ABSORPTION AND FLUORESCENCE SPECTRA OF PRASEODYMIUM IN KCl AND KBr MATRICES

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ABSTRACT

The observed fluorescence and absorption spectra of single crystals of KCl and KBr doped with praseodymium (Pr) show that the rare earth enters substitutionally as Pr^{3+} in these lattices. However, the site symmetry of the ion has at most a twofold axis. This is shown by the fact that the j-degeneracy of its energy levels is completely removed. Fluorescence is observed to occur only from $^3P_0$ level to $^3F_{2, 3, 4}$ and $^3H_6$ levels. The overall Stark splitting shows that the Pr^{3+} ion experiences a stronger field in these matrices than in $LaCl_3$ or $LaBr_3$.

1. INTRODUCTION

THE fluorescence and absorption spectra of several crystals such as $LaCl_3$, $LaBr_3$, etc., doped with praseodymium, (Pr) are now known.[1] In these crystals it is shown that the spectrum is due to Pr^{3+} ion which, however, is not free but subject to the electric field of the crystals in which the ion enters substitutionally for the cation. In the optical region the spectrum at low temperature is a line spectrum due to transitions among the energy levels of the ground state configuration $4f^2$. These are forbidden as ordinary electric dipole transitions in the free ion but are rendered allowed by crystal field perturbation as magnetic dipole or enforced electric dipole transitions in the ion-in-crystal. The free ion optical spectrum, therefore, does not contain any of these lines. The free ion energy levels of the $4f^2$ configuration, however, can be determined by a detailed analysis of the entire spectrum of the free ion which will involve these levels in certain allowed combinations with states of higher configurations of the ion. This has been recently achieved by the analysis of the emission spectrum of Pr^{3+} ion,[2] which is thus one of the better known of the trivalent rare earth ions for a study of the crystal field effects on its energy levels and their Stark splittings. The present paper deals with the absorption and fluorescence spectra of the alkali halides KCl and KBr having monovalent

240

ion lattices doped with corresponding trivalent Pr halides.* Fluorescence spectra of KCl and NaCl doped with samarium have been reported by Skorobogatov et al.[3]

2. EXPERIMENTAL

Single crystals of KCl and KBr containing 1, 3 and 5 atom % Pr were grown by the modified Stockbarger method. Melts containing 3 and 5 atom % Pr did not give good transparent single crystals. Single crystals containing one atom % Pr were transparent and these were used in the present studies. Polishing the crystal resulted in reducing the intensity of spectra both in absorption and fluorescence. Therefore, all spectra were taken with the unpolished crystal in the crystal growing tube. Multi-crystals of KCl and KBr containing 3 atom % Pr were also used in some experiments to record the higher Stark components of the ground state. The absorption spectra were recorded at 77° K on a three-prism Steinheil spectrograph (plate factor = 17 Å/mm at 5000 Å) and on a Jarrel-Ash grating spectrograph (plate factor = 5 Å/mm) in the first order. Tle fluorescence spectra at 77° K and polarization pictures of the single crystal absorption spectrum were recorded on the Steinheil spectrograph. The latter were taken with the light beam perpendicular to the growth axis of the crystal namely the axis of the cylindrical container. Fig. 1 (*a, b* and *c,d*) show the absorption and fluorescence spectra respectively of Pr in KCl and KBr matrices; Tables I and II give the wavelengths, wave numbers, visually estimated intensities, polarizations and the transitions involved.

3. OBSERVATIONS

The spectra consist of groups of sharp lines in the visible region. The spectral positions of the various absorption and fluorescence groups correspond to those of Pr^{3+} ion. This shows that Pr has gone into the lattices as Pr^{3+} ion. Analysis of the spectra indicates that all the Pr^{3+} ions have the same site symmetry in each matrix and that the spectra are free from lines due to superposed lattice vibrations or impurities. A comparative study of the various absorption groups shows that the lines are the sharpest in $^1D_2 \leftarrow {}^3H_4$ transition and become less and less sharp in absorption groups on the shorter wavelength side of this group.

Absorption Spectrum of Pr^{3+} in KCl and KBr Matrices

3.1.1. Pr^{3+} in KCl.—The absorption spectrum in the visible region consists of five groups of lines which arise from transitions from the ground state $^3H_4$, to excited states, $^1D_2$ (6000 Å group), $^3P_0$ (4900 Å group), $^3P_1$ (4700 Å group), $^1I_6$ (4600 Å group) and $^3P_2$ (4400 Å group).
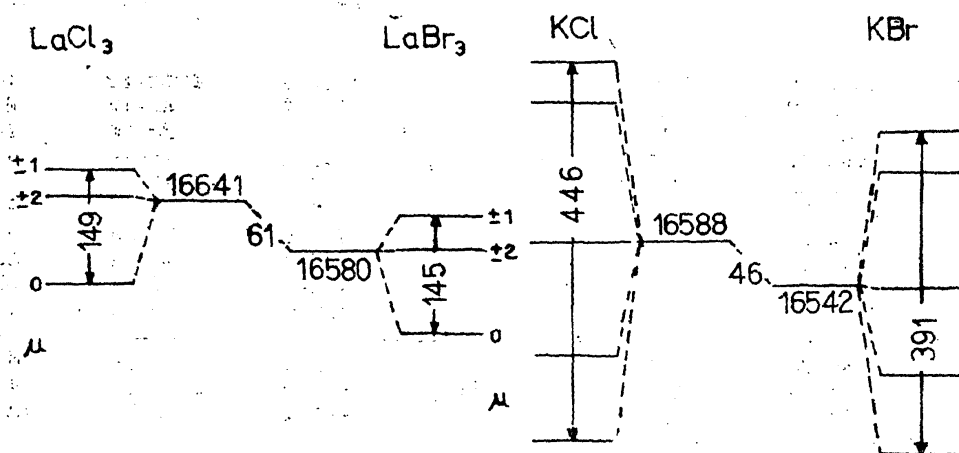

FIG. 2. $^1D_2$ level of Pr^{3+} and its splittings in different crystals. Energy values are in cm^{-1}.

The absorption group having the minimum number of lines is the 4900 Å group involving the transition $^3P_0 \leftarrow {}^3H_4$. $^3P_0$ being a non-degenerate state, this group gives the most direct and unambiguous information about the ground state splitting. The three lines observed in this group at 77° K are due to transitions to $^3P_0$ from three of the lowest Stark levels of the ground state $^3H_4$.

The next absorption group which is simple to analyse is the 4700 Å group involving the transition $^3P_1 \leftarrow {}^3H_4$. The splitting of the ground state known from the analysis of the 4900 Å group could be used for an analysis of this group. Thus the $^3P_1$ state is found to split into three Stark components showing that the degeneracy of the $^3P_1$ level is completely removed. In the region of 4600 Å to 4700 Å there are a number of very weak and diffuse lines which are possibly due to the transition $^1I_6 \leftarrow {}^3H_4$.

The absorption group at 4400 Å involves the transition $^3P_2 \leftarrow {}^3H_4$. The lines in this group are in general broad and diffuse. They involve transitions from the lowest Stark components of the ground state to all the five Stark components of $^3P_2$. Transitions from the higher Stark components of the ground state are observed only to the lowest Stark component of $^3P_2$. These lines are relatively less diffuse. The presence of five Stark components implies that the j-degeneracy of the $^3P_2$ level is completely removed.

TABLE I

Absorption spectrum data of Pr^{3+} in KCl and KBr at 77° K

	Pr^{3+} in KCl			Transition	Pr^{3+} in KBr			
Int.	Pol.	λ air Å	ν vac cm⁻¹		ν vac cm⁻¹	λ air Å	Int.	Pol.
1d	π	6039·20	17008·5		16515·8	6053·12	5	π
6	σ	36·13	16961·3		526·7	49·13	6	σ
3	π	00·36	952·6		578·2	30·36	1d	..
7	σ	5954·74	797·4	$^1D_2 \leftarrow {}^3H_4$	622·3	14·34	3	π
7	π	51·66	788·7		682·4	5992·69	0	..
3	π	5897·17	661·1		715·7	80·75	7b	σ
6	σ	94·13	562·3		727·1	76·66	7b	π
5	σ	77·79	553·9		856·2	30·90	3d	π
			..		866·8	27·15	6b	σ
			..		917·2	09·52	1d	σ
6	π	4889·20	20447·5		20372·7	4907·16	6	π
8	σ	75·46	505·2	$^3P_0 \leftarrow {}^3H_4$	406·0	4899·09	8	σ
10	π	73·46	513·6		417·5	96·39	10	π
1	..	4758·55	21008·9		20922·2	4778·28	1d	..
8	π	50·01	046·7		954·8	70·85	8	π
8	σ	48·05	055·4	$^3P_1 \leftarrow {}^3H_4$	966·0	68·30	8	σ
6	π	43·85	074·0		995·0	61·70	6	π
5bd	..	14·63	204·6		21101·7	37·63	5bd	..
1bbl		4704·17	21251·8		21028·9	4754·04	1d	
0		4695·94	289·0		064·9	45·90	1d	
0		87·95	325·3		207·4	14·01	0	
1dd	Not observed	64·99	430·3	$^1I_6 \leftarrow {}^3H_4$	380·2	4675·92	0	Not observed
1dd		51·67	491·6		408·2	69·30	0	
1dd		33·01	578·2		..	..	..	
0		21·41	632·4		..	..	..	
1dd		07·04	799·8		..	..	..	
1d	..	4515·64	22139·00		22076·9	4528·36	2bd	..
4d	σ	04·12	195·70		112·8	21·00	8b	σ
9	π	02·36	204·30		121·3	19·26	9	π
6	π	4486·50	282·80	$^3P_2 \leftarrow {}^3H_4$	195·8	04·09	6	..
5	σ	72·26	353·80		252·2	4492·68	5b	σ
3	..	67·71	376·60		264·6	90·17	3bd	..
1	..	60·56	412·40		275·9	87·89	6bd	..

The absorption lines of $^1D_2 \leftarrow {}^3H_4$ transition at 6000 Å are sharper than those in other absorption groups. Analysis gives five Stark components for the level $^1D_2$ thus showing that its *j*-degeneracy is completely removed.

From an analysis of all the observed absorption groups at 77° K the mean values of the ground level Stark components are found to be 0, 8·6 nd 65·5 cm⁻¹,

TABLE II

Fluorescence spectrum data of Pr^{3+} in KCl and KBr at 77° K

Int.	λair Å	νvac cm⁻¹	Transition	νvac cm⁻¹	λair Å	Int.
	Pr³⁺ in KCl				Pr³⁺ in KBr	
6	7410·64	13490·40		13452·1	7431·72	6
5	7392·91	522·70		482·0	15·23	5
7	81·60	543·50		500·5	05·12	7
6	53·21	595·80	$^3P_0{\to}^3F_4$	542·2	7382·31	6
5	37·02	625·80		566·5	69·06	5
7	21·93	653·80		590·3	56·14	7
5	05·95	683·70		618·1	41·12	5
10	7298·84	697·00		627·2	36·25	10
3	7115·16	14050·60		14005·8	7137·94	3
4	090·38	099·70		040·0	20·52	4
4	82·15	116·10	$^3P_0{\to}^3F_3$	052·9	14·02	1
4	74·85	130·70		063·6	08·61	4
10	6488·73	15407·10		15365·1	6506·44	10
10	78·31	431·90		386·6	6497·36	10
8	66·39	460·30	$^3P_0{\to}^3F_2$	416·3	84·86	8
10	59·31	477·30		429·0	79·53	10
2	44·17	513·60		457·9	67·38	2
2	6346·27	15752·90		15609·0	6368·08	1
1	09·60	844·50		812·9	22·21	2d
2	6297·03	876·10	$^3P_0{\to}^3H_6$	942·8	6270·69	4
4	41·09	16018·40		963·8	62·43	7
7	29·29	048·80		982·3	55·19	4
4	22·07	067·40		16031·6	35·95	4
4	07·87	104·10		059·5	25·14	3
3	6193·00	142·80		126·4	6199·31	10
0	73·27	194·40		··	··	··
10	56·84	237·60		··	··	··

3.1.2. *Pr^{3+} in KBr.*—The spectrum of (Pr^{3+} : KBr) resembles very much that of (Pr^{3+} : KCl) except that all groups are shifted slightly to the longer wavelength side. Also each of the groups covers a smaller range of wavelengths than in KCl. Analysis of the spectrum is similar to that in KCl. The mean values of the ground state Stark components in KBr are found to be 0, 10·9 and 44·3 cm⁻¹.

Fluorescence Spectrum of Pr^{3+} in KCl and KBr Matrices

3.2.1. *Pr^{3+} in KCl.*—It is found that only the $^3P_0$ level fluorescences in this matrix and fluorescence takes place from this level not only to $^3H_6$, $^3F_2$ and $^3F_4$, levels as in other fluorescing salts of Pr but also to the $^3F_3$ level which has not been recorded in matrices like $LaCl_3$, $LaBr_3$ etc. in, optically

excited fluorescence. However, Low, Makovsky and Yatziv[4] observed this transition in the case of $LaCl_3$ matrix under X-ray excitation when the total fluorescence was very intense. Since $^3P_0$ has no Stark splitting each fluorescence transition to a lower level must be to a different Stark component provided that there are no spurious or superposed lines due to impurities or lattice vibrations. Whereas in maitrces like $LaCl_3$, $LaBr_3$, etc, fluorescence of Pr^{3+} is observed from $^3P_1$, $^3P_0$ and $^1D_2$ levels, in KCl and KBr it occurs only from $^3P_0$ and is thus apparently similar to that of Pr^{3+} in $PrCl_3$. In both cases fluorescence is observed only from $^3P_0$ to the same lower levels $^3F_4$, $^3F_2$ and $^3H_6$, except that in KCl and KBr also the very weak transition to $^3F_3$ is observed. The important difference, however, lies in the structure of the fluorescence groups in the two cases. This is due to the difference in the site symmetry of Pr^{3+} in the two cases and is well shown in Fig. 1, *e*.

The fluorescence group at 6200 Å due to the transition $^3P_0 \rightarrow {}^3H_6$ consists of ten lines, each one locating a Stark level of the $^3H_6$ state. The total number of Stark components expected for $^3H_6$ if the *j*-degeneracy is completely removed, is thirteen. It is possible that lines involving the other three levels were not observed due to low intensity.

The fluorescence group at 6500 Å due to $^3P_0 \rightarrow {}^3F_2$ gives five Stark levels of the $^3F_2$ level showing that its degeneracy is completely removed by the crystal field.

The fluorescence group at 7300 Å due to transition $^3P_0 \rightarrow {}^3F_4$ consists of eight strong lines which locate eight of the possible nine Stark components of the $^3F_4$ level.

The weak fluorescence group at 7100 Å in both matrices is possibly due to the transition $^3P_0 \rightarrow {}^3F_3$. The absence of this group in other matrices is believed to be due to a selection rule according to which for an even number of electrons, transitions from J=0 to *odd* J should be very weak.[5]

3.2.2. *Pr³⁺ in KBr.*—As in absorption, the fluorescence spectrum is very similar to that in KCl with a few differences pointed out already.

3.3. Absorption Spectra at Higher Temperatures

Absorption spectra at temperatures intermediate between room and liquid nitrogen temperatures were recorded with a view to locate the higher Stark components of the ground level. The spectra observed at higher temperatures are in general broad and diffuse. Even at these high tempe-

ratures the $^3P_0 \leftarrow {}^3H_4$ group has fairly sharp lines whose intensity is governed by the Boltzmann distribution. The positions of most of the higher Stark components of the ground state could be obtained from measurements of lines in this group. In the case of (Pr^{3+} : KCl) apart from the three Stark components known from at spectra liquid nitrogen temperature, four and in the case of (Pr^{3+} : KBr) six, additional Stark levels of the ground state were identified. Thus all the nine expected Stark levels could be located in the latter case. Table III contains the combined data on Stark splittings of the levels obtained in the present experiments.

Table III

Observed Stark components (in cm^{-1}) of the energy levels of Pr^{3+} in KCl and KBr matrices

Level	Matrix		Level	Matrix	
	KCl	KBr		KCl	KBr
$^3H_4$	0·0	0·0	$^3F_4$	6811·6	6790·3
	8·6	10·9		6819·9	6799·4
	65·5	44·7		6859·8	6827·2
	*123	* 98		6887·8	6851·0
	*168	*140		6917·8	6875·3
	*243	*205		6970·1	6917·0
	*343	*293		6990·9	6935·5
	*438	*405		7023·2	6965·4
	*520	*491	$^1D_2$	16562·3	16526·7
$^3H_6$	4276·0	4291·1		16661·1	16622·3
	4319·2	4358·0		16797·4	16727·1
	4370·8	4385·9		16961·3	16866·8
	4409·5	4435·2		17008·5	16917·2
	4446·2	4453·7			
	4464·8	4474·7	$^3P_0$	20513·6	20417·5
	4495·2	4604·6			
	4637·5	4718·5	$^3P_1$	21055·4	20966·0
	4669·1	··		21074·0	20995·0
	4760·7	··		21204·6	21101·7
$^3F_2$	5000·0	4959·6	$^3P_2$	22204·3	22121·3
	5036·3	4988·5		22232·8	22195·8
	5053·3	5001·2		22353·8	22264·6
	5081·9	5030·9		22376·6	22275·9
	5106·5	5052·4		22412·4	22312·4
$^3F_3$	6382·9	6353·9			
	6397·5	6364·6			
	6413·9	6377·5			
	6463·0	6411·7			

* These values are deduced from data on room temperature absorption spectra. They are from rather broad and diffuse lines and have a lower precision than others,

4. DISCUSSION

The fact that the spectra of Pr^{3+} in KCl and KBr consist of sharp lines which show polarisation, shows that the Pr^{3+} ions have entered the lattice and occupy identical symmetry sites in it. The observation that the *j*-degeneracy is completely removed shows that the point symmetry around the Pr^{3+} ion in these matrices is very low and can have at most a twofold axis, the possible symmetry groups being C_1, C_i, C_s, C_2, C_{2v}, C_{2h}, D_2 and D_{2h}. The possible crystal quantum numbers for Stark levels in these symmetry groups are 0 and 1 when, as in the present case, the number of $4f$ electrons is even. The polarization of the lines in the absorption and fluorescence spectra enables one to fix the crystal quantum numbers of the Stark levels and in favourable cases to deduce the site symmetry of the ion. In the present investigation polarisation data could be obtained only for the absorption spectrum. The data obtained were not enough to fix unambiguously the crystal quantum numbers in all cases.

In the case of Pr^{3+} embedded in KCl and KBr matrices, fluorescence takes place only from the $^3P_0$ state. No fluorescence occurs from either the $^3P_1$ or the $^1D_2$ level both of which fluoresce in anhydrous $LaCl_3$ and $LaBr_3$. This shows stronger interaction of the rare earth ion with the KBr and KCl lattices than with the $LaCl_3$ or $LaBr_3$ lattices.

In cases where all the $(2J+1)$ Stark levels were detected, the centre of gravity of the state could be accurately determined. Where one or more Stark levels were missing approximate values of the missing levels were estimated. The centre of gravity of the Stark pattern of the ground state $^3H_4$ of Pr^{3+} is estimated to be 210 cm^{-1} in KCl and 190 cm^{-1} in KBr, above their respective lowest Stark levels. The energy levels of the various electronic states are then reduced relative to the centre of gravity of the ground state taken as zero and are compared to those obtained directly in the case of the free ion (Table IV). Using these experimental values the Slater integrals and spin-orbit coupling constants are evaluated by the method of Wong.[6] Adopting these parameters the theoretical energy levels are then calculated.

According to Wong's method, for ions like the triply ionised rare earth ions whose energy levels shift but little from one matrix to another, the energy E_j of a J level in any matrix can be expressed in the following form:

$$E_j = E_{0j} + \frac{\partial E_j}{\partial F_2} \triangle F_2 + \frac{\partial E_j}{\partial F_4} \triangle F_4 + \frac{\partial E_j}{\partial F_6} \triangle F_6 + \frac{\partial E_j}{\partial \xi} \triangle \xi,$$

TABLE IV

Energy levels (observed and calculated), Slater integral and Spin orbit interaction parameters (cm⁻¹) (For explanation see text)

Levels	Pr³⁺ in KCl		Pr³⁺ in KBr		Pr³⁺ free ion	
	Eobs.	Ecalc.	Eobs.	Ecalc.	Eobs.	Ecalc.
$^3H_4$	0	0	0	0	0	0
$^3H_5$	..	2111	..	2111	2152·09	2144·77
$^3H_6$	4275	4319	4275	4318	4389·09	4393·45
$^3F_2$	484?	4725	4817	4709	4996·61	4966·88
$^3F_3$	6205	6129	6187	6114	6415·24	6389·33
$^3F_4$	6702	6693	6680	6672	6854·75	6945·12
$^1G_4$	..	9639	..	9605	9921·24	9912·65
$^1D_2$	16588	16591	16542	16544	17304·39	17416·73
$^3P_0$	20304	20293	20228	20218	21389·81	21384·58
$^3P_1$	20901	20935	20831	20862	22007·46	22044·78
$^1I_6$	..	20975	..	2090?	22211·54	21949·22
$^3P_2$	22116	22119	2 044	22047	23160·61	23216·48
$^1S_0$	..	47915	..	47723	50000·29	50128·19
Slater integrals F_2	..	307·8	..	306·8	..	324·3
F_4	..	49·51	..	49·21	..	51·29
F_6	..	4·856	..	4·838	..	5·046
Spin-orbit coupling constant ξ	..	754·1	..	753·9	..	766·9

where E_{0j} is the zero order energy, F_2, F_4 and F_6 are the Slater integrals and ξ the spin orbit coupling constant. The partial derivatives have been evaluated by Wong for all the levels of the Pr^{3+} ion. For evaluating the constants F_2, F_4, etc., data on the levels, $^3P_2$, $^3P_1$, $^3P_0$, $^1D_2$, $^3F_2$ and $^3F_4$ were used. Values of the energy levels of Pr^{3+} in $LaCl_3$ calculated by Wong with the inclusion of configuration interaction were taken as the zero order spectrum. Energy levels and F_2, F_4, F_6 ξ parameters thus calculated are given in Table IV. Similar procedure was followed for obtaining F_2, F_4, F_6, ξ and from them the calculated values for the free ion are shown in Table IV.

It is seen that in general, there is a lowering of the energy levels of the ion in the crystal relative to those of the free ion and this follows the following pattern: free ion > ion-in-KCl > ion-in-KBr. This is also indicated in the F_2 values which are reduced by about 6% from the free ion value. This reduction is about 5% for Pr^{3+} in $LaCl_3$ and $LaBr_3$.

The effect of replacing Cl^- by Br^- on the energy levels of Pr^{3+} in KCl and KBr is illustrated in Fig. 2 which shows the $^1D_2$ level in KCl, KBr, $LaCl_3$ and $LaBr_3$ matrices. It is seen that the $^1D_2$ level lies lower in energy
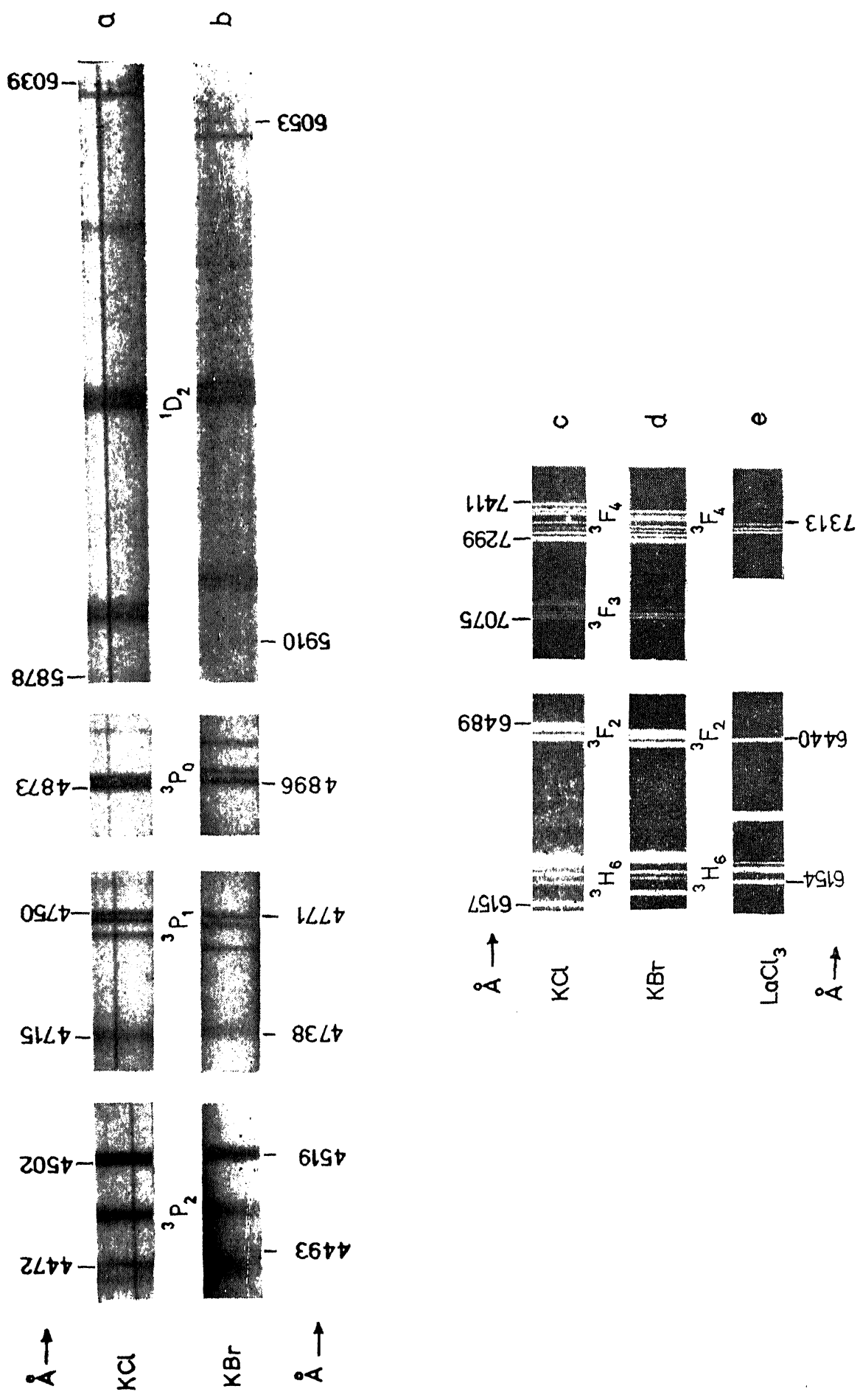
FIG. 1. (a) and (b) Absorption spectra of Pr^{3+} in KCl and KBr respectively. (c) and (d) Fluorescence spectra of Pr^{3+} in KCl and KBr respectively. (e) Same groups of fluorescence of Pr^{3+} in LaCl$_3$. The terminating levels of absorption are from the excited $^3P_0$ state.

All transitions in absorption are from the $^3H_4$ ground state and all transitions in fluorescence are from the $^3P_0$ state. The terminating levels of absorption and fluorescence are shown for all the groups.