 1 complex model may be sufficient as a first approximation. This assumption is reasonable since coupling between the three ligands is expected to be small as shown in the normal coordinate analysis of Cu^{2+} and Er^{3+} acetylacetonates [15, 16]. Considering only the immediate neighbours, the problem of force constants reduces to that of OMO molecules having symmetry C_{2v}. It should be mentioned that, though the δ vibration is not pure, the f_{MO} value is not very much influenced by the approximations made above.

The G matrix elements for such a molecule are given below [7]:

$$G_{11} = \mu_M(1+\cos\alpha) + \mu_0,$$

$$G_{12} = -\mu_M \sin\alpha, \qquad \text{for species } A_1,$$

$$G_{22} = [\mu_0 + \mu_M(1-\cos\alpha)],$$

$$G_{33} = \mu_M(1-\cos\alpha) + \mu_0, \qquad \text{for species } B_2.$$

As has been suggested by PEACOCK and MÜLLER [8], the F matrix elements for the species A_1 may be evaluated as follows:

$$F_{12} = -G_{12}\lambda_2/\det \mathbf{G},$$
$$F_{22} = G_{11}\lambda_2/\det \mathbf{G},$$
$$F_{11} = \lambda_1 \det \mathbf{G} + \lambda_2 G_{12}^2/(G_{11}\det \mathbf{G}),$$

where $\lambda_1 = 4\pi^2 c^2 \nu_1^2$ and $\lambda_2 = 4\pi^2 c^2 \nu_2^2$.

The symbols have used meaning.

The computed values of the stretching force constants, f_{MO} have been collected in Table 1. For all the complexes the value of f_{MO} is nearly constant suggesting similar MO bond strengths in all of them. For each metal ion the force constants show a slight decrease with the order of the ligands:

$$\boxed{A > TFA > DBM > BA}.$$

Table 1. Infrared frequencies and force constants of La^{3+}, Pr^{3+}, Nd^{3+} and Sm^{3+} β-diketonates.

Complex	I.R. Frequencies (cm^{-1})			Force constant f_{MO}
	ν_1 (A_1)	ν_2 (A_2)	ν_3 (B_2)	(10^5 dynes/cm)
La A_3	525	405	650	2.98
La $(TFA)_3$	565	430	600	2.88
La $(DBM)_3$	500	345	650	2.87
La $(BA)_3$	505	394	545	2.58
Pr A_3	522	395	650	2.97
Pr $(TFA)_3$	570	445	590	2.86
Pr $(DBM)_3$	505	350	625	2.75
Pr $(BA)_3$	515	402	555	2.44
Nd A_3	520	400	652	2.98
Nd $(TFA)_3$	579	450	600	2.96
Nd $(DBM)_3$	507	348	600	2.63
Nd $(BA)_3$	512	400	551	2.41
Sm $(TFA)_3$	580	450	600	2.98
Sm $(DBM)_3$	510	350	655	2.96
Sm $(BA)_3$	515	400	555	2.45

This shows that acetylacetone has the largest affinity towards the complex formation. A study of Table 1 reveals that the value of f_{MO} decreases approximately as the atomic number of the rare earth ion increases. This is in agreement with the general results of the study of the nephelauxetic effect [17] which predict that the bonding is more pronounced in the beginning of the $4f$ group than for the later members [3, 18]. Thus our results confirm the increase in contraction of $4f$ orbitals with increase in atomic number of lanthanides.

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