

Absorption and Emission Spectra of Difluorenyl-calcium and -strontium in Tetrahydrofuran and in Tetrahydropyran

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Difluorenylcalcium (Fl_2Ca) has been studied by absorption and emission spectrometry in tetrahydrofuran (THF) and in tetrahydropyran (THP). The absorption spectrum shows the presence of both contact and solvent-separated ion-pairs. The solvation of Fl_2Ca in THF is probably a stepwise process. In THP only contact ion-pairs are found. The emission spectrum in THF is independent of the excitation wavelength and of the concentration, and the relative intensities within the emission band do not change in the range of +20 to -40°C . The excitation spectrum shows only one maximum, at 373 nm.

The emission may be caused by an excited-state cation solvent relaxation process and appears to occur from a separated ion pair in the ion triplet. The emission spectrum of Fl_2Sr was examined in order to compare the characteristics of the Ba, Sr, and Ca salts; it depends on the excitation wavelength. The excitation spectrum also shows one maximum. The emission is probably due to a mechanism similar to that for Fl_2Ca .

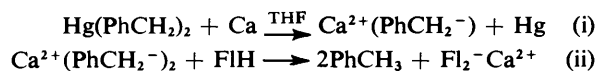
The electronic absorption and emission spectra of alkali metal carbanion salts have received considerable attention over the past few years.¹⁻⁵ The fluorenyl salts have been intensively studied because of their desirable spectral characteristics, allowing a distinction in absorption between at least two types of ion pair in ethereal solvents. The alkaline earth salts⁶⁻¹³ of fluorene or other hydrocarbons have received less attention. However, these salts are of considerable interest, arising from the proximity and interaction of the two carbanion moieties held together by a common ion. Previous workers have described the absorption spectra of barium and strontium fluoride salts in THF in the presence and in the absence of crown ethers or cryptands, as a function of temperature,^{11,12} and have pointed out the occurrence of a solvation process in THF involving the stepwise separation of the alkaline earth counterion from the first and the second carbanion moieties. Emission studies on difluorenylbarium in THF and in THP have indicated the occurrence of exciton interaction between the two carbanions, resulting in large emission red shifts as compared with the free anion.¹³ It was shown furthermore that the carbanion moieties may be initially tilted in order to allow counterion solvation.

In order to obtain a more complete picture of these phenomena, we have investigated the emission spectra of difluorenylcalcium (Fl_2Ca) and -strontium as well as the absorption spectra of the calcium salt.

Experimental

The preparation of the salts and the purification of the solvents were carried out under high vacuum following well known techniques.

The synthesis of the difluorenylcalcium involves two steps (i) and (ii). Dibenzylmercury affords dibenzylcalcium on



prolonged contact of a THF solution with a calcium mirror freshly prepared by sublimation in vacuum (procedure of Favier *et al.*¹⁴). After filtration of the coloured solution from the excess of metallic calcium, its spectrum showed λ_{max} 323 nm.

In step (ii) the dibenzylcalcium solution was mixed with a solution in THF of fluorene in slight excess (or with dry

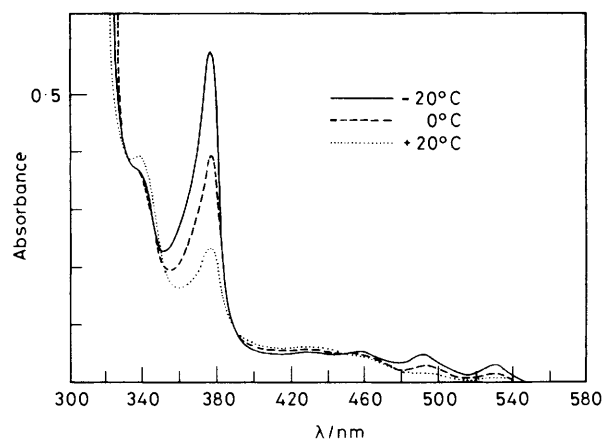


Figure 1. Absorption spectra of Fl_2Ca in THF at various temperatures

recrystallized and sublimed fluorene powder). The formation of difluorenylcalcium was instantaneous, as shown by precipitation of the yellow-orange salt, which is only very moderately soluble in THF even at room temperature. The solid salt was filtered off and washed with solvent in order to remove the excess of fluorene; it can be stored as a solid for prolonged periods at 0°C .

Absorption spectra were recorded with a Cary 17 spectrophotometer. Fluorescence spectra were recorded with a Fica 33 fluorescence spectrophotometer and on a Spex Fluorolog instrument. The latter permits a better observation of the weak emission bands and also allows measurements at higher wavelengths.

Results and Discussion

Absorption Spectra.—The absorption spectra of CaFl_2 in THF and in THP (10^{-5}M) were examined from +20 to -40°C (below -40°C the salts tended to crystallize slowly). The spectrum of CaFl_2 in THF at 20°C (Figure 1) shows two near-u.v. maxima, at 338 and 373 nm. Upon lowering the temperature, the band at 373 nm increases in intensity, and the 338 nm absorption slightly decreases. At 0°C , the two bands have

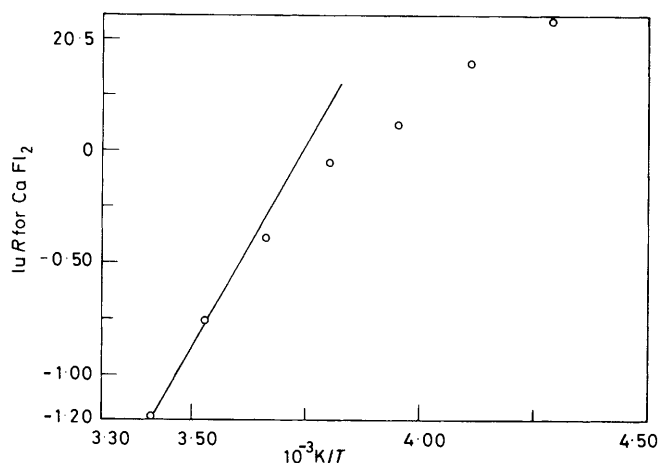


Figure 2. The ratio R for CaFl_2 in THF as a function of the temperature

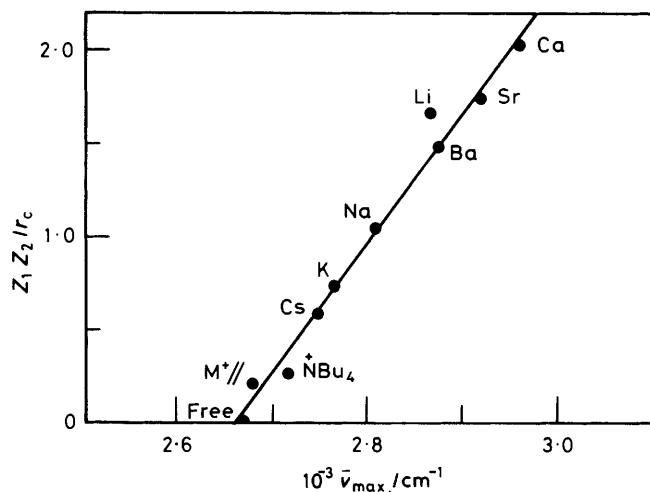
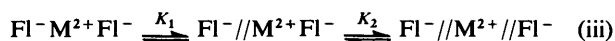


Figure 3. Correlation between wave number and $Z_1 Z_2 / r_c$ in THF at 25 °C for fluorenyl contact ion pairs

approximately the same intensity, but the 338 nm absorption remains visible even at -40°C .

Similar observations have been made for the Sr and Ba salts in THF, and there is little doubt that the absorptions at 338 and 373 nm are due to the presence of contact and separated ion pairs, respectively. A plot of the intensity ratio ($\log R$) of the two bands *versus* $1/T$ shows a pronounced curvature at lower temperatures (Figure 2).¹⁰ This behaviour is in contrast with the linear plots observed for the Li, Na, and K salts.² The observed curvature for the Sr salt¹⁰ was shown to be due to the occurrence of two distinct solvation steps [equation (iii)]. The two solvation steps were shown to have very



different enthalpies and entropies of formation ($\Delta H_1 = -51.5 \text{ kJ mol}^{-1}$, $\Delta S_1 = -196.8 \text{ J K}^{-1} \text{ mol}^{-1}$; $\Delta H_2 = -11.7 \text{ kJ mol}^{-1}$, $\Delta S_2 = -71.1 \text{ J K}^{-1} \text{ mol}^{-1}$). It appears reasonable that the curvature observed for the CaFl_2/THF system should also be due to such a stepwise solvation process.

Since the spectroscopic behaviour of the CaFl_2 solution could not be examined below -40°C , the relative participation of the first and second solvation steps could not be

Table 1. Dependence of λ_{max} on the radius of the cation of fluorenyl salts in THF at 25 °C

Cation	$r_c/\text{\AA}$	$\lambda_{\text{max.}}/\text{nm}$
Li^+	0.60	349
Na^+	0.95	356
K^+	1.33	362
Cs^+	1.69	364
N^+Bu_4	3.5	368
$//\text{M}^+{}^a$	4.5	373
Free ion	∞	374
Ca^{2+}	0.99	338
Sr^{2+}	1.13	343
Ba^{2+}	1.35	348

^a The solvent separated species.

reliably evaluated. However, if we assume that $K_2 \ll 1$ and use the previously derived equation (iv), where ΔH_1 and ΔH_2

$$\Delta H = \left(\frac{2}{2 + K_1} \right) \Delta H_1 + \left(\frac{2K_2}{1 + 2K_2} \right) \Delta H_2 \quad (\text{iv})$$

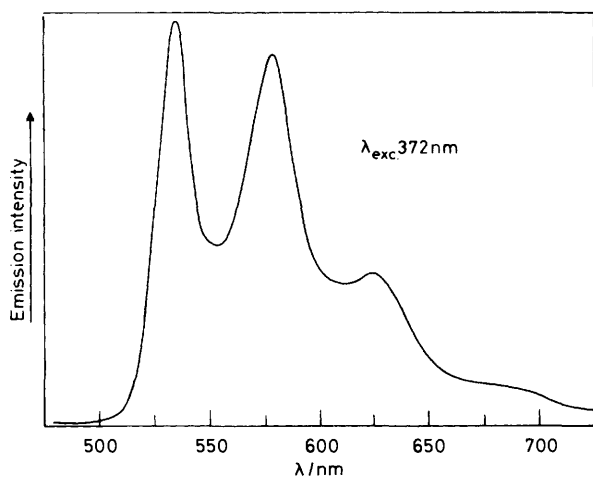
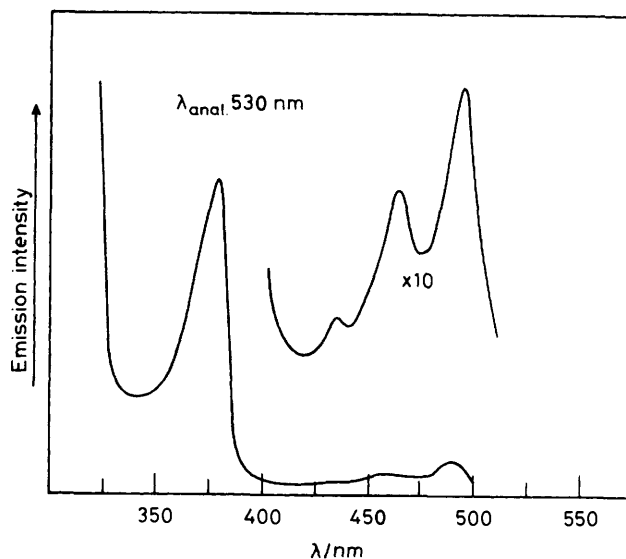
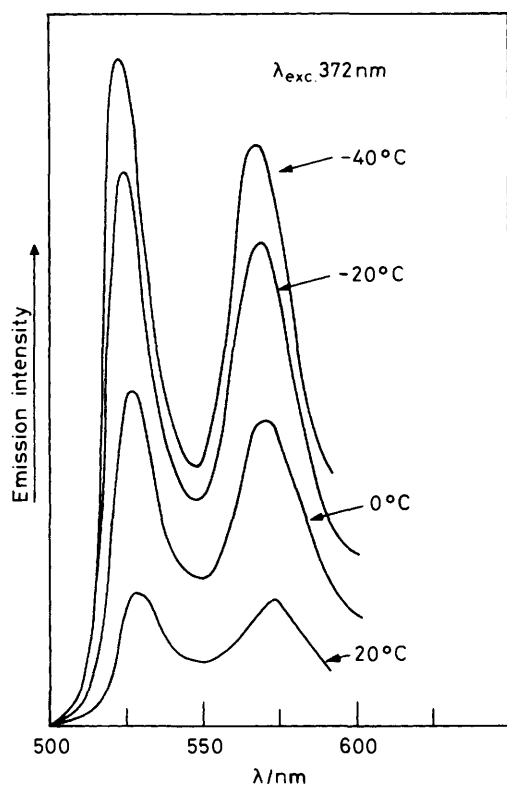
denote the enthalpy changes associated with the first and the second solvation steps, respectively, and H is the apparent enthalpy change associated with the formation of separated ion pairs, tentative values for ΔH_1 and ΔS_1 of 33.9 kJ mol^{-1} and $100.5 \text{ J K}^{-1} \text{ mol}^{-1}$ may be calculated. This would correspond to the participation of about two molecules of solvent in the first solvation step.

The spectrum of CaFl_2 in THF, in contrast, shows only the presence of contact ion pairs over the entire temperature range examined. For a given structure of the carbanion, in this case fluorenyl, the position of the absorption maximum of the contact ion pairs can be shown to depend on the cationic field of the counterion. This field depends not only on the cation radius but also on its charge.

If, in analogy with Hogen-Esch and Smid² and with Zaugg and Schaefer,³ we plot not $1/r_c$ (the inverse of the cation radius) but $Z_1 Z_2 / r_c$ (thus taking into account the differences in charge) as a function of $\tilde{\nu}_{\text{max}}$, a reasonably linear relationship is observed (Figure 3).

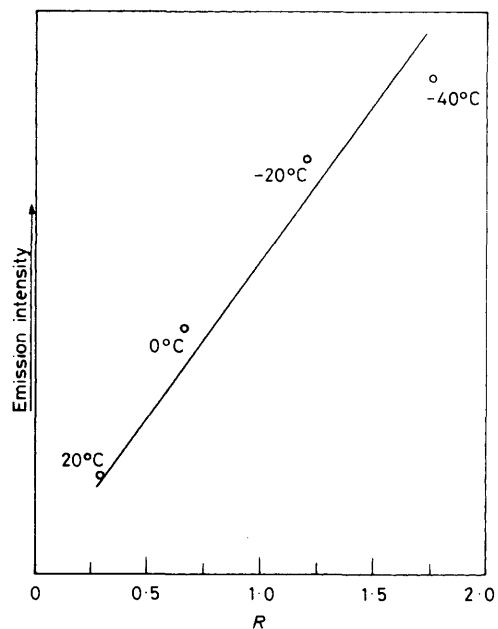
Thus if one compares the λ_{max} values of sodium and calcium fluorenyl salts or those of potassium and barium (cation radii are similar in each pair), it is seen (Table 1) that a hypsochromic shift occurs for the alkaline-earth derivatives with respect to the alkali analogues, due to an increased positive field of the cation.

Emission-Excitation Spectra.—Difluorenylcalcium. The emission spectra of difluorenylcalcium and -strontium were obtained in THF and in THP in the temperature range $+20$ to -40°C with the Spex Fluorolog or the FICA-33 fluorescence spectrometer. The emission spectrum of CaFl_2 in THF excited at 372 nm is shown in Figure 4. The emission signal, observed as four bands in the 500–750 nm region, has maxima at 531, 575, and 625 nm, and a shoulder at about 675 nm. Excitation at the absorption maxima of 338 and 373 nm produced an identical emission spectrum. The emission spectrum was concentration independent over a 100-fold range (10^{-3} to 10^{-5}M). This observation is in contrast to the BaFl_2/THF system (see later). Furthermore, the relative intensities in the emission spectrum do not change in the $+20$ to -40°C range, although the intensity of the spectrum is enhanced at lower temperature (Figure 5). The excitation spectrum (Figure 6) differs from the absorption spectrum in that only the 373 nm maximum is observed. Such a difference

Figure 4. Emission spectrum of Fl_2Ca in THFFigure 6. Excitation spectrum of Fl_2Ca in THFFigure 5. Emission spectra of Fl_2Ca in THF as a function of temperature

between absorption and excitation spectra has also been observed for the difluorenyl-barium and -strontium (see later).

The foregoing observations seem to indicate that the emitting species are ion pairs rather than free anions, which have been demonstrated to influence the emission spectra of BaFl_2 in THF below 10^{-5}M . Thus, no effect on emission is observed over a 100-fold concentration range. More intriguing is the absence of any effect on the shape of the emission spectrum due to excitation wavelength or temperature, although, for example, the molar ratio of separated to contact ion pairs increases with decreasing temperature. However, the emission at 531/575 nm does not change, and

Figure 7. Emission intensity for Fl_2Ca in THF as a function of R

appears to be due to a solvent separated ion pair as demonstrated for similar alkali metal⁵ or alkaline-earth salts.¹³ This interpretation is supported by the observed linear relation between emission intensity and the fraction of separated ion pairs in the CaFl_2/THF system (Figure 7). Free anions and separated ion pairs of these fluoride salts have been shown to have similar emissivities. Because dissociation of these salts is very low at the concentrations used, the emission of separated ion pairs should dominate. Apparently, the emissivity of the contact ion pair in the mixed ion triplet $\text{Fl}^-\text{Ca}^{2+}/\text{Fl}^-$ is very low; this has also been demonstrated for BaFl_2 .¹³ Excitation at the absorption maximum of this species (338 nm) produces emission typical of that of a separated ion pair. This may be caused by an excited state cation solvent relaxation process. In the present case, such a process could be formulated as (v). Emission would occur from the separated ion

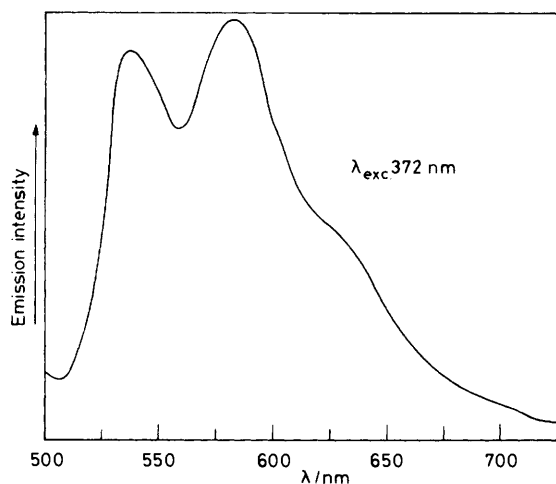
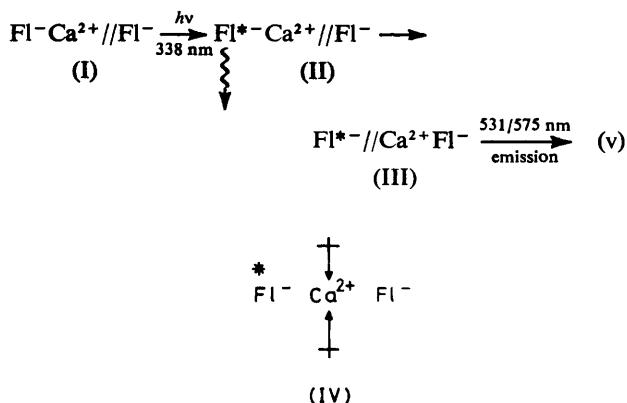


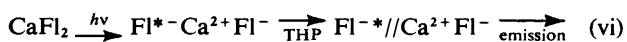
Figure 8. Emission spectrum of $F1_2Ca$ in THP



pair in the ion triplet (III). Competing non-radiative energy transfer from (II) is expected to reduce emissivity in this case. Emission directly from the contact ion pair is probably very low, as was also observed for the $BaFl_2/THF$ and the $CaFl_2/THP$ systems (see later).

The foregoing appears consistent with the observed excitation spectrum showing a maximum at 373 nm (Figure 6). From the shape of the band, a low wavelength contribution appears to be present. Such a shoulder may be consistent with the above, given the low absorptivity of the 338 nm peak coupled with the relatively low emission intensity.

The emission spectrum of $CaFl_2$ in THP (Figure 8) appears quite different from that in THF and is much less intense (25 times). The fine structure bands are much broader, and the relative intensities of the (slightly red-shifted) bands at 533 and 576 nm are reversed. This spectrum is puzzling, since it is not identical in appearance with the $BaFl_2/THP$ contact ion pair emission spectrum observed earlier.¹³ This spectrum showed an apparently single broad absorption at 570 nm and was attributed to emission from the lower excited state exciton level. The present case may be consistent with the simultaneous emission of two ion triplets, one of which is of the $BaFl_2/THP$ variety, the other being a very small concentration of separated ion pairs formed by an excited state cation solvent relaxation process (vi).



A simpler alternative explanation is that the emission is due to a solvated contact ion triplet in which exciton splitting due

Table 2. Absorption and emission maxima of alkali metal and alkaline earth salts of fluorene in THF and in THP at 25 °C, and the types of ionic species occurring in ground and excited states

Salt/solvent ^a	$\lambda_{max.}/nm$ (absorption)	Type of ion pair C/S ^b	$\lambda_{max.}/nm$ (emission)	Type of ion pair C/S/F ^b
$CaFl_2/THF$	338/373	70/30	531/575	S
$CaFl_2/THF$	338	C	540/580	C(S?)
Sr_2Fl/THF	343/373(S)	90/10	533/577	C, S(F?)
$SrFl_2/THP$	343	C	570—590	C
$BaFl_2/THF$	348	C	531/575	C(F)
$BaFl_2/THP$	347	C	570	C
$CsFl/THF$	364	C	537/578	C
$CsFl/THP$	364	C	537/580	C
$LiFl/THF$	349/373	20/80	531/575	S
$LiFl/THP$	349/373	70/30	531/575	S

^a Concentrations 10^{-3} — $10^{-5}M$. ^b C = contact ion pair, S = solvent-separated ion pair, F = free ion.

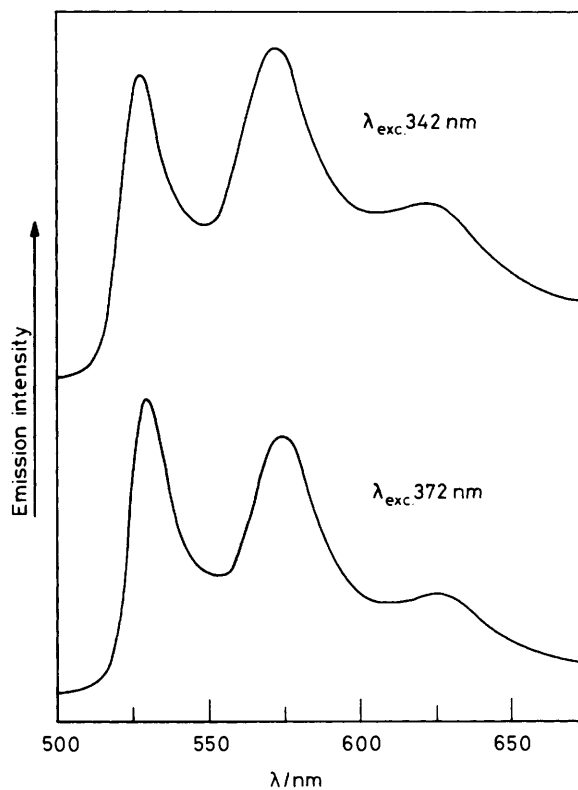


Figure 9. Emission spectra of $F1_2Sr$ in THF at various excitation wavelengths

to orbital overlap is obstructed by the residual solvation of the Ca ion schematically represented as (IV), or by an increased tilt in the relative positions of the two anions due to more extensive solvation of the Ca ion. Indeed the emission spectrum strongly resembles that of the fluorenylcaesium contact ion pairs in THF or THP (Table 2).

Difluorenylstrontium. Because of the observed differences in emission between the calcium and barium salts, the strontium salts were also examined. The emission spectrum in THF, unlike that of $CaFl_2$ but like that of $BaFl_2$, depends on excitation wavelength (Figure 9). The dependence in the $SrFl_2/THF$ system, however, is only slight and appears to involve

only the relative intensities of the 536 and 578 nm fine structure bands. The broad band at 570 nm observed in the BaFl₂/THF system, and attributed (like that in the BaFl₂/THP system) to exciton splitting,¹³ is clearly not present here. Perhaps exciton splitting is again prevented by residual solvation of the Sr ion, or by an increased tilt in the relative positions of the two anions due to more extensive ion solvation.¹³ Upon excitation at 373 nm, the emission spectrum again resembles that of separated ion pairs, consistent with the presence of an appreciable fraction of separated ion pairs in the ground state (ca. 10%). Upon excitation at 342 nm, partial cation-solvent relaxation occurs, and emission from both types of ion pairs appears to occur. As in the other two cases, the excitation spectrum has a single maximum at 373 nm, and the explanation for such a spectrum is probably similar to that given for CaFl₂ (see before).

In Table 2, the absorption and emission maxima of the Ca, Sr, and Ba fluorenyl salts are collected, together with those of a few alkali metal fluorenyl salts for comparison.

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