THE NEAR INFRARED TRANSITIONS OF THE TRIVALENT LANTHANIDES IN SOLUTION.[1] I. PRASEODYMIUM(III), NEODYMIUM(III), SAMARIUM(III), AND EUROPIUM(III) IONS

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The solution absorption spectra of Pr^{+3}, Nd^{+3}, Sm^{+3}, and Eu^{+3} were measured in molten $LiNO_3$–KNO_3 eutectic at 150° in the range 0.35–2.6 μ (28,600–3850 cm.$^{-1}$). New observations of a number of absorption bands in solution in the region 1.40–2.6 μ (7140–3850 cm.$^{-1}$) were made by taking advantage of the optical transparency of the $LiNO_3$–KNO_3 eutectic solvent in this region of the spectrum. Theoretical interpretations of the solution spectra are offered based on recent experimental and theoretical analyses of crystalline salts of the lanthanide ions.

Introduction

A great deal of progress has been made within the last five years in understanding the absorption and fluorescence spectra of crystalline salts of the lanthanides. This progress has resulted from a combination of experimental and theoretical analysis. In the present communication we have applied the results of these recent investigations with crystals to an interpretation of the solution spectra of the lanthanides.

With few exceptions, studies of the solution absorption spectra of the trivalent lanthanides have been confined to the region 0.2–1.4 μ, and have emphasized application to chemical analysis and to the characterization of complex ionic species. Previous communications[3-5] in which lanthanide solution absorption bands have been identified with certain excited multiplet components have been limited to a spectral range where in general considerable overlapping of multiplet levels occurs thus restricting the number of unique identifications to only a few of the observed bands.

The conditions for interpretation of lanthanide spectra are much more favorable in the near infrared region where the multiplet levels are fewer in number.

To study this spectral region, we have taken advantage of the wide range of optical transparency of the molten $LiNO_3$–KNO_3 eutectic which extends from ~0.35–2.6 μ. Primary interest in the present paper centers on the 1.4–2.6 μ (7140–3850 cm.$^{-1}$) region; however, since the most recent theoretical and experimental studies have revised many of the assignments appearing in the older literature, certain absorption bands occurring at wave lengths less than 1.4 μ also will be discussed.

In addition to giving a theoretical interpretation of the solution absorption bands of the light lanthanides, it is of interest to contrast the ligand field effects of the anhydrous nitrate media with those observed in aqueous solution. Therefore we also have measured the spectra of the elements concerned in D_2O (dilute $DClO_4$). The use of a deuterated solvent makes it possible to extend spectral investigations beyond the usual H_2O cut-off at 1.4 to ~1.8 μ, giving a wider region of comparison with the spectra obtained in the molten nitrate medium.

The transitions occurring in the near infrared region are associated with upper levels of the ground state multiplets or of the first excited multiplet levels of the lanthanides. Beyond the transparent range of the nitrate eutectic there are a few additional bands which could in principle be observed, but these are located at wave lengths much longer than the infrared cut-off of the nitrate eutectic.

Experimental

The spectral measurements were made using a Cary recording spectrophotometer Model 14. The aqueous solutions were measured at room temperature, 23 ± 2°, while the nitrate eutectic solutions were maintained at 150 ± 1°. Two types of furnaces were used for measurements on the molten salt samples, and have been described in the literature.[6] The eutectic mixture of $LiNO_3$ and KNO_3 employed as a solvent contains 43 mole % $LiNO_3$ and has a melting point of 132°.

Reagent grade chemicals were used without further purification. The lanthanide elements were obtained commercially as oxides and contained <1% impurities. The technique of preparing $DClO_4$ has been described previously.[7] Samples of the dried lanthanide oxides were weighed, then dissolved in the appropriate acid, $DClO_4$ or HNO_3. The HNO_3 solutions were evaporated to dryness in spectrophotometer cells before adding the required weight of solid $LiNO_3$–KNO_3 eutectic.

In some cases, the eutectic solutions remained turbid after essentially all of the dried lanthanide nitrates had dissolved in the melt. This was probably due to the formation of small amounts of lanthanide oxides or oxynitrates produced by partial thermal decomposition of the nitrates. Clear solutions could be obtained by addition of small amounts of solid NH_4NO_3 to the molten system at 150°, followed by bubbling dry N_2 through the solvent. Ammonium nitrate acts as an acid in the nitrate melt, and any excess of this salt can be removed by raising the temperature of the system to 220° for several hours. The existence of H_2O and/or undecomposed NH_4NO_3 in the melt is evidenced by the presence of intense characteristic absorption bands in the 1.9–2.5 μ region. Thus progress in the expulsion of these materials could conveniently be followed spectrophotometrically.

The ability of NH_4NO_3 to dissolve lanthanide oxides directly in the $LiNO_3$–KNO_3 melt already has been described[8] and represents an extention of the work of Audrieth, *et al.*,[9] with pure molten NH_4NO_3. The usefulness of this technique should, however, be emphasized.

(1) This work was performed under the auspices of the U. S. Atomic Energy Commission.

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(3) L. J. F. Broer, C. J. Gorter, and J. Hoogschagen, *Physica*, **11**, 231 (1945).

(4) C. K. Jørgensen, *Dan. Mat. Fys. Medd.*, **29**, No. 11 (1955).

(5) C. K. Jørgensen, *Acta Chem. Scand.*, **11**, 981 (1957).

(6) J. P. Young and J. C. White, *Anal. Chem.*, **31**, 1892 (1959); D. M. Gruen and R. L. McBeth, *J. Phys. Chem.*, **66**, 57 (1962).

(7) J. C. Sullivan, D. Cohen, and J. C. Hindman, *J. Am. Chem. Soc.*, **79**, 3672 (1957).

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(9) L. F. Audrieth and J. Kleinberg, "Non-aqueous Solvents," John Wiley and Sons, Inc., New York, N. Y., 1953, Chap. 14.
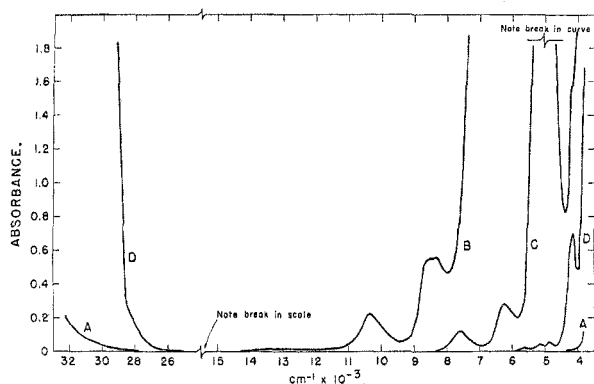
Fig. 1.—Absorption characteristics of (A) borosilicate glass cell with 1-cm. path length; borosilicate glass cell containing (B) H_2O, (C) D_2O, and (D) $LiNO_3$–KNO_3 at 150°.

The techniques used in the preparation and handling of the nitrate eutectic as well as the details concerning the procedure used in obtaining the data and calculating molar absorptivities for the molten salt solutions already have been described.[8]

As can be seen from Fig. 1, the range of optical transparency of the molten $LiNO_3$–KNO_3 eutectic corresponds approximately to that shown by borosilicate glass. Thus satisfactory spectrophotometer cells were fabricated from precision bore square borosilicate tubing. Both H_2O and D_2O absorb strongly in the near infrared, but the latter solvent is seen to have a greater range of transparency.

Results and Discussion

A very useful summary of the theory of lanthanide spectra, together with the necessary parameters required for calculating multiplet energy levels, has been presented by Elliot, et al.[10] The interaction of the crystal field with the 4f electrons of a lanthanide ion splits each multiplet level into a group of at most $2J + 1$ components. This splitting is considerably less in magnitude than that due to the Coulomb interaction between the 4f electrons or the spin–orbit coupling interaction. In solution, one would not expect to resolve all of the crystal field components individually, this being accomplished only at low temperature in crystals. The crystal field interaction may, however, shift the maximum of a given absorption band, broaden it and change its shape from one medium to another. Nevertheless, the transition generally can be identified with its analog in a crystal if it is well resolved from other multiplet levels.

For the most part, the absorption bands in the 1.4–2.6 μ region are due to transitions from the ground state to higher components of the ground state multiplet. In some cases the transitions are to levels of the first excited multiplet. It is useful to classify these levels according to the Russell–Saunders coupling scheme even though in many instances it is necessary to allow for deviations from this approximation in order to obtain satisfactory agreement between theory and experiment. Figure 2 shows recent results on multiplet assignments of the *light* lanthanides in the 0–14,000 cm.$^{-1}$ region obtained from studies of the spectra of crystalline salts. Each level is identified by suitable quantum numbers in the R–S system. Data of Pm^{+3} have been omitted since preliminary results

obtained to date have not been able to establish the existence of solution absorption bands in the 1.0–2.6 μ region,[8] and crystal studies in this spectral region have not been reported.

The absorption spectra of Ce^{+3} and Gd^{+3} are of little interest from the point of view of the present study. As seen from Fig. 2, Ce^{+3} with one 4f-electron has only one excited level near 4.44 μ[11] which cannot be observed in the $LiNO_3$–KNO_3 eutectic, both because of solvent absorption and because Ce^{+3} is not stable in the nitrate melt. Oxidation to CeO_2 occurs rapidly and the resulting oxide precipitates; an observation which is consistent with studies of the decomposition of hydrated $Ce(NO_3)_3$.[12] Due to the particular stability of the f[7] configuration, the transitions of Gd^{+3} within the 4f shell occur at relatively large energies. The corresponding absorption bands all are found in the ultraviolet region of the spectrum[13] and are masked by intense absorption of the solvent. It remains then to discuss the spectra of Pr^{+3}, Nd^{+3}, Sm^{+3}, and Eu^{+3}.

Pr^{+3}.—The well known spectrum of Pr^{+3} is due to transitions among the 13 multiplet levels arising from the $4f^2$ configuration. Dieke and Sarup[14] have studied the fluorescence spectrum of Pr^{+3} in $LaCl_3$ and were able to fix the centers of gravity of the $^3H_6$, $^3F_2$, $^3F_3$, and $^3F_4$ levels at approximately 4280, 4940, 6330, and 6770 cm.$^{-1}$, respectively. The corresponding absorption bands have now been observed in solution as shown in Fig. 3. Several of the near infrared transitions occur with considerable intensity relative to the bands observed in the visible region. The complex band centered near 2.1 μ can be resolved into two gaussians with maxima at 2.23 μ (4480 cm.$^{-1}$) and 1.93 μ (5180 cm.$^{-1}$). Since the $^3H_5$ level lies 2170 cm.$^{-1}$ above the $^3H_4$ ground state, it is not appreciably populated at 150°; thus there would appear to be little doubt that the two overlapping bands near 2.1 μ are due to the transitions $^3H_4$–$^3H_6$ and $^3H_4$–$^3F_2$. Similarly, the bands observed in the nitrate melt at 1.54 μ (6490 cm.$^{-1}$) and 1.45 μ (6900 cm.$^{-1}$) may be identified with transitions to the $^3F_3$ and $^3F_4$ levels, respectively.

The absorption bands of Pr^{+3} in $DClO_4$ near 1.5 μ show structure not observed in the molten nitrate system. This structure may be interpreted as due to transitions between partially resolved crystal field levels since the components of the bands are separated by ~ 160 cm.$^{-1}$. The over-all crystal field splitting of the ground term $^3H_4$ in $PrCl_3$ is 131 cm.$^{-1}$,[15] and splittings of similar magnitude occur within the excited $^3F_3$ and $^3F_4$ levels in the same crystal.[12]

As a result of the relative simplicity of the Pr^{+3} spectrum and the large separation between multiplets and multiplet components, other absorption bands shown in Fig. 3 also can be identified. In recent years, general agreement has been reached

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(14) G. H. Dieke and R. Sarup, *ibid.*, **29**, 741 (1958).

(15) E. V. Sayre, K. M. Sancier, and S. Freed, *ibid.*, **23**, 2060 (1955) (partial revision, *ibid.*, **29**, 242 (1958).

Lanthanide Ion	Ce+3	Pr+3	Nd+3	Sm+3	Eu+3
Configuration	4f¹	4f²	4f³	4f5	4f6
Number of J Levels	2	13	44	206	301
Wavelength in Microns	μ	μ	μ	μ	μ

Fig. 2.—Energy levels of the light lanthanide ions from 0–14.000 cm.$^{-1}$. References: Ce^{+3}[11], Pr^{+3}[14,15], Nd^{+3}[18,19], Sm^{+3}[24], Eu^{+3}[30]. Centers of gravity of multiplet levels as given in ref. 10 are: Pr^{+3}....^{3}F = 4072 cm.$^{-1}$, 1'G = 5106 cm.$^{-1}$; Nd^{+3}....^{4}S = 10,548 cm.$^{-1}$, ^{4}F = 10,548 cm.$^{-1}$, ^{2}H = 11,087 cm.$^{-1}$; Sm^{+3}....^{6}F = 4958 cm.$^{-1}$.

concerning the assignment of the bands centered at ~1.0 and 0.59 μ and the system centered at ~ 0.47 μ to transitions from the ^{3}H$_4$ ground state to the excited levels ^{1}G$_4$, ^{1}D$_2$, and ^{3}P$_{0,1,2}$ plus ^{1}I$_6$, respectively.[14] It is of interest to note that with the exception of ^{3}H$_4$–^{3}H$_5$ and ^{3}H$_4$–^{1}S$_0$, the transitions from the ground state to all of the excited multiplet components in the 4f^2 configuration lie in a spectral region that can be studied using the LiNO$_3$–KNO$_3$ eutectic as a solvent.

It is clear from Fig. 3 that spectra of Pr^{+3} in DClO$_4$ and in the nitrate melt are very similar. The small shifts of the band maxima toward the infrared found in the nitrate melt are paralleled by observations in aqueous solutions where similar shifts are found with increasing NO$_3^-$ concentration[16] and with acetylacetone chelate formation.[17]

Nd^{+3}.—Crystal spectra of Nd^{+3} have absorption bands in the 1.4–2.6 μ region and similar transitions have now been observed in LiNO$_3$–KNO$_3$ eutectic as shown in Fig. 4. The transitions ^{4}I$_{9/2}$–^{4}I$_{13/2}$ and I$_{9/2}$–^{4}I$_{15/2}$ with centers of gravity at ~4010 and ~6060 cm.$^{-1}$ were identified by Varsanyi and Dieke[18] from absorption and fluorescence spectra of Nd^{+3} in solid solution in LaCl$_3$. The crystal field splitting of the ground multiplet components of Nd^{+3} in LaCl$_3$ has been reported to be 249 cm.$^{-1}$ for ^{4}I$_{9/2}$; 85 cm.$^{-1}$ for ^{4}I$_{11/2}$; 151 cm.$^{-1}$ for ^{4}I$_{13/2}$; and 285 cm.$^{-1}$ for ^{4}I$_{15/2}$.[18,19] In the nitrate eutectic, the 2.5 μ (4000 cm.$^{-1}$) band is complex. It can be resolved into two gaussian bands with maxima at 2.35 μ (4260 cm.$^{-1}$) and 2.51 μ (3980 cm.$^{-1}$), respectively. The energy difference of 280 cm.$^{-1}$ is close to the energy separation of the lowest and

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(17) T. Moeller and W. F. Ullrich, J. Inorg. Nucl. Chem., 2, 164 (1956).

(18) F. Varsanyi and G. H. Dieke, J. Chem. Phys., 33, 1616 (1960).
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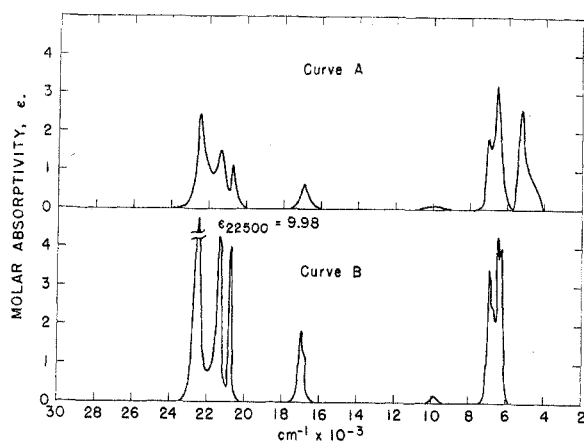
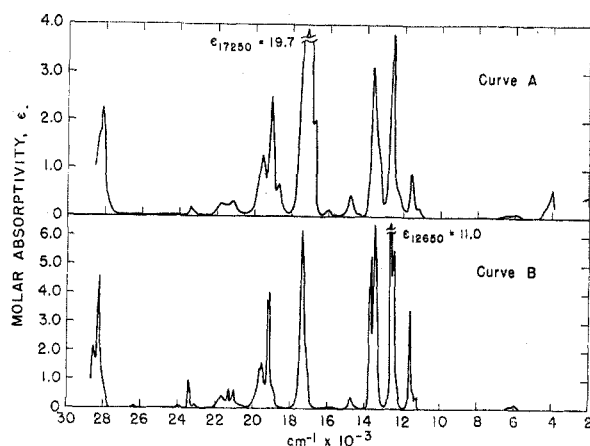Fig. 3.—The absorption spectrum of Pr^{+3} in (A) molten $LiNO_3$–KNO_3 eutectic at 150°, and (B) in 0.4 M $DClO_4$ at 23°.

Fig. 4.—The absorption spectrum of Nd^{+3} in (A) molten $LiNO_3$–KNO_3 eutectic at 150°, and (B) in 0.3 M $DClO_4$ at 23°.

highest crystal field components of $^4I_{9/2}$ for Nd^{+3} in $LaCl_3$. Assuming that the crystal field splittings are similar in nitrate melts and in $LaCl_3$, one may interpret the structure of the 2.5 μ band in the eutectic as arising from transitions originating from the lowest and highest crystal field levels of $^4I_{9/2}$ and terminating in $^4I_{13/2}$. A temperature study of the intensities of the components of this band would help to indicate the correctness of this assignment.

It should be pointed out that the $^4I_{9/2}$–$^4I_{15/2}$ transition was observed for the first time only recently.[18] In the nitrate melt and in $DClO_4$ solution, this transition appears as a weak, broad band centered at 1.63 μ (6130 cm.$^{-1}$) and could easily have been missed in the absence of information predicting its location.

Transitions to the excited multiplet levels of Nd^{+3} give rise to a much more complicated band structure in the visible region of the spectrum than in the case of Pr^{+3}. All except four of the 44 possible multiplet levels in the $4f^3$ configuration lie at wave lengths < 0.9 μ (11,100 cm.$^{-1}$). Krumholz has shown that under high resolution and at a temperature of 3° the absorption spectrum of Nd^{+3} in dilute $HClO_4$ in the 0.4–0.9 μ range approximates that reported for Nd^{+3} in $Nd(BrO_3)_3 \cdot 9H_2O$

crystals where the symmetry of the crystal field appeared to be trigonal (C_{3v}).[20]

The visible absorption bands of Nd^{+3} show a shift of the band maxima toward the infrared with increasing NO_3^- concentration when comparing the spectra of an aqueous solution of 1.0 N $Nd(NO_3)_3$ with that of a crystal of $Nd(NO_3)_3 \cdot 6H_2O$.[16] Similarly, a small red shift is observed in comparing an aqueous to a molten nitrate medium.

Oetjen[21] noted a significant increase in oscillator strength of the band near 0.58 μ (17,250 cm.$^{-1}$) with increasing $Nd(NO_3)_3$ concentration and reported a molar absorptivity $\epsilon_{0.578\mu}$ of 22 for 2.421 M $Nd(NO_3)_3$, the highest concentration measured. By comparison, it was found that the concentration of Nd^{+3} in the $LiNO_3$–KNO_3 eutectic can be varied up to ~0.2 M Nd^{+3} by using neutral density filters and the band at 0.58 μ was shown to follow Beer's law with ϵ = 19.7. At higher concentrations of Nd^{+3} the band was too intense to permit quantitative measurements to be made. Similar effects with this particular absorption band have been reported in molten $LiCl$–KCl system[22] and in a study of Nd^{+3} chelate formation,[17] but not in aqueous chloride solutions.[21] In the investigation in which the acetylacetone chelate of Nd^{+3} was dissolved in various organic solvents, it was found that the extinction coefficient of the 0.58 μ band obeyed Beer's law at low concentrations giving an ϵ-value that varied between 21 and 23 depending on the solvent, but in any event close to the value found in the present study.

The remarkable sensitivity of the intensity of the 0.58 μ band to changes in anion environment has recently been justified theoretically by Judd,[23] who found that the oscillator strength P corresponding to the transition $\Psi_J \rightarrow \Psi_J'$ is given by

$$P = \Sigma T_\lambda \nu (\Psi_J || U^{(\lambda)} || \Psi_J')^2$$

where $U^{(\lambda)}$ is a tensor operator of rank λ, and the sum runs over the three values 2, 4, and 6 of λ. Sets of parameters T_2, T_4, and T_6 can be chosen to fit the experimental data. The parameter T_2 often plays only a minor role in determining the oscillator strengths because of selection rules. However, the matrix elements of $U^{(2)}$ for the transitions $^4I_{9/2} \rightarrow ^2G_{7/2}$, $^4G_{5/2}$ which give rise to the 0.58 μ band are of the two largest in magnitude and it is the intensities these transitions which are most sensitive to the size of T_2. It is to be hoped that a detailed understanding of the relation between the magnitude of T_2 and the physical model of the rare earth anion complex can ultimately be gained. The interpretation of intensity changes in terms of chemical interactions then will become possible.

Sm^{+3}.—An experimental and theoretical study of many of the 206 possible multiplet levels in the $4f^5$ configuration (Sm^{+3}) has been made by Magno and Dieke,[24] whose experimental results appear to agree with those obtained by Gobrecht.[25] The

(20) P. Krumholz, *Spectrochim. Acta*, **10**, 274 (1958).
(21) G. W. Oetjen, *Z. Naturforsch.*, **4a**, 1 (1949).
(22) C. V. Banks, M. R. Heusinkveld, and J. W. O'Laughlin, *Anal. Chem.*, **33**, 1235 (1961).
(23) B. R. Judd, UCRL-10019, January, 1962.
(24) M. S. Magno and G. H. Dieke, NYO-8098 (June 18, 1959).
(25) H. Gobrecht, *Ann. Physik.*, **31**, 755 (1938).

absorption spectra in the 1.0–2.6 μ range have been interpreted in terms of an overlapping of the terms of the [6]F state with the upper levels of the [6]H ground state multiplet (Fig. 2). The first excited component of the ground state multiplet, [6]H$_{7/2}$, lies at an energy which is large compared with kT so that it is not populated at 150°. The crystal field splitting of the ground component, [6]H$_{5/2}$, in Sm(NO$_3$)$_3$ crystals was found to be ~136 cm.$^{-1}$,[26] but neither the bands observed in DClO$_4$ solution nor those in the nitrate melt (Fig. 5) give any evidence of structure traceable to this splitting.

The transitions of Sm^{+3} observed in the near infrared in the nitrate melt are summarized in Table I, and compared to the data reported by Magno and Dieke,[24] and to multiplet levels calculated from theory assuming pure R–S coupling.[10] Judd has shown that intermediate coupling calculations lead to a much better agreement between theory and experiment for the lower levels of the ground term multiplet.[27] The assignment of the level at 6600 cm.$^{-1}$ to [6]H$_{15/2}$ is in very good agreement with experimental results of Gobrecht.[25] There is some confusion respecting the order in which [6]H$_{15/2}$ and [6]F$_{5/2}$ are assigned by Magno and Dieke.[24]

The degree of agreement between theory and experiment for the [6]F multiplet is of particular interest here since the transition to [6]F$_{1/2}$ which was reported in crystals near 1.75 μ (5710 cm.$^{-1}$)[24] is not observed in the nitrate melt. We therefore must assume either that this transition is extremely weak or that, as indicated by theory, it occurs at a somewhat higher energy than reported by Magno and Dieke. In this event it would be masked by the relatively intense band at 1.56 μ (6410 cm.$^{-1}$).

TABLE I

A COMPARISON OF THEORY AND EXPERIMENT FOR THE
[6]H AND [6]F MULTIPLET LEVELS OF Sm^{+3}

Transition	Exptl. obsd.[24] in crystals (cm.$^{-1}$)	Exptl. obsd. LiNO$_3$–KNO$_3$ (cm.$^{-1}$)	Calcd.[a] Pure R–S coupling (cm.$^{-1}$)
[6]H$_{5/2}$	0	0	0
[6]H$_{7/2}$	1100	..	840
[6]H$_{9/2}$	2300	..	1920
[6]H$_{11/2}$	3600	..	3240
[6]H$_{13/2}$	5000	4950	4800
[6]F$_{1/2}$	5700	..	6158
[6]F$_{3/2}$	6300	6410	6518
[6]H$_{15/2}$	6750	6711	6600
[6]F$_{5/2}$	7100	7194	7118
[6]F$_{7/2}$	7950	8000	7985
[6]F$_{9/2}$	9050	9174	9038
[6]F$_{11/2}$	10400	10530	10358

[a] Calcd. as shown in ref. 10 using F_2 = 370 cm.$^{-1}$ and ζ = 1200 cm.$^{-1}$.

Although the [6]H$_{9/2}$ and [6]H$_{11/2}$ transitions lie beyond the experimental limits of the present study, it is of interest to note that absorption bands at ~4.1 μ (2440 cm.$^{-1}$) and 2.62 μ (3820 cm.$^{-1}$) were reported in the absorption spectrum of a glass containing Sm$_2$O$_3$.[28]

(26) A. Friedrick, K. H. Hellwege, and H. Lammermann, Z. Physik, 158, 251 (1960).

(27) B. R. Judd, Proc. Phys. Soc. (London), A69, 157 (1956).

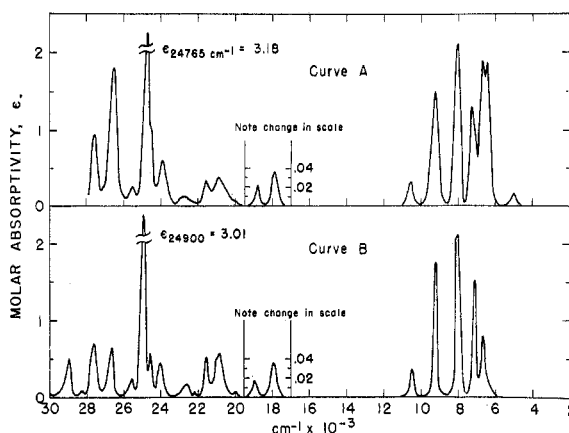Fig. 5.—The absorption spectrum of Sm^{+3} in (A) molten LiNO$_3$–KNO$_3$ eutectic at 150°, and (B) in 0.4 M DClO$_4$ at 23°.

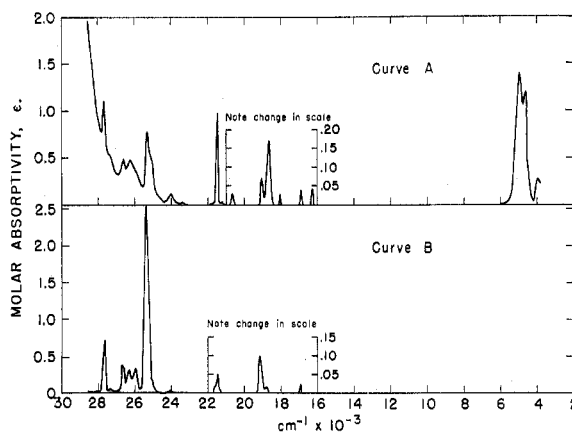
Fig. 6.—The absorption spectrum of Eu^{+3} in (A) molten LiNO$_3$–KNO$_3$ eutectic at 150°, and (B) in 0.3 M DClO$_4$ at 23°.

Except for the two band structure near 1.5 μ in molten LiNO$_3$–KNO$_3$, the spectra of Sm^{+3} in DClO$_4$ and in the nitrate eutectic are very similar with no appreciable shift in the energies of the band maxima. Moeller and Ullrich[17] have shown that chelate formation can give rise to modifications of several Sm^{+3} bands in the visible region, but the effects are strongly dependent upon the chelating agent employed.[29]

Eu^{+3}.—A study of the fluorescence spectrum of Eu^{+3} in crystalline Eu(C$_2$H$_5$SO$_4$)$_3$·9H$_2$O has been made by Sayre and Freed[30] and their results have been interpreted theoretically by Judd.[31] According to an analysis by Gruber and Conway[32] of the energy levels of the f^6 configuration, the highest component of the [7]F ground state multiplet is separated by more than 10,000 cm.$^{-1}$ from the lowest component of the first excited multiplet, [5]D$_0$. The centers of gravity of the [7]F$_{1,2,3,4,5,6}$ multiplet components occur at approximately

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(31) B. R. Judd, Mol. Phys., 2, 407 (1959).

(32) J. B. Gruber and J. G. Conway, J. Chem. Phys., 34, 632 (1961).

377, 1050, 1900, 2910, 3960, and 4990 cm.$^{-1}$, respectively, as shown in Fig. 2.[30] The magnitude of the crystal field splitting of the ground state multiplet components in Eu(C$_2$H$_5$SO$_4$)$_3$·9H$_2$O was found to vary from ~40 cm.$^{-1}$ for ^{7}F$_1$ to ~270 cm.$^{-1}$ for ^{7}F$_4$,[30] while the ^{7}F$_0$ ground state is not split in a crystal field. Since the ^{7}F$_1$ level lies very close in energy to the ground state, both levels are populated at room temperature.[33]

The absorption spectrum of Eu^{+3} in molten LiNO$_3$–KNO$_3$ eutectic (Fig. 6) is clearly in consonance with the results of Sayre and Freed.[30] The bands with centers at ~2.1 and ~2.5 μ thus are to be identified with transitions between ground state multiplet components, while the very weak bands near 0.55 and 0.6 μ are due to transitions to the ^{5}D state. We propose that the two maxima at 2.17 μ (4610 cm.$^{-1}$) and 2.03 μ (4930 cm.$^{-1}$) arise from the transitions ^{7}F$_0$–^{7}F$_6$ and ^{7}F$_1$–^{7}F$_6$, respectively, since the energy difference of 320 cm.$^{-1}$ corresponds reasonably well to that found in Eu(C$_2$H$_5$SO$_4$)$_3$·9H$_2$O. The band with maximum at 2.56 μ (3910 cm.$^{-1}$) thus is to be identified with the ^{7}F$_0$–^{7}F$_5$ transition. Since the latter occurs so near the experimental limit in the present investigation, it cannot be established whether it too possesses a satellite on the infrared side.

(33) K. H. Hellwege, U. Johnsen, H. G. Kahle, and G. Schaack, Z. Physik, 148, 112 (1957).

The assignment of the absorption bands of Eu^{+3} near 0.579, 0.525, and 0.465 to the ^{5}D configuration has been discussed by Bayer-Helms.[34] These are all low intensity bands in the solution spectra, (Fig. 6), but sufficiently separated in energy to make possible their characterization. Calculation showed that the oscillator strengths for the ^{7}F$_0$–^{5}D$_2$ transition (0.465 μ) increased both with increasing temperature and with increasing NO$_3$$^-$ concentration. This is consistent with the present results since in the nitrate melt, the 0.465 μ band shows a very significant increase in intensity similar to the effect of NO$_3$$^-$ ion on the 0.58 μ band of Nd^{+3}. Selwood[14] has also noted the sensitivity of the 0.465-μ Eu^{+3} band to NO$_3$$^-$ concentration.

The correlation between the absorption maxima of the bands found in the present study and those found in crystal spectra suggests that a careful investigation of relatively high concentrations of Pm^{+3} in the LiNO$_3$–KNO$_3$ eutectic may lead to information on the structure of the ground state multiplet of that system. Such studies are presently being carried out. The applicability of the infrared bands to analytical studies has already been stressed in an earlier publication.[8]

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(34) F. Bayer-Helms, Z. Naturforsch., 13a, 161 (1958).

A KINETIC STUDY OF TELOMER PRODUCTION FROM CHLOROFORM–ETHYLENE MIXTURES INITIATED BY COBALT-60 γ-RADIATION
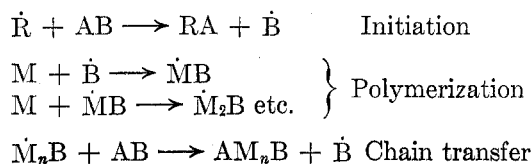
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Radiolysis of chloroform–ethylene mixtures in an autoclave produces the addition compounds C$_2$H$_5$CCl$_3$, C$_4$H$_9$CCl$_3$, and C$_6$H$_{13}$CCl$_3$ with G-values as high as 3000 at 100° and 300 at 28°. A study of product distribution as a function of ethylene pressure yields transfer constants for the radicals involved in the chain reaction: at 28° the values for the radicals C$_2$H$_4$CCl$_3$, C$_4$H$_8$CCl$_3$, and C$_6$H$_{12}$CCl$_3$ are 0.21, 1.3, and 1.5, respectively; at 100° they decrease to 0.15, 0.54, and 0.45. A study of the chloroform–carbon tetrachloride–ethylene system using both high energy radiation and thermal decomposition of benzoyl peroxide as initators confirms that the radiation-initiated chain reaction is radical, and not ionic, in nature. The effect of non-polar solvents on the transfer constants suggests that increase in transfer constants with increasing chain length is a result of a decrease in rate of the radical–olefin addition reaction. G-values for pure carbon tetrachloride–ethylene mixtures have not been determined, but indirect evidence indicates G(telomer) of the same order as those obtained with chloroform.

Introduction

In production of telomers (low molecular weight polymers) from radical-initiated chain reactions, the reactants, an olefin M and an adduct AB, usually are sensitized by thermal decomposition of a peroxide to produce high yields of telomers of the type AM$_n$B. The reaction scheme for production of telomers from these systems usually is given as

$$\dot{R} + AB \longrightarrow RA + \dot{B} \qquad \text{Initiation}$$

$$\left.\begin{array}{l} M + \dot{B} \longrightarrow \dot{M}B \\ M + \dot{M}B \longrightarrow \dot{M}_2B \text{ etc.} \end{array}\right\} \text{ Polymerization}$$

$$\dot{M}_nB + AB \longrightarrow AM_nB + \dot{B} \quad \text{Chain transfer}$$

Kharasch and his co-workers, who performed much of the earlier work, found that many polyhalogen compounds give high yields of telomers with olefins Walling[2] gives an extensive review of this field. For the systems that are pertinent to this work, chloroform–ethylene and carbon tetrachloride–ethylene, the telomers produced have the general formula H(C$_2$H$_4$)$_n$CCl$_3$ and Cl(C$_2$H$_4$)$_n$CCl$_3$, respectively.[3-7]

(1) The Radiation Laboratory is operated under contract with the Atomic Energy Commission.

(2) C. Walling, "Free Radicals in Solutions," John Wiley and Sons, Inc., New York, N. Y., 1957.

(3) I.C.I., British Patent 581,899 (October 29, 1946).

(4) M. S. Kharasch, E. V. Jensen, and W. H. Urry, J. Am. Chem. Soc., 69, 1100 (1947).