Electronic energy transfer in actinyl crystals

I. Non-resonant transfer in Cs$_2$UO$_2$Cl$_4$

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Low-temperature time-resolved luminescence measurements on single crystals of Cs$_2$UO$_2$Cl$_4$ doped with small concentrations of U$^{18}$O$_2^{3+}$ and U$^{16}$O$_2^{4+}$ permit the measurement of nearest neighbour non-resonant electronic energy transfer rates. The rates are consistent with a direct phonon emission process and electric quadrupole–quadrupole coupling.

1. INTRODUCTION

The mobility of electronic excitation energy in crystalline solids is most directly detected by the change in the spectral characteristics of the emission as a function of time. In organic crystals the most satisfactory detector is an isotopic trap which does not physically perturb the lattice. In inorganic materials it is not usually possible to create suitable isotope shifts in the emission spectrum so that the majority of studies have been restricted to solids which contain sites which are chemically distinct from the absorbing centres. In some cases the nature of these sites may be known, for example in the migration between single and Cr$^{3+}$ pair sites in ruby [1], but in other cases may not be clearly identifiable [2]. The mobility of the excitation in pure crystals often leads to quenching of the emission so that the majority of energy transfer studies refer to dilute absorbing centres. The dilution, however, brings with it the danger that the donor and acceptor sites may not be perfectly dilute, so that the range of the transfer becomes uncertain.

Pure solids, where they can be studied, offer a clearly identifiable elementary energy transfer step, but the dynamics are complicated by the statistical variations in the range of the detecting trap and the dimensionality of the transport pathway [3]. Almost invariably absorption occurs in the host material so that the time dependence of the trap emission is a composite of the diffusion of the excitation and the subsequent trapping step.

Proper characterization of the diffusion process depends on a knowledge of the rate of the trapping process. Direct measurement of the trapping rate is difficult. In this work we approach this rate by selectively exciting isotopic anti-traps whose energy levels lie above those of the bulk. The time evolution of the

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emission is then a direct measure of the rate of transfer to the immediately neighbouring sites. This rate will be equivalent to the trapping step when the isotopic species has energy levels below those of the bulk. Here we report the observation of this rate in the pure crystal Cs$_2$UO$_2$Cl$_4$, which can be isotopically substituted in the UO$_2^{2+}$ ion, and investigate the variation of the rate as a function of both temperature and the energy defect.

2. THE ELECTRONIC ABSORPTION SPECTRUM OF Cs$_2$UO$_2$Cl$_4$

The polarized single crystal absorption spectrum of Cs$_2$UO$_2$Cl$_4$ has been extensively investigated [4, 5]. The first electronic excited state is nearly degenerate. Both electronic origin bands, I and II, are observed, in different polarizations, separated by 1.6 cm$^{-1}$, near 20 095 cm$^{-1}$; they are both allowed by a magnetic-dipole mechanism. This state together with its vibronic sidebands is responsible for all the emission intensity. In the course of our analysis...
of the absorption spectrum [4, 5] we have prepared crystals containing various concentrations of $\text{U}^{16}\text{O}_{2}^{2+}$, $\text{U}^{18}\text{O}_{2}^{2+}$. Figure 1 shows the polarized absorption spectrum of such a crystal containing approximately 80 per cent oxygen-18, in the region of origin I, compared with a natural abundance crystal. The isotope shifts of 5.1 cm$^{-1}$ arise as a consequence of differences in the ground and excited state zero-point vibrational energy, and clearly permit selective pumping of any of the isotopic species with a tunable dye laser. A third electronic origin band, origin III, is pure electric-quadrupole allowed [4] and occurs at 20 405 cm$^{-1}$.

3. EXPERIMENTAL

The emission was excited by a tunable nitrogen-pumped dye laser (Molectron Type DL 200) operating at 20 Hz, with a bandwidth of 0.5 cm$^{-1}$ and a pulse length of about 5 ns. The emission was analysed by a Spex 1404 double monochromator with an effective spectral bandpass of 2.5 cm$^{-1}$. In the region between 18 600 cm$^{-1}$ and 18 300 cm$^{-1}$ the emission corresponds to the creation, in the electronic ground state, of either two quanta of the UO$_2$ symmetric stretching frequency, or to one quantum of this mode together with one quantum of the asymmetric stretching frequency. The isotope shift caused by the substitution of one atom of oxygen-18 for one of oxygen-16 is about 50 cm$^{-1}$ so that it is easy to separate spectrally the emission from all three isotopic species. The emission was measured orthogonal to the pump beam in a pumped helium cryostat having a base temperature of 0.8 K.

![Single crystal polarized absorption spectrum of natural abundance Cs$_2$UO$_2$Cl$_4$ at 4.2 K, thickness 2.3 mm.](image)
The time evolution of the luminescence was recorded by a Biomation 8100 transient digitizer having a minimum interval between digitization of 10 ns and a 2048 8-bit word memory. The results from successive laser pulses were averaged in real time by transfer of the data to a Research Machines Ltd. 380-Z micro-computer via an interface which has been described in detail elsewhere [6].

4. RESULTS

Figure 2 shows the absorption spectrum of a thick crystal, 2.3 mm, of pure natural abundance Cs2UO2Cl4 in the $X(z)$ and $X(y)$ polarizations [4]. The feature at 20 101 cm$^{-1}$ corresponds to the 0.4 per cent abundance U16O18O2$^{2+}$; it is completely polarized and is superimposed on a steadily rising background absorption which is presumably associated with the dispersion of the lattice phonons.

The energy transfer measurements were made on another crystal having the composition U18O2$^{2+}$ : U16O16O2$^{2+}$ : U16O2$^{2+}$ of 0.005 : 0.005 : 1. This material was made by growing crystals from a natural abundance solution to which a small concentration of U18O2$^{2+}$ had been added. The evaporation was carried out in a chlorine atmosphere to prevent isotopic exchange [5]. The isotopic composition was determined by careful measurements of the Raman scattering intensity in the UO2$^{2+}$ symmetric stretching frequency of the three isotopic species, making allowance for the mixing of the symmetric and asymmetric modes in the non-centrosymmetric U16O18O2$^{2+}$ ion.

Figure 3 shows (a) the time evolution of the luminescence spectrum measured at 4.2 K when the exciting laser is turned to the U18O16O2$^{2+}$ feature at 20 101 cm$^{-1}$ and (b) the equivalent when excited on the U18O2$^{2+}$ feature at 20 106 cm$^{-1}$. The
Figure 3. Time evolution of the emission spectrum at 4.2 K of a single crystal of $\text{Cs}_2\text{UO}_2\text{Cl}_4$ containing 0.5 per cent $\text{U}^{18}\text{O}_2^{2+}$ and 0.5 per cent $\text{U}^{18}\text{O}^{16}\text{O}_2^{2+}$ (a) when pumped on $\text{U}^{18}\text{O}^{16}\text{O}_2^{2+}$ absorption, (b) when pumped on $\text{U}^{18}\text{O}_2^{2+}$ absorption.

notation in the figure is that of [5]. The spectra illustrate the complementary rise and fall of the directly pumped anti-trap emission and the corresponding $\text{U}^{16}\text{O}_2^{2+}$ emission. In both figures 3 (a) and 3 (b) the acceptor emission has an appreciable amplitude only 2 $\mu$s after the laser pulse, reflecting the 3 $\mu$s width of the software channel average imposed on the data and some residual absorption of the acceptor at the pump wavelength. The (1/\(e\)) lifetime of the acceptor is 3.3 ms so that it shows negligible decay on the time scale of figure 3. The efficiency of the energy transfer is shown by the observation that the intensity of the donor emission at 2 $\mu$s delay is comparable with that of the acceptor emission at 152 $\mu$s, after allowing for that portion of the acceptor emission which is directly pumped. The lower initial acceptor emission in figure 3 (a) reflects the smaller background absorption at the $\text{U}^{18}\text{O}^{16}\text{O}_2^{2+}$ pump-wavelength as indicated in figure 2. Figure 4 illustrates the complementary rise and fall of donor and acceptor emission when $\text{U}^{18}\text{O}^{16}\text{O}_2^{2+}$ is pumped and shows the quality of the lifetime data. Figure 5 illustrates that at 4.2 K the decay of both donor centres is perfectly exponential. The absence of back-transfer, particularly in the case of $\text{U}^{18}\text{O}^{16}\text{O}_2^{2+}$, for which the energy defect is 5 cm\(^{-1}\), indicates that the rate of diffusion of the exciton away from the acceptor centre into the bulk $\text{U}^{16}\text{O}_2^{2+}$ lattice is fast compared with the rate of back transfer. This figure also shows how much faster the energy transfer occurs from the $\text{U}^{18}\text{O}_2^{2+}$ donor, with the larger energy defect.

Figure 6 illustrates the temperature dependence of the rate for both donor species. The presence of back transfer, at higher temperatures, means that some of the rates are calculated from the initial exponential decay rate of the donor.
Figure 4. Time evolution of the emission from $^{18}O^{18}O^{2+}$ and $^{18}O^{2+}$ in $Cs_2UO_2Cl_4$ at 4.2 K.

Figure 5. Comparison of the rate of decay of $^{18}O^{2+}$ and $^{18}O^{18}O^{2+}$ emission at 4.2 K.
Figure 6. Temperature dependence of the energy transfer rates from $U^{180}O^{16}O^{2+}$ and $U^{18}O_2^{2+}$ to $U^{16}O_2^{2+}$, compared with a one-phonon first order model (A and C) and a composite one-phonon first and second order model (B and D).

The transfer process is, in part, thermally activated, the transfer from $U^{18}O^{16}O^{2+}$ being much more sensitive to temperature than that from $U^{18}O_2^{2+}$. Below 3 K there is negligible temperature dependence and at 1.2 K the rate of transfer from $U^{18}O_2^{2+}$ is eight times faster than that from $U^{18}O^{16}O^{2+}$.

5. THE TRANSFER MECHANISM

The rate of energy transfer is dependent on two factors, the nature of the electronic coupling between adjacent uranyl ions and the mechanism by which the energy defect is compensated. These are considered in turn.

5.1. The electronic coupling

Several mechanisms for excitation exchange have been investigated theoretically by Orbach [7]. Besides the direct coupling mechanisms it is possible that the transfer may occur radiatively. It can be shown [8] that the importance of this mechanism can be estimated by replacing the non-radiative ion-ion coupling $J$ by $J' = \lambda A/2\pi R$ where $\lambda$ is the wavelength associated with the intermediary photon, $A$ is the radiative decay probability and $R$ is the ion-ion distance. The quantum efficiency for radiative decay in uranyl salts is close to 100 per cent so that the measured lifetime gives a value for $A$ of approximately $3 \times 10^3$ s$^{-1}$. However, the resonance line, which is the only feature relevant to this mechanism, represents less than one twentieth of the total emission intensity. Including this factor and using an ion-ion distance of 6 Å we estimate $J' = 1.5 \times 10^{-7}$ cm$^{-1}$. It will transpire that the magnitude of the direct coupling matrix elements are much larger.
Cs₂UO₂Cl₄ is a C₉/m monoclinic crystal, containing one molecule per primitive unit cell. The uranyl ion, incorporated in the molecular [UO₂Cl₄]²⁻ unit, is separated from its immediate neighbours by 5.83, 7.10, 7.71 and 8.53 Å. The equatorial field parameter describing the interaction of the excited f electron with the immediately coordinated chloride ion is ~ 500 cm⁻¹ [9]. The small magnitude of this parameter, compared to the values found for transition metal ions, and the absence of bridging atoms suggests that the exchange interaction involving these electrons may be small. At any rate it is hard to estimate and we therefore examine the magnitude of the electro-magnetic multipole coupling between neighbouring ions.

Cs₂UO₂Cl₄ accommodates the UO₂²⁺ ion in a centrosymmetric, C₂h, site, the pure electronic transitions obeying parity forbidden magnetic-dipole and electric-quadrupole selection rules [4, 5]. At first sight the situation approaches that found in the energy transfer between lanthanide ions in halide lattices [10] with two important differences; the chromophore is strongly anisotropic and the electronic excitation is strongly coupled to the O–U–O stretching frequency of the uranyl group. Careful account must therefore be taken of the directional properties of the multipolar coupling instead of performing the usual orientational average [11]. The strong coupling to the O–U–O stretching mode requires vibronically coupled wavefunctions so that the relevant multipole moments are attenuated by a Franck-Condon factor. As a result the resonant transfer rate at low temperature is reduced by a factor reflecting the intensity in the 0–0 or pure exciton component of the transition, and the excitation is said to be self-trapped as a result of the relaxation in the O–U–O distances. Fortunately, in Cs₂UO₂Cl₄ the progression in the O–U–O stretching mode is very well resolved so that the appropriate multipole transition moment can be calculated directly from the area of the resonance line.

The site symmetry in Cs₂UO₂Cl₄ is close to D₄h, with a small orthorhombic, D₂h, distortion which is manifest in the 1.6 cm⁻¹ splitting of the first, E_{g(D₄h)}', excited state. Both components are, formally, both magnetic-dipole and electric-quadrupole allowed in D₄h and in D₂h'. The electric-quadrupole polarization characteristics [4] are not observed in these transitions so that the principal intensity mechanism is magnetic-dipole.

The interaction energies are

\[ J_{qq} = \frac{e^2 \alpha \tilde{N}_d \tilde{N}_a}{4\pi\varepsilon_0 R^5} \tag{1} \]

\[ J_{\mu\nu} = \frac{e^2 \mu_0 \alpha (\mathbf{L} + 2\mathbf{S})_d (\mathbf{L} + 2\mathbf{S})_a}{16\pi m^2 R^3} \tag{2} \]

where \( R \) is the internuclear distance, \( \alpha \) is the angular factor describing the interaction, \( \tilde{N}_d \) is the donor or acceptor quadrupole transition moment, expressed in terms of the traceless quadrupole tensor \( \tilde{N}_{d\beta} = (\hat{r}_d \hat{r}_d - 1/3 r^2 \delta_{d\beta}) \), and \( (\mathbf{L} + 2\mathbf{S})_i \) is the equivalent angular momentum operator. We have ignored the difference of the dielectric constant from unity and assumed a negligible magnetic susceptibility.

The most important and difficult estimation is that of the quadrupole–quadrupole interaction associated with origins I and II. Since the intensity mechanism is not directly observable in these origins it must be approached by
way of the intensity of origin III which is known to be pure electric–quadrupole allowed [4]. We begin by a purely illustrative calculation of the transfer rate associated with origin III. This rate is not measurable in practice because the non-radiative relaxation from origin III to origins I and II is sufficiently fast that no luminescence is detectable from it.

The oscillator strength of origin III is $f = 2.7 \times 10^{-9}$. In view of the observed polarization of this transition we calculate $|\mathcal{N}_{xy}|^2 = 1.05 \times 10^{-48}$ m$^4$. The angular factors, $\alpha$, appropriate to equation (1), are collected in the Appendix. They refer to the pairs of ions indicated and are based on the structural data in [12]. The disposition of neighbouring ions is indicated in figure 7; using these values in equation (1) gives the interaction energies in table 1 (column 1).

![Figure 7. Physical relationship of neighbouring pairs of uranyl cations in the unit cell of Cs$_2$UO$_2$Cl$_4$](image-url)

<table>
<thead>
<tr>
<th>Atom pair</th>
<th>$J_{qq}/\text{cm}^{-1}$</th>
<th>$W_{ij}/\text{s}^{-1}$</th>
<th>$J_{qq}/\text{cm}^{-1}$</th>
<th>$W_{ij}/\text{s}^{-1}$</th>
<th>$J_{qq}/\text{cm}^{-1}$</th>
<th>$W_{ij}/\text{s}^{-1}$</th>
<th>$J_{qq}/\text{cm}^{-1}$</th>
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<tr>
<td>1–2</td>
<td>0.268</td>
<td>$2.39 \times 10^{11}$</td>
<td>0.256</td>
<td>$2.18 \times 10^{11}$</td>
<td>0.057</td>
<td>$1.08 \times 10^{10}$</td>
<td>0</td>
</tr>
<tr>
<td>1–3</td>
<td>0.084</td>
<td>$2.35 \times 10^{10}$</td>
<td>0.037</td>
<td>$4.56 \times 10^{9}$</td>
<td>0.024</td>
<td>$1.92 \times 10^{9}$</td>
<td>0.036</td>
</tr>
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<td>1–4</td>
<td>0.33</td>
<td>$5.88 \times 10^{10}$</td>
<td>0.014</td>
<td>$6.52 \times 10^{8}$</td>
<td>0.057</td>
<td>$1.08 \times 10^{10}$</td>
<td>0</td>
</tr>
<tr>
<td>2–3</td>
<td>$5.4 \times 10^{-4}$</td>
<td>$9.7 \times 10^{5}$</td>
<td>0.026</td>
<td>$2.25 \times 10^{9}$</td>
<td>0.014</td>
<td>$6.52 \times 10^{8}$</td>
<td>0</td>
</tr>
</tbody>
</table>
By way of illustration the pairwise resonant transfer rate between sites (1) and (2) can be calculated using the expression derived by Dexter [11]

\[ W_{1-2} = (2\pi/\hbar^2)J_{12}^2 \int g(\nu)^2 d\nu. \]  

(3)

It has been pointed out by Orbach and others [13-15] that the line-shape function \( g(\nu) \) in this expression should only be applied to a homogeneously broadened line. Only the homogeneous width is a measure of the final density of states available to a pair of coupled ions. Unfortunately, the homogeneous width of origin III is not known. A lower limit on the transfer rate between adjacent ions exactly in resonance can be estimated on the assumption that the observed width (0.72 cm\(^{-1}\) FWHM) is comparable with the homogeneous width. Transfer rates based on this assumption are included in table 1 (column 2). It is, however, likely that the homogeneous width of the line is considerably smaller.

The effect of inhomogeneous broadening on the transfer rate is particularly interesting. As the homogeneous width falls below the inhomogeneous width the rate of transfer between adjacent ions in resonance increases. However, Orbach [16] suggests that the probability that an ion spectrally in resonance with the donor lies spatially close to it will decrease as the inhomogeneous broadening increases. The transfer rate, as reflected in spectral diffusion, then depends on the functional dependence of the rate on the energy defect [17]. The validity of this argument depends on the assumption of microscopic strain inhomogeneity, so that there is no correlation of strain energies between nearest neighbour ions. While this may easily be true in dilute materials it may not be true in a pure crystal, in which it is difficult to imagine a source of strain which is random on the scale of a single lattice spacing. If the strain varies slowly on the scale of a lattice spacing then quite rapid spatial and spectral transport may persist despite the inhomogeneous broadening.

We now attempt an estimate of the transfer rate \( W_{1-2} \) for the luminescent origins I and II. Because the quadrupole component of the intensity is not observable the quadrupole transition moments \( \tilde{N}_{xz} \) and \( \tilde{N}_{yz} \) are calculated from the appropriate wavefunctions. The nature of the wavefunctions and an empirical calculation of the relative energies of the excited states is discussed in [9]. The success of this calculation gives some value to the eigenvectors and they are used here to estimate the transition moments. In terms of a \( \Lambda-\Sigma \) basis [9] the relevant allowed transition moments are

\[ \langle \Sigma^+_g | \tilde{N}_{xy} | \Delta_g (xy) \rangle, \quad \langle \Sigma^+_g | \tilde{N}_{xz} | \Pi_g (x) \rangle. \]

These excited states are to be associated with the \( \sigma_u \delta_u \) and \( \sigma_u \pi_u^* \) configurations respectively. There is ample evidence for the dominant role of the \( \sigma_u \delta_u \) configuration in the observed excited states [9], while the location of the \( \sigma_u \pi_u^* \) configuration can be inferred from the 15 000 cm\(^{-1}\) separation of the \( \delta_u \) and \( \pi_u^* \) orbitals in the neptunyl (VI) ion [18].

Recent relativistic self consistent field calculations [19] indicate that the \( \sigma_u \) orbital in these configurations is 59 per cent uranium \( f \) while the \( \delta_u \) and \( \pi_u^* \) orbitals are 94 and 71 per cent \( f \) respectively. Considering the uranium \( f \) orbital contribution alone, with the reasonable approximation that \( \int_0^\infty f(r)^2 r^4 dr \) is the same for both \( f_g \) and \( f_\pi^* \) orbitals, we find by way of the angular part of these
The eigenvectors from the energy calculations of [9] we denote as \( \lambda_3 \) for the component of \( |\Delta_g(x,y)\rangle \) in the excited state associated with origin III and \( \lambda_1 \) for the component of \( |\Pi_g(x)\rangle \) in origin I. Then

\[
\langle 1\Sigma^+_g | \hat{N}_{xy} | \lambda_1 \rangle = (\lambda_1 / \sqrt{10}) \langle 1\Sigma^+_g | \hat{N}_{xy} | \Pi_II \rangle .
\]  

Using the parameters of reference [9] and a difference in energy of \( \omega_u \) and \( \omega_7u^* \) of 15 000 cm\(^{-1} \) we obtain \( \lambda_1 = 0.185 \) and \( \lambda_3 = 0.137 \). These wavefunctions predict \( |\hat{N}_{xz}|^2 = 4.48 \times 10^{-43} \) m\(^4\).

It is well to summarize the main assumptions of this procedure. First the Franck-Condon factors applying to origins I and III are assumed equal. The intensity pattern in their progressions [5] suggests that this is an excellent approximation. Secondly the validity of the one-centre procedure for the transition moments should be questioned. In an LCAO description the \( f_{\sigma_u} \) orbital has equal weight in each excited configuration, but SCF calculations [19] show some difference between the \( f \) orbital weight in the \( \delta_u \) (94 per cent) and \( \pi_u^* \) (71 per cent) molecular orbitals, which has been ignored. This factor would reduce the calculated transition moment for origin I. On the other hand the inclusion of two centre contributions may have the opposite effect. Again taking an LCAO description, \( \langle r^2 \rangle \) for the oxygen orbitals will be sufficiently small that one-centre contributions on oxygen may be ignored, but it is likely that the two-centre integral, \( \langle 2p_o | xy | f_u \rangle \), will be much smaller than \( \langle 2p_o | xz | f_u^* \rangle \) on overlap grounds. In the absence of satisfactory quantitative procedures we use \( |\hat{N}_{xz}|^2 = 4.48 \times 10^{-43} \) m\(^4\) to calculate the relevant transfer integrals.

Using the angular factors in the Appendix this transition moment is used to calculate the interaction energies in table 1 (column 3). Identical assumptions apply for the transition moment, \( \hat{N}_{yz} \), applicable to origin II but the different angular factors give the interaction energies shown in table 1 (column 5). Table 1 (column 7) includes the cross-term linking origins I and II. With the same assumption about the homogeneous linewidth discussed in connection with origin III we obtain illustrative lower limits on the transfer rates which are also included in table 1 (columns 4 and 6).

It is also possible to estimate the magnitude of the transfer integral associated with the magnetic-dipole mechanism which dominates the intensity of origins I and II. Using the observed oscillator strength \( (f = 1.83 \times 10^{-8}) \) for origin I [5] the transition moment \( \mu_y = 0.084 \mu_B \). With the angular factors in the Appendix, the interaction energies and notional transfer rates are collected in table 2. The

<table>
<thead>
<tr>
<th>Atom pair</th>
<th>( J_{xu} \times 10^8 / \text{cm}^{-1} )</th>
<th>( W^{12} / \text{s}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-2</td>
<td>31.4</td>
<td>3283</td>
</tr>
<tr>
<td>1-3</td>
<td>0.96</td>
<td>3.04</td>
</tr>
<tr>
<td>1-4</td>
<td>6.78</td>
<td>153</td>
</tr>
<tr>
<td>2-3</td>
<td>1.90</td>
<td>12.0</td>
</tr>
</tbody>
</table>

Table 2. Magnetic dipole interaction energies and transfer rates.
observed non-resonant transfer rates are $\sim 10^4$ s$^{-1}$ so that the magnetic dipole mechanism can be of no importance. The rates shown in table 2 are resonant transfer rates and, as the next section shows, are strongly attenuated by the phonon-assisted compensation for the non-resonant energy defect.

The most important conclusion from table 1 is that the energy transfer rate is predicted to be strongly anisotropic and pseudo one-dimensional, being an order of magnitude faster (see columns 4 and 6) along the molecular $c$ axis (see figure 7) than in any other direction. The Appendix shows that this is a consequence of both the angular factors and the strong power dependence on the internuclear distances.

5.2. Energy defect compensation

In the present experiments the temperature is low enough for there to be negligible back-transfer to the donor. We are therefore concerned with processes which lead to a net creation of thermal energy in the lattice; several mechanisms have been proposed [7]. The simplest involves the emission of a single phonon, of wavevector $\mathbf{k}$ and polarization $j$, whose energy $E = h\omega_{\mathbf{k},j}$ is equal to the energy defect $E_1 - E_2$. The rate is given by [14]

$$W = \frac{(2\pi\hbar^2)}{(h^2)} J^2 \omega_{\mathbf{k},j}^{-2} \sum_{i,j} \left[ \sum_{q_{\mathbf{k},m}} M_{11}(\Gamma_{q,m}) \langle n_{\mathbf{k}} + 1 | \psi_{\Gamma_{q,m}} \rangle \langle \psi_{\Gamma_{q,m}} | n_{\mathbf{k}} \rangle ight]$$

$$- \sum_{q,\mathbf{m}'} M_{22}(\Gamma_{q',m'}) \langle n_{\mathbf{k}} + 1 | \psi_{\Gamma_{q,m'}} \rangle \langle \psi_{\Gamma_{q,m'}} | n_{\mathbf{k}} \rangle \exp \left( i\mathbf{\Delta k} \cdot \mathbf{R}_{12} \right) \delta(\omega_1 - \omega_2 - \omega_{\mathbf{k},j}),$$

where $J$ is the multipole–multipole coupling energy, $\mathbf{R}_{12}$ is the ion–ion separation, $M_{11}(\Gamma_{q,m})$ is the difference in the orbit–lattice interaction energy in the electronic excited and ground states, transforming as the $m^{th}$ component of the $\Gamma_q$ representation of the point group at the $i^{th}$ ion site, and $\langle n_{\mathbf{k}} + 1 | \psi_{\Gamma_{q,m}} \rangle \langle \psi_{\Gamma_{q,m}} | n_{\mathbf{k}} \rangle$ is the strain associated with the same component, arising from a change in the phonon number of wave-vector $\mathbf{k}$ by one unit. Since every site in Cs$_2$UO$_2$Cl$_4$ is translationally equivalent and the difference between sites 1 and 2 is only in an isotopic substitution (in an atom well decoupled from lattice phonons) it is an excellent approximation to set $M_{11}(\Gamma_{q,m}) = M_{22}(\Gamma_{q',m'})$ and

$$\langle n_{\mathbf{k}} + 1 | \psi_{\Gamma_{q,m}} \rangle \langle \psi_{\Gamma_{q,m}} | n_{\mathbf{k}} \rangle = \langle n_{\mathbf{k}} + 1 | \psi_{\Gamma_{q,m'}} \rangle \langle \psi_{\Gamma_{q,m'}} | n_{\mathbf{k}} \rangle.$$

For the very low frequency, 10 cm$^{-1}$, phonons, assuming a speed of sound of $2 \times 10^8$ m s$^{-1}$, the phonon wavelength is about 70 Å or twelve lattice spacings. The argument of the exponential in equation (6) is therefore small and we find

$$W = \frac{(2\pi\hbar^2)}{(h^2)} J^2 \omega_{\mathbf{k},j}^{-2} \sum_{i,j} \left[ \sum_{q_{\mathbf{k},m}} M_{11}(\Gamma_{q,m}) \langle n_{\mathbf{k}} + 1 | \psi_{\Gamma_{q,m}} \rangle \langle \psi_{\Gamma_{q,m}} | n_{\mathbf{k}} \rangle \right]$$

$$\times \mathbf{\Delta k} \cdot \mathbf{R}_{12} \delta(\omega_1 - \omega_2 - \omega_{\mathbf{k},j}).$$

We follow the usual approximate procedure in assuming that strain matrix elements can be evaluated by a harmonic oscillator model which does not distinguish between the mass of the vibrating atoms [20], and that the summation over $\sum_{\mathbf{k},j}$ can be replaced by an integral over the density of phonon states derived
from the Debye model, and obtain

$$ W = \left( \frac{2\pi}{\hbar^2} \right) \frac{\omega_p}{J^2} \frac{\hbar}{\rho} \left( \frac{1}{v_L^5} + \frac{2}{v_L^5} \right) |M_{11}(\Gamma_{q,m}) \cdot \Delta k \cdot R_{12}|^2 \left[ n_k + 1 \right]. \quad (8) $$

The meaning of equation (8) is that the rate is proportional to the probability of creating a phonon of frequency $\omega_p$, whose amplitude is sufficiently different at the donor and acceptor sites, that the resultant difference in strain energies at the two sites can bring the electronic excited states into resonance with one another. The rate then depends on the phonon-frequency on two grounds: (a) linearly on account of the density of states, (b) as the square through the increase in the phonon amplitude difference at the two sites as the wavelength shortens. Equation (8) therefore predicts that in the low temperature limit ($n_k = 0$) the rate is proportional to the cube of the energy defect. Transfer from $\text{U}^{180} \text{O}^{180} \text{O}^{2+}$ creates a phonon of exactly half the frequency of that created by the transfer from $\text{U}^{180} \text{O}^{2+}$ so that the transfer in the latter case should be eight times faster. Experimental values at 0 K can be extrapolated from six measurements between 4.2 K and 1.1 K, over which range the temperature dependence is small (see figure 6). The results are $W(\text{U}^{180} \text{O}^{2+} \rightarrow \text{U}^{180} \text{O}^{2+}) = 9.5 \pm 0.3 \times 10^4 \text{ s}^{-1}$ and $W(\text{U}^{180} \text{O}^{180} \text{O}^{2+} \rightarrow \text{U}^{180} \text{O}^{2+}) = 1.2 \pm 0.1 \times 10^4 \text{ s}^{-1}$. Their ratio is in excellent agreement with the theory, providing strong support for this mechanism.

It is also possible from equation (8) to make an estimate of the absolute transfer rate within the limitations of this model. The principal difficulty lies in the assessment of the quantity $M_{11}(\Gamma_{q,m})$, which represents the difference between the excited state and the ground state orbit-lattice interaction energies. The only guide we have to these energies is that, where they are experimentally accessible through strain measurements, they are comparable with crystal field splitting parameters [21]. For transition metal ions a reasonable value would be 10 000 cm$^{-1}$, for the lanthanides 100 cm$^{-1}$ and for the actinides 1000 cm$^{-1}$. It is probable that the principal perturbation of these low-frequency phonons occurs, in the present case, through the interaction of the $f$ electrons with the four equatorially coordinated chloride ions. The parameter which measures the angular part of this interaction is $<f^2|V_{oe}|f^{-2}> = 655 \text{ cm}^{-1}$ [9] and with this as a guide we adopt $M_{11} = 1000 \text{ cm}^{-1}$. For a 10 cm$^{-1}$ phonon we take $\Delta k \cdot R_{12} \approx 1/3$. Using $v_L = 2 \times 10^3 \text{ m s}^{-1}$, $\rho = 4.26 \times 10^3 \text{ kg m}^{-3}$ and $J = 0.256 \text{ cm}^{-1}$ and ignoring $v_L > v_p$, equation (8) gives $W_{12} = 1.1 \times 10^4 \text{ s}^{-1}$. There are two neighbours related to the donor ion as are the pair of ions 1 and 2. Table 1 implies that this type of interaction dominates the rate, so that we might anticipate a measured rate of transfer of $2.2 \times 10^4 \text{ s}^{-1}$. This rate is in good agreement with the observed value of $9.5 \times 10^4 \text{ s}^{-1}$.

Before the significance of this calculation is accepted it is best to look at the sources of uncertainty. First, no effective field approximation has been made in deriving the electric–quadrupole transition moment and from it the transfer integral. Adopting the Lorentz approximation $|\hat{N}_{xx}|^2$ would be reduced by the factor $9/n(n^2+2)^2$. With $n = 1.5$ the transfer integral would be reduced by a factor of three giving a ninefold reduction in transfer rate. Similarly, because the transition moments occur as the fourth power in the transfer rate, the sources of uncertainty in the procedure used for the estimation of $\hat{N}_{xx}$ can easily produce an order of magnitude change in the calculated rate. The estimate of $M_{11}$ is probably correct within a factor of 3, but such a factor would also create a ninefold
change in the rate. The other major area of difficulty is that \( v_l \) is unknown. We have taken the value of \( v_l \) by analogy with the values for NaCl, RbCl, TlCl for which \( v_l = 2.6, 1.66, 1.15 \text{ kms}^{-1} \) respectively. An order of magnitude decrease in the rate would result if \( v_l \) were taken as \( 3 \times 10^3 \text{ ms}^{-1} \). With these reservations it nevertheless seems probable from the success of the calculation that the quadrupole–quadrupole interaction is the source of the inter-ion coupling.

Figure 6 shows that the temperature dependence of the transfer rate is not well described by the phonon occupation number, or Bose–Einstein factor, \( n_k = 1/\left[ \exp \left( \frac{\hbar \omega}{kT} \right) - 1 \right] \) appearing in equation (8), which predicts a relatively small sensitivity to temperature. Above 6 K there appears to be an auxiliary mechanism with a stronger temperature dependence. Orbach describes two types of two-phonon assisted energy transfer [7]. Both may be viewed as Raman processes in that the energy defect is found from the difference in energy of two phonons [20]. In the two-phonon first-order process the phonons are absorbed and emitted at the same centre. At low temperatures such a process has a \( T^7 \) temperature dependence and varies inversely as the square of the energy defect [7]. The process is actually equivalent to the increase in the spectral overlap associated with the phonon-broadening of the homogeneous linewidth. In the one-phonon second-order process [7] the phonons are absorbed and emitted at different centres. The rate is effectively independent of the energy defect and varies as \( T^3 \) at low temperatures. Both these processes require the elimination of a phonon and approach zero rate at very low temperatures. Our experiments clearly converge on a non-zero limiting rate consistent with the one-phonon process. When the one-phonon rate is slow there is some evidence in the temperature dependence that the one-phonon second-order process starts to become important at higher temperatures. Figure 6 shows the composite of a Bose-factor and a \( T^3 \) dependence. The data in this figure fit the composite model well but it is not possible at present to explain the greater sensitivity of the species with the small energy defect which leads to a relative inversion of the transfer rates at temperatures above 12 K. At higher temperatures the data used in figure 6 represent initial rates prior to the onset of back-transfer.

5.3. Comparison with other systems

Because of the absence of suitable isotope shifts most previous workers have used the technique of fluorescent line-narrowing to study the transfer of energy between the components of an inhomogeneously broadened line [22, 23]. By definition spectral transport occurs between sites which differ in their strain energy, so that the simplification that \( M_{11}(\Gamma_{\alpha,m}) = M_{22}(\Gamma_{\alpha,m}) \) used in this work cannot be applied. The essential feature of the oxygen-isotope substitution is that the electronic strain energy associated with the substitution is not reflected in the lattice phonons which predominantly involve the displacement of chloride ions with respect to the cations. In effect we are assuming that the covalently-bonded UO\(_2^{2+}\) ion acts as a single rigid oscillator with respect to the elastic waves of the lattice. The decoupling is a consequence of the difference between the uranium-oxygen stretching frequencies which are near 900 cm\(^{-1}\) and which dominate the isotope shift, and the lattice modes which have frequencies below 100 cm\(^{-1}\). The merit of this approach is that the relative transfer rates at
different energy defects are then only a reflection of the phonon wavelength and
the density of phonon states.

It is striking that fluorescence line-narrowing experiments generally show
evidence for the one-phonon second-order process, at least for inhomogeneous
lines of approximately 1 cm\(^{-1}\) in width [22]. On the other hand, in pure PrF\(_3\) the
transfer-rate between minority sites separated by 32 cm\(^{-1}\) shows the temperature
dependence of a direct one-phonon emission. The results of the present work
show clearly how the rate of the direct process falls off sharply with the decreasing
energy defect, until at liquid helium temperatures and small defects two-phonon
processes can dominate. The sharp temperature dependence of the latter
processes implies that they can be dominant at higher temperatures, whereas only
the direct emission will be possible at the lowest temperatures. Localization of
the excitation within an inhomogeneously broadened line, at the lowest tempera-
tures, may well be complete unless the nature of the strain inhomogeneity is such
as to permit overlap between the homogeneous linewidths of neighbouring ions.

In summary, we have shown that the energy-transfer from isotopic anti-traps
in Cs\(_2\)UO\(_2\)Cl\(_4\) occurs by the one-phonon direct process at temperatures below
5 K. The transfer rates are in good agreement with those calculated by a
quadrupole–quadrupole coupling mechanism. These rates are the equivalent
of the trapping step in the transfer to isotopic traps. The theory of the coupling
suggests that the transfer integral is highly anisotropic.

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APPENDIX

(a) Definition of axes

The axes are unconventional. They are consistent with those of [4] where \(y\)
is coincident with the crystallographic \(b\) axis and \(z\) is coincident with the UO\(_2^{2+}\)
axis. The polar angle, \(\theta\), is defined with respect to \(y\) and the azimuthal angle, \(\phi\),
with respect to \(z\).

(b) The electric quadrupole–quadrupole interaction

The interaction energy can be computed by evaluating the field gradient of
the relevant tensor components at a general point \(P(R, \theta, \phi)\). The results, for
the angular factor, \(\alpha\), in the energy are

\[
\begin{align*}
\alpha_{xx,xx} &= \frac{3}{4} \left( 1 - 5 \sin^2 \theta + \frac{35}{4} \sin^4 \theta \sin^2 2\phi \right), \\
\alpha_{yz,yz} &= \frac{3}{4} \left( 1 - 5 \left( \sin^2 \theta \cos^2 \phi + \cos^2 \theta \right) + \frac{35}{4} \cos^2 \phi \sin^4 \theta \right), \\
\alpha_{xx,yz} &= \frac{1}{4} \left( \sin \theta \cos \theta \sin \phi \left( 7 \sin^2 \theta \cos^2 \phi - 1 \right) \right), \\
\alpha_{xy,xy} &= \frac{3}{4} \left( 1 - 5 \left( \cos^2 \theta + \sin^2 \theta \sin^2 \phi \right) + \frac{35}{4} \sin^2 \theta \phi \sin^2 2\phi \right).
\end{align*}
\]

Using the coordinates of the various pairs of atoms shown in figure 7, the follow-
ing angular factors are obtained.
The angular factor \( \alpha = 3 \cos^2 \psi - 1 \) is determined by the angle, \( \psi \), made by the line joining the two atoms with the direction of the relevant transition moment. The results are

\[
\begin{array}{cccc}
\text{Atom pair} & \psi(x, x) & \psi(y, y) & \alpha_x, x & \alpha_y, y \\
1-2 & 39.4^\circ & 90^\circ & 0.79 & 2 \\
1-3 & 129.4^\circ & 57^\circ & 0.21 & -0.11 \\
1-4 & 90^\circ & 0^\circ & 2 & -1 \\
2-3 & 90^\circ & 63^\circ & 2 & -0.38 \\
\end{array}
\]

References