

Absorption, excitation and fluorescence spectra of thallium activated cesium bromide

V B SHARAN, D N S SRIVASTWA and S C SEN*

Physics Department, H. B. Technological Institute, Kanpur 208 002

*Physics Department, Indian Institute of Technology, Kanpur 208 016

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Abstract. Absorption, excitation and fluorescence spectra of Tl^+ doped cesium bromide have been investigated at various thallium concentrations. At very low thallium concentration two absorption bands are obtained at 225 nm and 264 nm. With rise of thallium concentration additional absorption bands are obtained at 230, 244, 258, 270 and 285 nm. A single bell-shaped fluorescence band at 357 nm in the ultraviolet region is obtained at low thallium concentration. Two additional visible fluorescence bands appear at 440 and 540 nm with rise in thallium content. The excitation spectra for ultraviolet emission band and visible emission bands are found to be different. Accordingly the ultraviolet emission band is attributed to the characteristic A emission in Tl^+ ion and the visible bands are attributed to dimer centers having D_{4h} site symmetry.

Keywords. Luminescence; cesium bromide; thallium; fluorescence spectra.

1. Introduction

The optical absorption and fluorescence spectra of thallium activated alkali halides have been widely investigated by many authors. Although a great amount of work has been done on thallium doped alkali chlorides and alkali iodides, relatively little attention has been paid to alkali bromides (Seitz 1938; Teegarden 1966; Joshi and Prasad 1977). It has also been reported that the absorption and fluorescence spectra of thallium doped alkali chlorides having CsCl like structure differ considerably from those obtained for thallium doped alkali chlorides having NaCl like structure (Zazubovich 1970; Srivastwa 1973; Pathak and Sen 1974). Some attempts have been made to examine absorption and fluorescence spectra of thallium doped alkali bromide hosts having NaCl structure (Ivanova *et al* 1961; Edgerton and Teegarden 1964; Tsuboi 1970; Gindina *et al* 1973 and Casalboni *et al* 1977). However, only recently Sharan *et al* (1977) have reported dimer center luminescence in $NH_4Br:Tl$ where the host has a CsCl like structure. In this paper, we report a similar study of absorption, excitation and fluorescence spectra of CsBr:Tl phosphor and their thallium concentration dependence.

2. Experimental procedure

2.1. Preparation of the phosphor

All the raw materials used in preparing CsBr:TlBr mixed phosphor were of analar

grade. The CsBr:Tl samples have been prepared by mortar grinding CsBr with TlBr and keeping the mixture in platinum crucible at 100°C for an hour (Hutten and Pringsheim 1948). The samples were prepared with thallium concentrations 4.13, 1.03, 0.25, 0.063, 0.016 and 0.004 m%. These were named Cs-11, Cs-12, Cs-13, Cs-14, Cs-15 and Cs-16 respectively.

2.2. Diffuse absorption spectra

According to Kubelka's model (Kubelka 1948; Kortum 1969) the absorption coefficient and the reflectivity are related by the equation

$$K/S = (1-R)^2/2R,$$

where K is the coefficient of absorption, S is the coefficient of scattering of light and R is the reflectivity. The function (K/S) which characterises the absorption can be computed using this equation from the reflectivity data. Using this method we obtained the absorption spectra from the reflection spectra. The reflection spectra relative to $MgCO_3$ surface were recorded using a double monochromator arrangement. An AH4 lamp with outer glass envelope removed was used as the source. The incident radiation was monochromatised by a Gaertner L-234-150 quartz monochromator. The reflected intensity from the phosphor was recorded at right angles to the incident light using another identical monochromator with RCA 1P 28 photomultiplier and a DC electrometer.

2.3. Fluorescence and excitation spectra

Fluorescence and excitation spectra have been recorded using the same double monochromator arrangement described in §2.2. The details of the method of measurement are described elsewhere (Sharan *et al* 1977). The corrections in the fluorescence as well as excitation spectra due to spectral distribution of exciting radiation, dispersion of monochromators and the relative sensitivity of the photomultiplier tube have been applied. The slit widths of the exciting and analysing monochromators were kept at 0.15 and 0.25 mm respectively, so that radiations other than the exciting and emitting ones may not be effective.

3. Experimental results

Diffuse absorption spectra of CsBr:Tl mixed phosphors Cs-16 to Cs-11 recorded at room temperature ($\approx 300^\circ K$) are reproduced in figure 1. The sample Cs-16 containing the lowest thallium concentration shows two clear absorption bands at 225 and 264 nm. With the increase in thallium content these bands grow in intensity and additional absorption bands appear around 230 and 244 nm. Moreover, on the long wavelength side of 264 nm the absorption extends upto 300 nm.

The emission spectra obtained for Cs-11 to Cs-16 with various thallium contents under 258 nm excitation are shown in figure 2. Only a single bell-shaped fluorescence band peaking at 357 nm is obtained for Cs-16 as reported by Masunaga *et al* (1966) under excitation at 258 nm. The intensity of this band initially increases with the

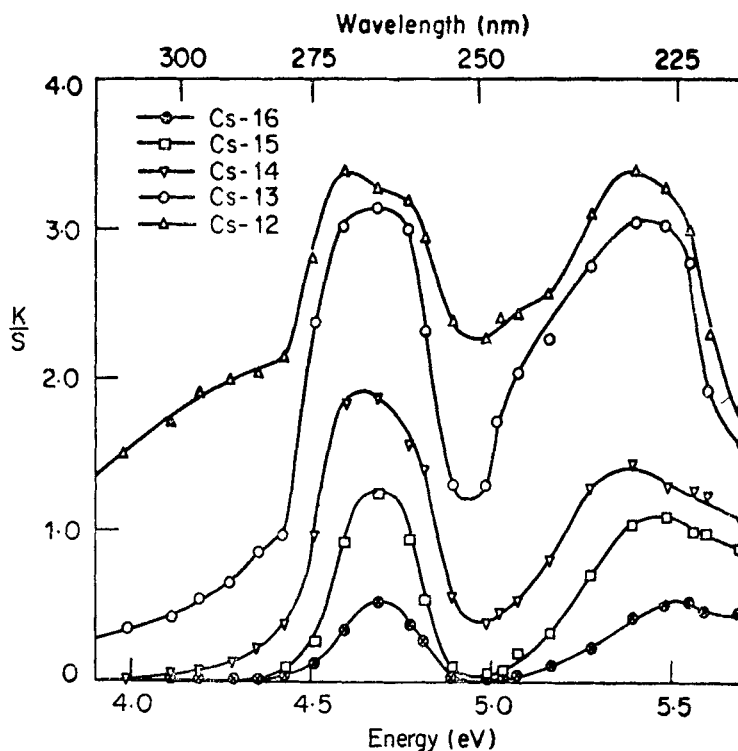


Figure 1. The diffuse absorption spectra of CsBr+TlBr mixed phosphor for different concentrations of thallium at 300°K.

increase in thallium content but diminishes for large concentration e.g. Cs-12. The visible emission which extends from 400 nm to 650 nm has maximum intensity for Cs-12 which has thallium content around 1.0 m%. But with a further rise in thallium concentration this too diminishes.

When the phosphor sample Cs-11 was excited at 240, 258, 265, 275 and 285 nm the visible emission band clearly shows its composite structure (figure 3). On fitting gaussian bands it is found that the constituent bands peak at 440 nm and 540 nm respectively (figure 4). The emission spectra were also recorded under 275 nm excitation for samples Cs-16, Cs-13, Cs-12 and Cs-11. These are shown in figure 5. The emission excited in these samples for this excitation is strongest at 540 nm for Cs-12. The emission spectra obtained for various samples when excited at 230 nm were similar to those obtained for excitation at 275 nm. The emission spectra for samples Cs-15 and Cs-12 under 230 nm excitation are shown in figure 6.

The excitation spectra were recorded for Cs-12 for the emission bands peaking at 357, 440 and 540 nm (figure 7) keeping the analysing monochromator position fixed at 360, 440 and 540 nm. From the nature of the excitation spectra it is concluded that the fluorescence bands obtained at 357, 440 and 540 nm are most efficiently excited by 264, 270 and 276 nm respectively. Excitation bands for visible emission bands are also obtained at 230 nm and 244 nm.

All the three emission bands have been obtained when the different samples were excited at 240 nm; however, the strength of the visible emission bands is stronger compared to the ultraviolet emission band for all concentrations (figure 3).

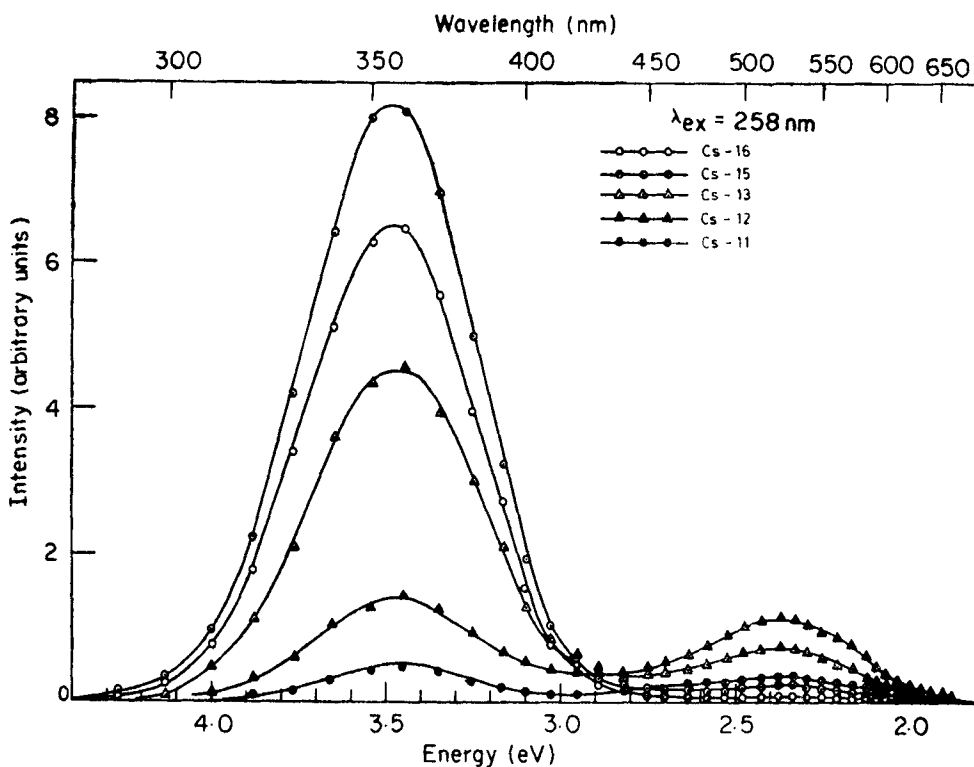


Figure 2. The emission spectra of CsBr + TlBr mixed phosphors under 258 nm excitation at 300°K.

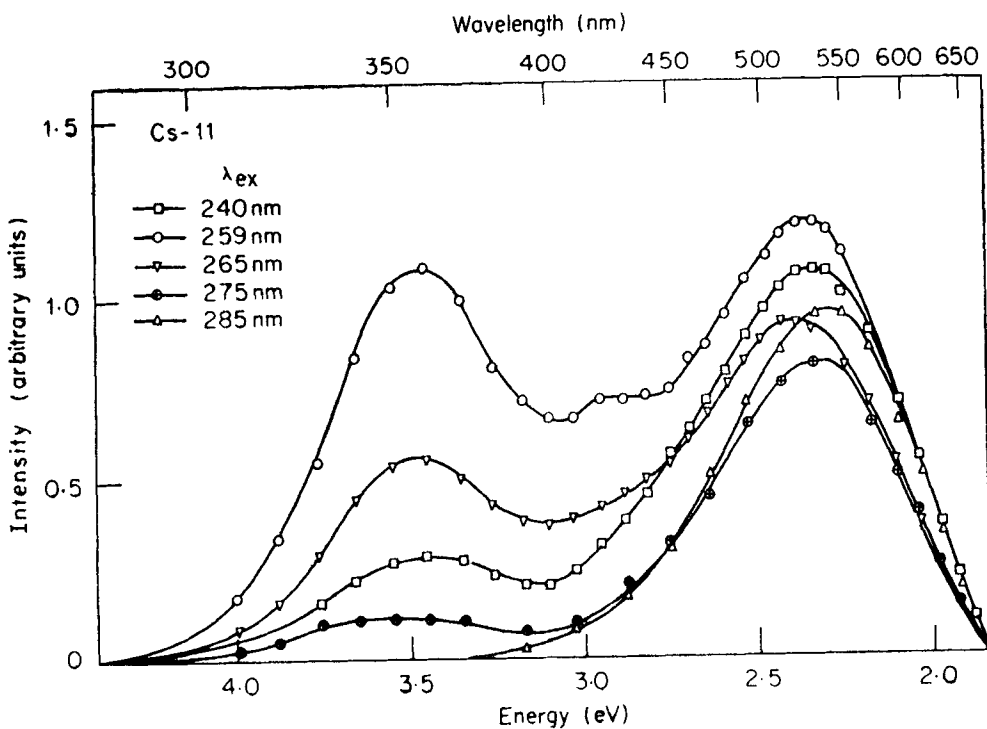


Figure 3. The emission spectra of Cs-11 under 240 nm, 258 nm, 265 nm, 275 nm and 285 nm excitation at 300°K.

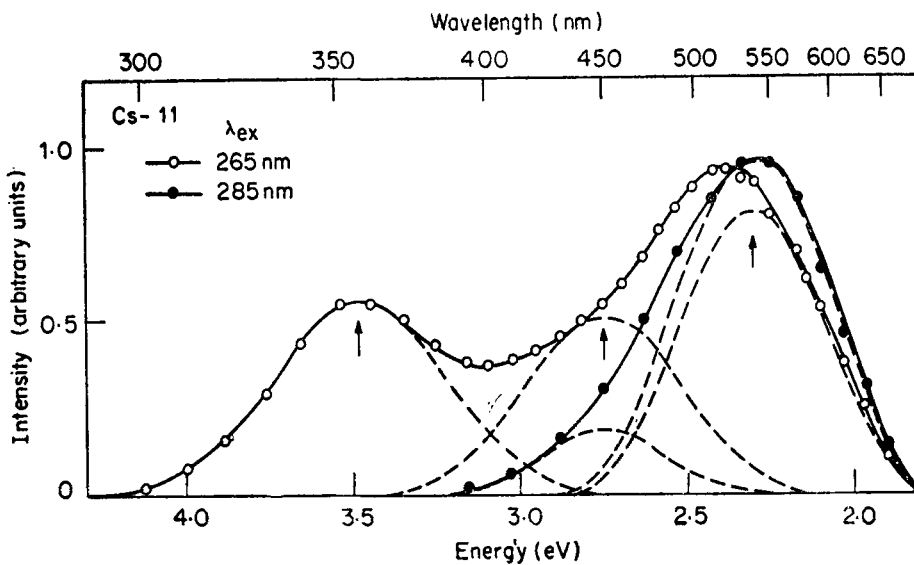


Figure 4. The emission spectra of Cs-11 under 265 nm and 285 nm excitation shown resolved into three gaussian emission bands peaking at 357, 440 and 540 nm at 300°K.

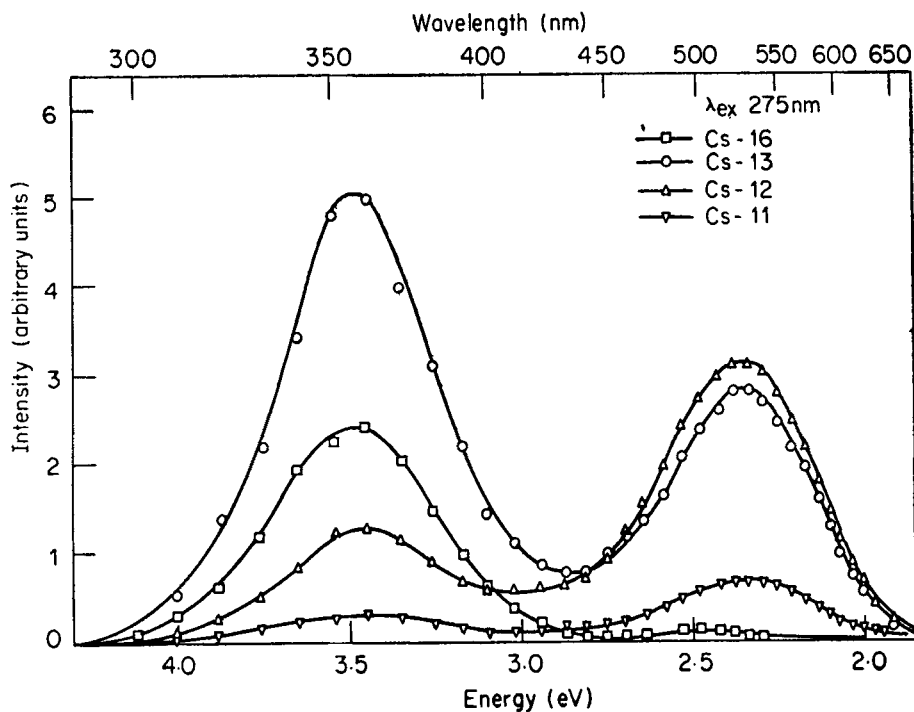


Figure 5. Emissions spectra of Cs-16, Cs-13, Cs-12 and Cs-11 under 275 nm excitation at 300°K.

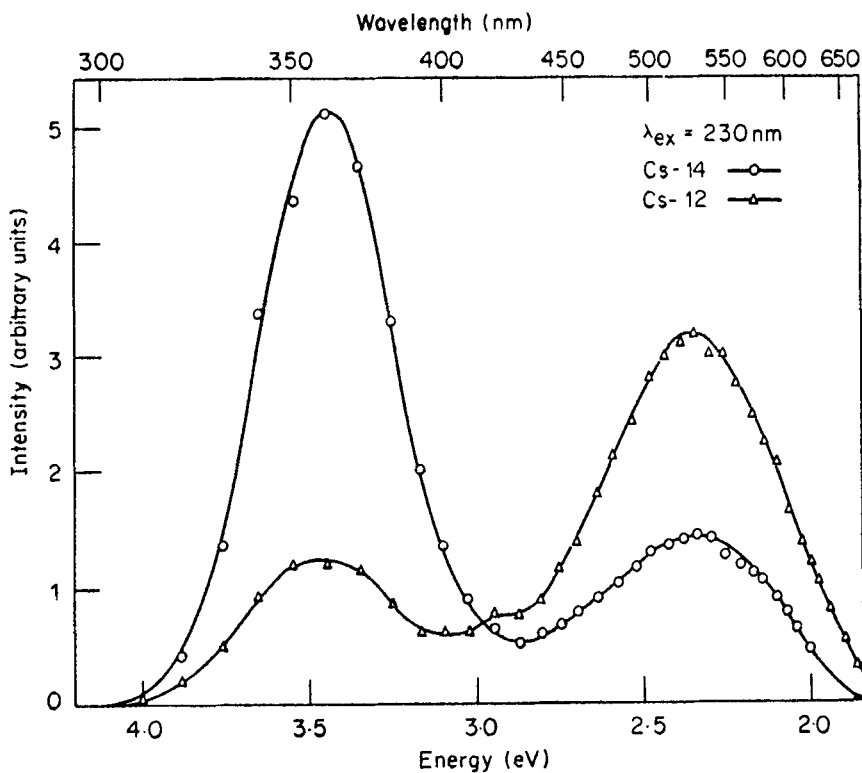


Figure 6. Emission spectra of Cs-12 and Cs-14 under 230 nm excitation at 300°K.

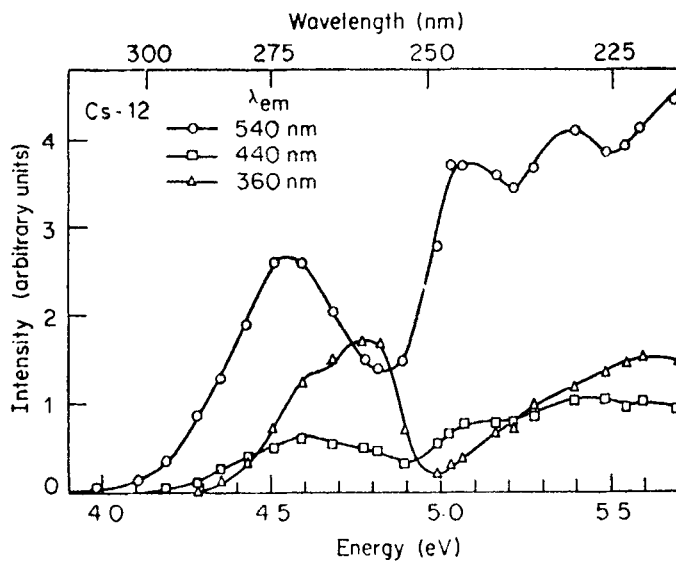


Figure 7. Excitation spectra for Cs-12 for emission bands at 540 nm, 440 nm and 360 nm at 300°K.

4. Discussion

Introduction of a small amount of thallium in an alkali halide results in the so-called *A*, *B* and *C* absorption bands in increasing order of energy (Seitz 1938; Fukuda 1964). These are assigned to $(a_{1g})^2 \rightarrow (a_{1g})(t_{1u})$ or $(s)^2 \rightarrow (s)(p)$ electronic transitions in Tl^+ entering substitutionally in the host lattice. The *C* band corresponds to the dipole allowed transition ${}^1A_{1g} \rightarrow {}^1T_{1u}$ (${}^1S_0 \rightarrow {}^1P_1$), the *B* band to ${}^1A_{1g} \rightarrow {}^3T_{2u} + {}^3E_u$ (${}^1S_0 \rightarrow {}^3P_2$) which gets partially allowed by the spin orbit and electron lattice interactions and the *A* band to the spin orbit allowed ${}^1A_{1g} \rightarrow {}^3T_{1u}$ (${}^1S_0 \rightarrow {}^3P_1$) transitions.

The *A*, *B* and *C* absorption peaks and the fluorescence bands obtained under *A* excitation reported for the phosphors NaBr: Tl, KBr: Tl, RbBr: Tl, NH_4Br : Tl and CsCl: Tl are shown in table 1. Keeping these reports in view we propose that the absorption band obtained for lowest thallium concentration at 264 nm is the *A* band for CsBr: Tl and the one obtained at 225 nm is the *B* band. This agrees well with single crystal absorption data reported by Masunaga *et al* (1966). Fixing *C* band tentatively at 210 nm for CsBr: Tl we may compute the ratio *R* of the dipole strength of the *C* band to the *A* band using Sugano's formula (Sugano 1962). According to this formula

$$R = \frac{4 - 2x + [6 - 2(2x - 1)^2]^{\frac{1}{2}}}{2 + 2x - [6 - 2(2x - 1)^2]^{\frac{1}{2}}},$$

$$x = \frac{W_B - W_A}{W_C - W_A},$$

where W_A , W_B and W_C are the observed positions of the *A*, *B* and *C* bands respectively. The value of *R* for CsBr: Tl then comes out to be 9.8.

The excitation band of the bell shaped emission band obtained at 357 nm for low thallium content is at 264 nm. Hence this emission band is attributed to the electronic transition ${}^3T_{1u} \rightarrow {}^1A_{1g}$ in an isolated Tl^+ , the monomer center. The two visible emission bands peaking at 440 and 540 nm which appear at relatively high thallium concentration are excited efficiently at 270 and 276 nm (figure 7). Recently Pathak and Sen (1974, 1975) and Pathak (1975) have reported visible emission bands for NH_4Cl : Tl, CsCl: Tl and RbCl: Tl and attributed these to dimers. Herb *et al* (1968) have ascertained the symmetry of the dimer centres as D_{4h} . In D_{4h} symmetry ${}^3T_{1u}$ level of Tl^+ splits into a non-degenerate ${}^3A_{2u}$ and doubly degenerate 3E_u and the electric dipole transitions from the ground state ${}^1A_{1g}$ to both

Table 1. Absorption and emission bands of Tl^+ in some alkali halides

Phosphor	Absorption band in nm			Fluorescence bands under <i>A</i> excitation	Reference
	<i>A</i>	<i>B</i>	<i>C</i>		
NaBr:Tl	265	227	211	287, 310	Casalboni <i>et al</i> (1977)
KBr:Tl	259	222	210	317, 364	Edgerton and Teegarden (1964)
RbBr:Tl	260	224	—	317, 365	Sharan <i>et al</i> (1978)
NH_4Br :Tl	259	224	—	390	Sharan <i>et al</i> (1977)
CsCl:Tl	243	222	197	350	Pathak and Sen (1975)

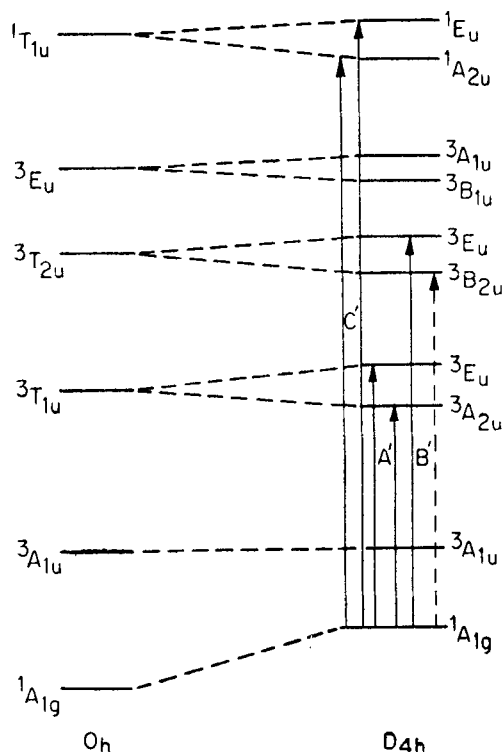


Figure 8. Schematic energy level diagram showing the dimer transitions in D_{4h} symmetry.

these split states are allowed. Accordingly the additional excitation bands at 270 and 276 nm obtained for visible luminescence are attributed to electronic transitions ${}^1A_{1g} \rightarrow {}^3E_u$ and ${}^1A_{1g} \rightarrow {}^3A_{2u}$ respectively in the dimers having D_{4h} symmetry. The fluorescence bands at 440 and 540 nm are then the deexcitation of 3E_u and ${}^3A_{2u}$ to ${}^1A_{1g}$ respectively in these dimers (figure 8).

Excitation bands for visible fluorescence are also obtained at 230 and 244 nm (figure 7). When the various samples are excited at these wavelengths the fluorescence spectra obtained are similar to those obtained for excitation around 275 nm. This seems to be due to the fact that the emission corresponding to these absorptions overlaps considerably with dimer absorption bands at 270 nm. Accordingly due to reabsorption the dimers get excited by even 230 and 244 nm. Considering the strength of these excitation bands we attribute these to transitions in dimers from ${}^1A_{1g}$ to ${}^1T_{1u}$ split states. In D_{4h} site symmetry ${}^1T_{1u}$ also splits into 1E_u and ${}^1A_{2u}$. The 230 nm absorption corresponds to ${}^1A_{1g} \rightarrow {}^1E_u$ (${}^1T_{1u}$) and 244 nm absorption to ${}^1A_{1g} \rightarrow {}^1A_{2u}$ (${}^1T_{1u}$) transitions (figure 8).

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