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To cite this version:
J. Thorne, R. Denning, T. Barker, D. Grimley. EXCITON MIGRATION AND LOCALISATION IN PURE INORGANIC SOLIDS. Journal de Physique Colloques, 1985, 46 (C7), pp.C7-125-C7-128. <10.1051/jphyscol:1985724>. <jpa-00225048>

HAL Id: jpa-00225048
https://hal.archives-ouvertes.fr/jpa-00225048
Submitted on 1 Jan 1985

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EXCITON MIGRATION AND LOCALISATION IN PURE INORGANIC SOLIDS

J.R.G. Thorne, R.G. Denning, T.J. Barker and D.I. Grimley

Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR, U.K.

Abstract: Energy Transfer in Uranyl Compounds for T>0.4K is discussed.

It is not easy to devise experiments which will measure rates of resonant energy transport in pure inorganic solids, and distinguish between the migration and capture processes [1]. We have taken two approaches to this problem which are unusual in that they exploit isotopic effects in these materials. In the first case we use isotopic substitution in a mode which is so weakly coupled to the electronic transition, that the isotope shift in the pure exciton energy is small compared with the excitonic coupling, and use the emission properties to characterise the energy transfer rate. In the second case we characterise the trapping process, by studying the properties of analagous 'anti-traps'. We are able to show that, at rather low temperatures transport over the 'lip' of the trap is rate determining, and that the presence of biexciton annihilation at 0.4K, implies a delocalised exciton in the bulk material.

In single crystals of CsUO₂(NO₃)₃, both the absorption and emission spectrum show features associated with the internal modes of the nitrate ions. Three of these ions act as bidentate ligands, occupying the equatorial region surrounding the linear UO₂²⁺ ion. These modes show large isotope shifts on nitrogen-15 substitution but the difference in their frequency in the ground and excited states is such that the difference in zero-point vibrational energy is <0.1 cm⁻¹. There are two symmetry-related molecules per unit cell, and the polarisation in absorption can be used to assess the magnitude of the Davydov coupling. This measurement must be carefully analysed because the effect of inhomogenous broadening is to amplify the apparent Davydov splitting [2]. We find \( J = 0.05 \text{cm}^{-1} \). Although \( J \) is comparable to

Figure 1. Time resolved emission spectrum of CsUO₂(NO₃)₃, 14-N excitation, at 4.2K. The isotope shift the time resolved emission (Figure 1) shows a transfer rate constant of \( 10^{5} \text{s}^{-1} \). We interpret this to mean that the much larger spectral
inhomogeneity (FWHM=2cm⁻¹) is manifest as disorder with a range which is comparable
to the intermolecular spacing. This disorder effectively localises the exciton, and
may be a consequence of the scope for small deviations in the nitrate geometry.

We have also made a study of trapping mechanisms in Cs₂UO₂Cl₄. We use data from the
rate of transfer between isotopic 'anti-traps' and the bulk material, using both
oxygen-18 and oxygen-17 [3]. These results give a trapping rate at absolute zero
given by

\[ W_{2+1} = 140(\Delta E_{12})^{2.82}s^{-1} \]  

(1)

where $\Delta E_{12}$ is the energy defect expressed in wavenumbers. At higher temperatures
the rate is controlled by a two-phonon, one-site, Raman process with a rate given by

\[ W_{2+1} = P(\Delta E_{12})^{-1.63}f(\omega, \Delta\omega, T) \]  

(2)

where $P$ is a constant incorporating the electron-phonon coupling, and $f(\omega, \Delta\omega, T)$
describes the temperature dependence attributable to an integration over the density
of states, in the Debye approximation, of two phonons differing in frequency by $\Delta\omega$.
Using these expressions it is possible to compute a set of expected rate constants
for any temperature and any energy defect for non-resonant processes in this
material (Figure 2).

![Figure 2. Non-resonant transfer rates in Cs₂UO₂Cl₄, as a function
of energy defect and temperature.](image-url)
We have investigated the rate of trapping in crystals containing small concentrations of bromide ion. This trap is easily observed spectroscopically and is 30 cm$^{-1}$ deep [4]. The primary trapping rate can be assessed directly, because the 'lip' sites are spectrally resolved, having a typical depth of 3 cm$^{-1}$. There is considerable anisotropy in the trapping process as shown by the time-resolved excitation spectrum of trap emission in the region where the 'lip' sites absorb (Figure 3). The fastest rate is $1.5 \times 10^6$ s$^{-1}$, at 5K which is consistent with the rate expected from Figure 2 for this trap depth. Moreover the rate of trapping above 5K from the bulk is consistent with rapid migration to the trap sites, followed by a rate determining capture. Below 5K Figure 2 predicts that if the 30 cm$^{-1}$ trapping process is rate determining the rate should stay effectively constant with temperature. In fact the trapping rate falls by over an order of magnitude in the range between 1.2K and 0.4K, and shows increasing deviation from exponential decay. These low temperature data are included in Figure 2 where the extrapolation to zero temperature suggests a rate determining step of the order of 5 cm$^{-1}$. This is close to the 3.9 cm$^{-1}$ interval which describes the depth of the 'lip' site.

To summarize, the data is consistent with fast resonant bulk migration followed by a rate determining step which, above 5K, is the primary capture at the trap, but below 5K is the transfer to the lip site. In support of the hypothesis that resonant migration is still rapid at 0.4K, Figure 4 shows that biexciton annihilation is still significant at this temperature. Because the spectral inhomogeneity is less than 0.3 cm$^{-1}$, the 'resonant' process cannot proceed by a series of non-resonant steps with rates predicted by Fig. 2 and we infer that the excitation is delocalised, despite our conclusion that in this material J=0.02 cm$^{-1}$[3].

![Figure 3. Time Resolved Excitation Spectra of Trap Emission in Cs$_2$UO$_2$Cl$_{4-x}$Br$_x$.](image)
Figure 4. Effect of laser intensity on decay of Cs$_2$UO$_2$Cl$_4$ emission at 0.4K.

REFERENCES