The temperature dependence of the fluorescence intensity and a nonradiative de-excitation process in sodium cryptand sodide

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Abstract. To account for the strong temperature dependence of the photoluminescence intensity from sodium cryptand sodide, we introduce a spatially extended excitonic state into which exciton–polaritons can be scattered. The relevancy of such a state is discussed. By considering the exciton–polariton transport equation which includes the annihilation process for exciton–polaritons, we derive the dependence of the fluorescence intensity on temperature. It is shown that the annihilation process is completed very early during the time evolution of the exciton–polaritons, which is consistent with the experimental observation. The nonradiative transition of the spatially extended state is described in terms of a spherically symmetric lattice relaxation induced by the diffuse wavefunction of the spatially extended state. Continuum elasticity theory and variational principles are combined in an effort to find the electron–lattice coupling that is responsible for a polaron state in sodium cryptand sodide. Bartram and Stoneham's criterion is employed in establishing the maximum allowable speed of sound in sodium cryptand sodide.

1. Introduction

Optical and electrical properties of alkalides have been investigated by absorption measurements [1, 2], photoluminescence experiments [3, 4, 5], and by conductivity measurements [6]. The alkalide films whose anions are Na^-, K^-, Rb^-, and Cs^- have shown broad absorption spectra [1, 2]. Many alkalides including $Na^+(C222)Na^-$, $Rb^+(15C5)_2Na^-$, $K^+(15C5)_2Na^-$, $K^+(15C5)_2K^-$, and $K^+(HMHCY)Na^-$ have yielded fluorescence with lifetimes of the order of a few ns at low temperature [4]. In $Na^+(C222)Na^-$ (sodium cryptand sodide), C222 represents the bicyclic polyether, cryptand [2.2.2] [1]. The unusual anion state of Na^- is stabilized by confining the sodium positive ion in the cage structure of the multi-atomic cryptand molecule C222, which prevents the Na^+ and Na^- ions from forming sodium metal. The cryptands shield the enclosed cations from the anions. In other alkalides, $(15C5)_2$ and HMHCY are also the complexants that stabilize the ionic structures. 15C5 and HMHCY represent a crown ether 15-crown-5 and hexamethyl hexacyclen, respectively [1].

Since $Na^+(C222)Na^-$ has the strongest photoluminescence and is the most stable among all the alkalides, it has been investigated extensively. Bannwart *et al* [3] showed that the time-integrated fluorescence from sodium cryptand sodide has a peak at 1.84 eV at a nominal temperature of 7 K with an excitation photon energy of 2.1 eV. The photoluminescence from $Na^+(C222)Na^-$ was attributed to the 3p $\rightarrow$ 3s bound–bound transition of Na^-. Conductivity measurements have revealed that sodium cryptand sodide behaves as an

intrinsic semiconductor with a band gap of about 2.5 eV [6]. It was also shown by time-resolved photoluminescence experiments that the lineshape of the fluorescence is red-shifting with time [3, 5]. In addition to this, the optical excitation was observed to be spatially migrating and the fluorescence lineshape was dependent on crystal size [5]. In [5] all of those observations were consistently explained in terms of an exciton–polariton (EP) [7, 8] picture. In this case the 3p state of the Na$^-$ constitutes an excitonic state which couples with a photon to form the EP state.

It was also experimentally observed that while the fluorescence intensity decreases drastically with increasing temperature [3], the lifetime of the spectrally integrated fluorescence (or the time evolution of the lineshape peak) was independent of temperature [9]. The purpose of this paper is to explain this thermal behaviour of the fluorescence. We also propose that while the EP state that arises from the coupling of the exciton and the photon is responsible for the fluorescence in sodium cryptand sodide, a polaron state arising from the strong coupling of the electron in a spatially extended state and the spherically symmetric lattice deformation is necessary in quenching the photoluminescence.

In section 2, we introduce a spatially extended state and discuss the relevancy of its presence in sodium cryptand sodide. The scattering of the EP into the spatially extended state is considered. The transition rate is also calculated. In section 3, we derive the relationship between the fluorescence intensity and the temperature and compare that with the experiment. In section 4, the nonradiative de-excitation process by which the spatially extended state makes a transition into the ground state is described. The lattice deformation induced by the spatially extended state is considered.

2. The rate of transition of exciton–polaritons into spatially extended states

The wavefunction of the sodide anion's 3p state is presumably confined within the octahedron of radius 2.5 Å formed by six surrounding cryptated sodium cations. This 3p state constitutes an excitonic state which couples with the photons to form the EP state. To understand the thermal quenching of the EPs, let us first introduce another excitonic state whose wavefunction is more extended than that of the 3p state. Unlike the localized 3p state, such a spatially extended state (SES) may have a wavefunction that extends significantly beyond the octahedron mentioned above.

The density of the SES produced by the EPs in the low-laser-excitation limit is small. Thus it is appropriate to assume that the interaction between adjacent SESs is not large. We also assume a negligible interaction between the SES and the ground states of the adjacent sites, so the SES does not propagate. We simply regard the SES as having a stationary hydrogen-like wavefunction that does not belong to a band state. As we shall see in section 4, the SES also provides a suitable mechanism for the nonradiative transition of the EPs: the reduced amount of negative charge inside the octahedron induces relaxation of the lattice in a breathing mode, and the SES de-excites nonradiatively via this lattice deformation. Also note that the coupling strength of the exciton and the photon depends on the dipole matrix element between the ground state and the excitonic state [8]. Since the SES has a spherically symmetric wavefunction, it is obvious that it will not couple with the photon to form another EP state. Thus if the EP makes a transition into the SES then it will de-excite nonradiatively and there will be a reduction in the intensity of the photoluminescence. This behaviour will provide an adequate basis for explaining the thermal dependence of the photoluminescence. (To be consistent with experimental observations, the transition to the SES should be finished very early. See the discussion in section 3.) In this section we first calculate the matrix element between the EP state and the SES. The SES $|n\rangle$ centred at site

R_n is written as

$$|n\rangle = \sum_m D(m)a_{2n+m}^+ a_{1n} |n_0\rangle = \sum_m D(m)a_{2n+m}^+ a_{0n} |o\rangle \tag{1}$$

where m denotes the site R_m, $D(m)$ is the distribution function of the electron–hole internal motion and satisfies

$$\sum_m D(m)D^*(m) = 1$$

to ensure that the normalization condition $\langle n| \, n\rangle = 1$ is satisfied, a_{1n} is the annihilation operator of a sodide anion's 3p electron at site R_n, a_{2n+m}^+ is the creation operator of an electron at site $R_n + R_m$, a_{0n} is the annihilation operator of a sodide anion's 3s electron at site R_n, $|n_0\rangle = a_{1n}^+ a_{0n} |o\rangle$ is the sodide anion's 3s3p excited state that is localized at site R_n, and $|o\rangle$ is the crystal ground state. In its ground state, Na$^-$ has two electrons in the 3s state.

For our purposes we can approximate the EP state with an excitonic state. This is possible because in the early stage of the time evolution of the EP, the lower-polariton-branch (LPB) EPs dominate over the upper-polariton-branch (UPB) EPs and the former have a negligible amount of the photon component (it will be shown in section 3 that the scattering from the EP to the SES is completed while the EP is exciton-like). (From now on, the EP means the exciton-like LPB polariton state.) Thus, for the EP state in the early time region, we have

$$|k_{i0}\rangle = \frac{1}{\sqrt{N}} \sum_m e^{ik_i \cdot m} |m_0\rangle = \frac{1}{\sqrt{N}} \sum_m e^{ik_i \cdot m} a_{1m}^+ a_{0m} |o\rangle \tag{2}$$

where N is the number of sites in the crystal.

The transition of the EP into the SES is caused by the scattering of the former by acoustic and optical phonons. For the optical phonon–electron interaction we use the Fröhlich interaction and for the acoustic phonon–electron interaction we use the deformation potential interaction [10]:

$$H_{E-L} = \sum_{J=LA,LO} \sum_{k,q} P^J(q)(b_q^J - b_{-q}^{J+})a_{2k+q}^+ a_{1k} \tag{3}$$

where b_q^{LO+} and b_q^{LA+} are the creation operators of a longitudinal optical (LO) phonon and a longitudinal acoustic (LA) phonon with wave vector q respectively, a_{ik} is the Bloch representation (Fourier transform) of a_{in}, $P^{LO}(q) = C^{LO}/q$, and $P^{LA}(q) = C^{LA}\sqrt{q}$ where

$$C^{LO} = i\left[\frac{2\pi\hbar\omega_{LO}e^2}{V}\left(\frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_0}\right)\right]^{1/2} \qquad C^{LA} = i\left(\frac{\hbar D_e^2}{2\rho\mu V}\right)^{1/2}.$$

Here, $\hbar\omega_{LO}$ ($\hbar\omega_{LA}$) is the energy of a LO (LA) phonon, V the crystal volume, e the electron charge, ε_∞ (ε_0) the optical (static) dielectric constant, D_e the electron deformation potential, ρ the density of the crystal, and μ the speed of sound.

The total transition rate with which the EPs are scattered into the SES centred at any site is then given by, using equations (1)–(3) after converting the Wannier representation into the Bloch representation,

$$W_{total} = \frac{2\pi}{\hbar} |D(0)|^2 |C^{LO}|^2 \sum_q \frac{1}{q^2} [n_{LO} \, \delta(E_S - \hbar\omega_{LO} - E)$$

$$+ (n_{LO} + 1) \, \delta(E_S + \hbar\omega_{LO} - E)]$$

$$+ \frac{2\pi}{\hbar} |D(0)|^2 |C^{LA}|^2 \sum_q q \, [n_{LA} \, \delta(E_S - \hbar\omega_{LA} - E)$$

$$+(n_{LA} + 1)\,\delta(E_S + \hbar\omega_{LA} - E)] \tag{4}$$

where n_{LO} and n_{LA} are the LO and LA phonon occupation numbers, respectively, E_S the energy of the SES, and E the EP energy. $|D(0)|^2$ is the probability that the electron in the SES will be found in the site (octahedral cavity) where it originally belonged in the ground state or in the 3p state before making the transition into the SES. In equation (4) the first and second terms in the parentheses describe the conservation of energy for the phonon absorption process and the phonon emission process respectively.

3. The temperature dependence of photoluminescence intensity

Let us consider the transport process of the (LPB) EPs. The LPB EPs are constantly scattered by phonons into themselves (intra-branch scattering) and into the UPB (inter-branch scattering). They undergo radiative decay when they reach the crystal-to-vacuum boundary and undergo nonradiative decay at defect sites. In addition to these decays they are scattered into the SES by phonons.

However, within our time-scale (a few ps) we need to consider only the intra-branch scattering and the transition into the SES. This is due to the fact that in the exciton-like dispersion region of the LPB the density of states of the UPB is negligible compared to that of the LPB and the radiative decay is also negligible (only the photon component of the polariton escapes from the crystal). The nonradiative decay at defect sites is also negligible within our time-scale. Since the experimentally measured lifetime of the fluorescence from the $Na^+(C222)Na^-$ is about 5 ns [3], the nonradiative decay rate is of the order of 10^8 s^{-1} or smaller. As will be discussed later, it takes a few ps before the EPs are scattered into the SES after they are produced by a laser pulse. Therefore, during that period the nonradiative decay at defect sites does not make a sizable contribution to reducing the number of EPs.

Let the population $\phi(E, t)$ be the number of the (LPB) EPs per unit energy interval at time t. Then, the transport equation relevant within our time-scale is

$$\frac{\partial}{\partial t}\phi(E, t) \cong -W_{total}\phi(E, t) + \int dE'\,\left[\phi(E', t)Z(E' \to E) - \phi(E, t)Z(E \to E')\right] \tag{5}$$

where the first term on the right-hand side represents the scattering into the SES and the second term represents the intra-branch scattering mentioned before. $Z(E' \to E)$ signifies the intra-branch scattering of the EP with energy E' into the one with energy E within the LPB by LA phonons via deformation potential interaction.

If we integrate equation (5) over entire energy span, then the second term vanishes (because the intra-branch scattering conserves the total number of EPs) and we obtain

$$\frac{d}{dt}\int dE\phi(E, t)$$

$$= -\frac{2\pi}{\hbar}\,|D(0)|^2\,\left|C^{LO}\right|^2\,S\left(\sum_q \frac{1}{q^2}\right)\left[n_{LO}\phi(E_-, t) + (n_{LO} + 1)\phi(E_+, t)\right]$$

$$-\frac{2\pi}{\hbar}\,|D(0)|^2\,\left|C^{LA}\right|^2\,\sum_q \{qn_{LA}(\hbar\mu q)\phi(E_S - \hbar\mu q, t)$$

$$+q\left[n_{LA}(\hbar\mu q) + 1\right]\phi(E_S + \hbar\mu q, t)\} \tag{6}$$

where the LO phonon energy was assumed to be dispersionless, S is the number of LO phonon branches, $E_- = E_S - \hbar\omega_{LO}$, and $E_+ = E_S + \hbar\omega_{LO}$. Note that, because of energy conservation, the scattering of the EPs into the SES occurs only in a limited region of the dispersion curve (see figure 1).

Figure 1 shows the dispersion curves of the EP schematically. It also describes the energy relaxation process of the EPs and the scattering of them into the SES. The thick line segment between E_+ and E_- denotes the region where the EP can be scattered into the SES. The bell-shaped curves schematically represent the EP population $\phi(E, t)$. When the EPs are produced by a laser pulse initially, their energy is greater than E_+. The energy of the EP begins to decrease gradually along the LPB dispersion curve due to the intra-branch scattering by LA phonons (see the discussion later). When its energy reaches E_+ at t_+, it is also scattered into the SES and it continues to be scattered into the SES until it reaches E_- at t_-. As a consequence, the number of EPs is reduced when its energy is lowered below E_-. Since the number of phonons available for the scattering of the EP into the SES increases with temperature the fluorescence intensity decreases at higher temperatures.
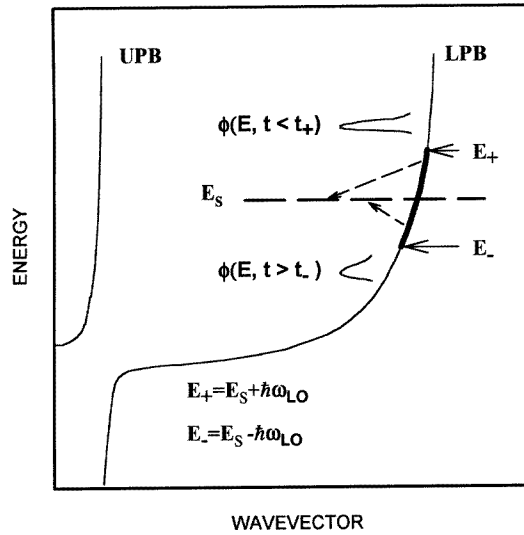

Figure 1. A schematic representation of the EP evolution. The energy of the EP decreases along the LPB dispersion curve due to the intra-branch scattering by phonons. E_S denotes the energy of the SES and the scattering of the EP into the SES occurs between E_+ and E_-, by energy conservation. Bell-shaped curves represent schematically the EP population. The scattering of the EPs into the SES makes the population reduce when the energy is lowered below E_-.

To solve equation (6) approximately, we assume that the annihilation of the EPs by the LO and LA phonons does not affect the energy relaxation process of the EP population along the LPB dispersion curve and we note that the intra-branch scattering lowers the energy of the EPs on average (see figure 1). Let us consider the annihilation of the EPs by LO phonon emission processes. For convenience, we assume that the LO phonon has a narrow band width Δ. Let us assume that the energy of an EP population of unit width is lowered from just above E_+ to just below E_+ by the intra-branch scattering. Then the rate equation involving just this LO phonon emission process is obtained by using equation (6):

$$\frac{\partial}{\partial t}\phi(E_+, t) = -\frac{1}{\Delta}\left[\frac{2\pi}{\hbar}|D(0)|^2|C^{LO}|^2 S\left(\sum_q \frac{1}{q^2}\right)(n_{LO} + 1)\right]\phi(E_+, t). \tag{7}$$

Let the energy relaxation speed at energy E be $\eta(E)$ (for the expression for $\eta(E)$, see the discussion below equation (11)). Then the time required for the EP to transit this band width Δ is $\Delta/\eta(E_+)$. Thus the EP population at just below E_+ is obtained by integrating

equation (7) for the time duration $\Delta/\eta(E_+)$:

$$\phi\left(E_+^<, t_0 + \frac{\Delta}{\eta(E_+)}\right)$$

$$= \phi(E_+^>, t_0) \exp\left\{-\frac{1}{\Delta}\left[\frac{2\pi}{\hbar}|D(0)|^2 |C^{LO}|^2 S\left(\sum_q \frac{1}{q^2}\right)(n_{LO}+1)\right]\frac{\Delta}{\eta(E_+)}\right\} \tag{8}$$

where $E_+^<$ and $E_+^>$ are the energies just below E_+ and just above E_+ respectively. Thus we see that after the scattering by the LO phonon emission process the total number of EPs is reduced by a factor

$$\exp\left\{-\left[\frac{2\pi}{\hbar}|D(0)|^2 |C^{LO}|^2 S\left(\sum_q \frac{1}{q^2}\right)(n_{LO}+1)\right]\frac{1}{\eta(E_+)}\right\}.$$

Similar calculations can be done with LO phonon absorption, LA phonon absorption and LA phonon emission processes. Therefore, one has as the total number $\bar{N}$ of polaritons in the LPB, when all of them have energies sufficiently lower than E_-,

$$\bar{N} = \bar{N}_0 \exp\left\{-A\int_0^{E_D} du\, u^3 \left[\frac{n_{LA}(u)}{\eta(E_S-u)} + \frac{(n_{LA}(u)+1)}{\eta(E_S+u)}\right] - B\left[\frac{n_{LO}}{\eta(E_-)} + \frac{(n_{LO}+1)}{\eta(E_+)}\right]\right\} \tag{9}$$

where $\bar{N}_0$ is the total number of polaritons at $t = 0$, A and B are defined by

$$A = |D(0)|^2 D_e^2/2\pi\hbar^4\rho\mu^5 \qquad B = 2\omega_{LO}e^2(\varepsilon_\infty^{-1} - \varepsilon_0^{-1})Sk_D|D(0)|^2$$

and also $E_D = \hbar\mu k_D$ where k_D is the radius of a sphere whose volume is equal to that of the Brillouin zone, $k_D = (6\pi^2 N/V)^{1/3}$. The summations over q in equation (6) were replaced with integrations in equation (9) the usual way. The spectrally and temporally integrated intensity I of the fluorescence from $Na^+(C222)Na^-$ is proportional to $\bar{N}$. Rewriting equation (9), one obtains, as the relationship between the fluorescence intensity I and the temperature T [11],

$$\ln(I) \cong -K_1 T^4 \int_0^{E_D/(k_B T)} du\, \frac{u^3}{e^u - 1} - \frac{K_2}{\exp(\hbar\omega_{LO}/k_B T) - 1} + \text{constant} \tag{10}$$

where k_B is the Boltzmann constant and

$$K_1 = \frac{2A}{\eta(E_S)} \qquad K_2 = B\left[\frac{1}{\eta(E_-)} + \frac{1}{\eta(E_+)}\right]$$

are temperature-independent quantities. In equation (10), a Bose distribution of the phonons was used, and η was taken outside the integral since its energy dependence is much slower than that of the other terms in the integrand. Equation (10) gives an excellent fit to the experimental fluorescence intensity data in [3] with the parameter values $K_1 = 6.34 \times 10^{-6}$, $K_2 = 4.71$, $\mu = 4.44 \times 10^4$ cm s^{-1} (for the choice of this speed of sound, see section 4) and $\hbar\omega_{LO} = 4.3$ meV. The value of the ratio K_1/K_2 gives a reasonable magnitude in this case.

Let us summarize the experimental observation with fluorescence from sodium cryptand sodide. At a fixed temperature, the fluorescence linewidth is nearly constant (increases very slowly) over time after about 1 ns. However, the lineshape is red-shifting with time and the decay of the spectrally integrated fluorescence can be expressed in terms of a mono-exponential decay. In that case it is easy to see that the fluorescence decay at a

fixed wavelength can be approximated well by a bi-exponential function containing two lifetimes. As was mentioned previously, the intra-branch scattering of the LPB EPs by acoustic phonons makes the fluorescence red-shift with time, making the bi-exponential fitting an adequate choice.

We found experimentally that at a fixed wavelength the fluorescence from sodium cryptand sodide decays faster at a higher temperature [9]. (As a result of more frequent scattering by acoustic phonons at a higher temperature, the fluorescence broadens and red-shifts. It can be seen that this red-shift of the fluorescence at a higher temperature is responsible for the faster decay.) However, when the temperature-dependent fluorescence is fitted with the bi-exponential decay we find that (1) the longer lifetime is temperature independent (and also nearly wavelength independent); it was also observed that (2) the time evolution of the spectrally integrated fluorescence is independent of temperature [9]. It is easily seen that the two observations (1) and (2) above are equivalent to each other.

Note that this means that, although the fluorescence intensity decreases with temperature, the observed lifetime of the spectrally integrated fluorescence is independent of temperature. The radiative decay of the EP occurs at the surface of the crystal via the photon component of the EP and is independent of temperature. The nonradiative decay which occurs at the defect sites via the exciton component of the EP is also independent of temperature (if it were temperature dependent, then the lifetime of the spectrally integrated fluorescence would be also temperature dependent). The only major temperature-dependent factor is the process of annihilation of the EPs by phonons. Thus we require that the transitions of the EPs to the SES do not affect the (apparent) decay rate of the EPs, although the transition reduces the number of fluorescing EPs with increasing temperature.

Considering that the longer lifetime of the photoluminescence is about 5 ns, this observation states that the transition to the SES is completed very early (earlier than the resolution time of the detection apparatus). Otherwise, the apparent decay of the spectrally integrated fluorescence will be accelerated as the temperature increases. (For example, let us assume that the lifetime of the photoluminescence is 5 ns at 20 K. If the rate of transition to the SES increases from $(1 \text{ ns})^{-1}$ at 20 K to $(5 \text{ ns})^{-1}$ at 50 K then the decay rate of the photoluminescence will also increase with temperature. However, if the rate of transition to the SES increases from $(1 \text{ ps})^{-1}$ at 20 K to $(5 \text{ ps})^{-1}$ at 50 K *and* the transition is completed within 10 ps after the EPs are produced, then the decay rate after 10 ps will be independent of temperature although the photoluminescence intensity is reduced with increasing temperature.)

Therefore to check the consistency, let us estimate the time t_- at which an average EP relaxes to the energy E_- after it is produced by a laser pulse (see figure 1). It is mainly determined by the intra-branch scattering process. When the LPB EPs are scattered by LA phonons they either lose energy by phonon emission or gain energy by phonon absorption. Therefore, the energy distribution of the EPs becomes wider as the number of the scatterings increases. On average, the LPB EPs lose energy after being scattered by a phonon since the transition probability for phonon emission is larger than that for absorption, the former being proportional to $n_{LA} + 1$ while the latter is proportional to n_{LA} where n_{LA} is the LA phonon occupation number. In short, the role played by the intra-branch scattering by the LA phonons is to broaden and red-shift the distribution of the EP population with time along the LPB dispersion curve.

For calculating t_- we use the deformation potential interaction for the intra-branch scattering of the (LPB) EPs and use the exciton-like dispersion relation $E(k) = E_0 + \hbar^2 k^2/2m^*$ for the energy of the EP where m^* is the effective exciton mass, $\boldsymbol{k}$ the wave vector of the EP, and E_0 the transverse exciton [12] minimum energy. (When the excited 3p states

of the sodium anions are perpendicular to the wave vector, they form the transverse exciton. Only transverse excitons couple with photons to form EPs.) By using the approximation of Tait and Weiher [13] we obtain, as the average energy relaxation rate $\langle \mathrm{d}E/\mathrm{d}t \rangle$ of the EPs,

$$\left\langle \frac{\mathrm{d}E}{\mathrm{d}t} \right\rangle = -\left(\frac{2\sqrt{2}D^2 m^{*5/2}}{\pi \hbar^4 \rho} \right)(E - E_0)^{3/2} \tag{11}$$

where D is the exciton deformation potential. In equation (5), the main effect of the term $-W_{total}\phi(E,t)$ is to reduce the number of EPs. Therefore, $\eta(E)$ in equation (9) can be approximated by the magnitude of the energy relaxation rate due to the intra-branch scattering: $\eta(E) \cong -\langle \mathrm{d}E/\mathrm{d}t \rangle$.

t_- is then obtained by integrating equation (11):

$$E_- = E_0 + \left(\frac{\sqrt{2}}{\pi \hbar^4} \frac{D^2 m^{*5/2}}{\rho} t_- + \frac{1}{\sqrt{\alpha - E_0}} \right)^{-2} \tag{12}$$

where α is the initial onset energy at which the EP begins to be scattered by the LA phonons. Among the various physical quantities appearing in equation (12), only the density of the $Na^+(C222)Na^-$ is known: $\rho = 1.064$ g cm^{-3}. However, with reasonable combinations of the parameter values, equation (12) yields good results. For example, with $\alpha = 2.1$ eV (laser excitation energy), $E_0 = 1.9$ eV, $E_- = 1.95$ eV, $D = 9$ eV, $m^* = 0.5$ electron masses, one obtains $t_- \cong 6$ ps, $\eta(E_-) \cong 9 \times 10^9$ eV s^{-1}. Also if we follow [5] the FWHM of the EP distribution at t_- is about 1.6 meV at 20 K . Therefore, nearly all the EP energies are lowered below E_- in about 6 ps after they are produced. Consequently the transition of the EPs into the SES is completed within about 6 ps, which is a much shorter time than the measured lifetime.

4. The nonradiative de-excitation process

In $Na^+(C222)Na^-$, the sodide anions are placed in octahedral cavities that are formed by six surrounding sodium cations [1, 14]. If an EP makes a transition to a SES, then the electron's wavefunction changes from the compact 3p state to a more diffuse state, described by $D(m)$ in equation (1). Thus, the amount of negative electronic charge inside the cavity is reduced by this transition. This results in a decrease of the attractive Coulomb interaction between the sodide anion and the surrounding lattices (positive ions), leading to a relaxation of the latter (figure 2). If the magnitude of the relaxation is sufficiently large, then nonradiative de-excitation from the SES to the sodide anion's ground state, the 3s state, will occur.

For simplicity, let us regard the octahedral cavity as a spherical one and assume that the six cations are placed at the same distance from the centre of the cavity. We also assume that the wavefunction of the SES is spherically symmetric. The 'positive' charge induced by the SES establishes an electric field that causes the cations and the anions to deviate from their normal configurations. Consider the effect of the electric field on a dipole consisting of the sodium cation and the sodide anion. This electric field will have the largest effect on the six dipoles surrounding the cavity. While the directions of the six dipoles are radial, the directions of other dipoles at larger distances from the cavity are less correlated. Thus, in evaluating the lattice deformation caused by the electric field, we neglect the force from dipoles other than the six surrounding the cavity.

The radii of the sodide anions and the cryptated sodium cations are about 2.5 Å and 4.5 Å respectively [1, 14]. The latter are in van der Waals contact, making octahedral cavities of sufficient size to allow the anions to fit snugly into them. Therefore we can assume that only the cryptated sodium cations are elastically connected with each other in the crystal
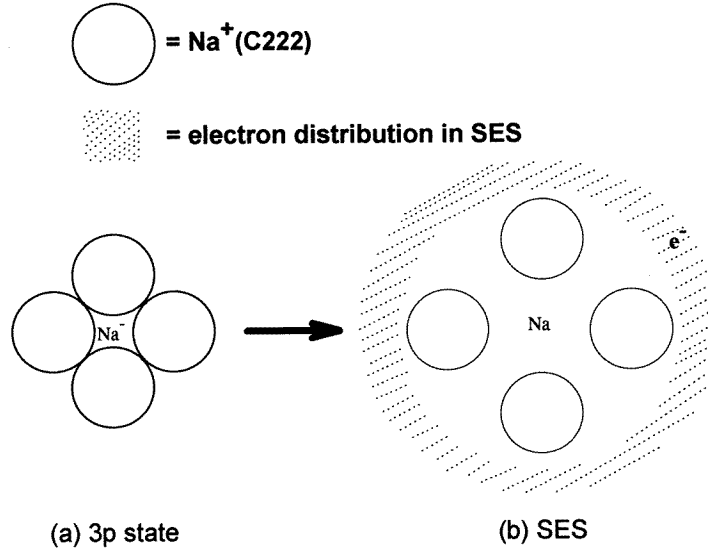
Figure 2. A schematic illustration of the lattice relaxation induced by the electronic transition from the compact 3p state to the diffuse SES. With the SES the reduced amount of negative charge inside the octahedron causes the attraction between negative and positive ions to decrease. This results in the relaxation of the lattice.

and the smaller anions contribute to the elastic property through the interaction with the cations. Thus the force on one of the six dipoles is acting at the position of the cation in the radial direction with a spherically symmetric electric field.

We suppose that all the cations and the anions move according to the continuum elasticity theory. The displacement of a cation at one site will make all other cations and anions displace also. In continuum approach, the kth component of the lattice displacement $u_k(\boldsymbol{r})$ at position $\boldsymbol{r}$ due to the force density distribution $\boldsymbol{f}(\boldsymbol{r})$ is described by [15, 16]

$$u_k(\boldsymbol{r}) = \int U_{km}(\boldsymbol{r} - \boldsymbol{r}') f_m(\boldsymbol{r}') \, \mathrm{d}^3 r' \tag{13}$$

where f_m is the mth component of the force density $\boldsymbol{f}$ and the Green's function U_{km} is defined by [16]

$$C_{ijkl} \frac{\partial^2}{\partial x_l \, \partial x_j} U_{km}(\boldsymbol{r}) + \delta_{im} \delta(\boldsymbol{r}) = 0. \tag{14}$$

$U_{km}(\boldsymbol{r})$ represents the displacement $u_k(\boldsymbol{r})$ at a point $\boldsymbol{r}$ arising from a point force at the origin in the x_m-direction and C_{ijkl} is elastic constant. For simplicity, we assume an isotropic case for sodium cryptand sodide. In this case the elastic constants C_{ijkl} reduce to two independent constants and are given by [16]

$$C_{ijkl} = \lambda \delta_{ij} \delta_{kl} + G(\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}). \tag{15}$$

For a spherically symmetric force density distribution $S(r)$ in an isotropic material, the lattice displacement is also spherically symmetric. Using equation (13) and the Green's function [16] in equation (14) which is solved by a Fourier transform method, we obtain

$$\boldsymbol{u}(r) = \frac{1}{3(\lambda + 2G)} \left[\frac{1}{r^2} \int_0^r \mathrm{d}r' \, S(r') r'^3 + r \int_r^\infty \mathrm{d}r' \, S(r') \right] \widehat{\boldsymbol{r}}_0 \tag{16}$$

where $\widehat{r}_0$ is the unit radial vector. Let the origin of the coordinate be the centre of the cavity and the radial force due to the induced electric field on one of the six dipoles be $F\widehat{r}_0$. Then in the continuum approximation the force density acting on the six dipoles whose sodium cations are located at radius $r = R$ is given by

$$f(r) = \frac{6F}{4\pi R^2}\,\delta(r - R)\widehat{r}_0. \tag{17}$$

From equations (16) and (17) we obtain the desired expression for the lattice relaxation $u^0(r)$ caused by the electronic transition to the SES,

$$u^0(r) = \frac{FR}{2\pi(\lambda + 2G)}\frac{1}{r^2}\widehat{r}_0 \qquad (R \leqslant r). \tag{18}$$

The total Hamiltonian H of the system consisting of an electron and the deformable lattice is written as

$$H = H_e + H_{lattice} + H_{int} \tag{19}$$

where H_e, $H_{lattice}$, and H_{int} represent the Hamiltonian of the electron, lattice, and the electron–lattice interaction respectively. The lattice Hamiltonian $H_{lattice}$ is composed of the lattice strain energy and kinetic energy. When expressed in terms of the normal coordinate S_{kl} it has the form

$$H_{lattice} = \sum_k \left[-\frac{\hbar^2}{2\rho V}\frac{\partial^2}{\partial S_{kl}^2} + \frac{1}{2}\rho V\omega_k^2 S_{kl}^2 \right]. \tag{20}$$

In a spherically symmetric lattice deformation only longitudinal acoustic phonons are involved. Thus in equation (20) S_{kl} represents the normal coordinate of the longitudinal lattice deformation with wave vector k and is defined by

$$u(r) = \sum_k -\mathrm{i}S_{kl}\widehat{\varepsilon}_{kl}\mathrm{e}^{\mathrm{i}k\cdot r} \tag{21}$$

where $\widehat{\varepsilon}_{kl}$ is the lattice polarization unit vector. From the dispersion relation

$$\rho\omega^2\varepsilon_{k\mu} = \sum_{\sigma\nu\tau}C_{\mu\sigma\nu\tau}k_\sigma k_\nu\varepsilon_{k\tau}$$

[17] we have, with the elastic constants defined by equation (15), the angular frequency ω_k of the longitudinal acoustic phonon with wave vector k as follows:

$$\omega_k = \sqrt{\frac{2G + \lambda}{\rho}}k. \tag{22}$$

To find the electron–lattice interaction Hamiltonian H_{int}, we use the variational principle and the result obtained in equation (18). Let

$$H_{int} = -\sum_k J_k S_{kl} \tag{23}$$

where J_k is the coupling constant to be determined and let us represent the total wavefunction Ψ by using Born–Oppenheimer approximation:

$$\Psi = \psi_e(r)\prod_k \phi_k(S_{kl}) \tag{24}$$

where ψ_e and ϕ_k are the electron and phonon wavefunctions respectively. Variation of $E = \langle\Psi|\,H\,|\Psi\rangle$ with respect to $\phi_k^*(S_{kl})$ gives

$$\left[-\frac{\hbar^2}{2\rho V}\frac{\partial^2}{\partial S_{kl}^2} + \frac{1}{2}\rho V\omega_k^2 S_{kl}^2 - J_k S_{kl} \right]\phi_k(S_{kl}) = \lambda_k\phi_k(S_{kl}) \tag{25}$$

which is an equation for a displaced oscillator with the equilibrium value at $S_{kl} = S_{kl}^0$ where

$$S_{kl}^0 = \frac{J_k}{\rho V \omega_k^2}. \tag{26}$$

Now S_{kl}^0 is determined by the Fourier transformation of $u^0(r)$ in equation (18). Since $\widehat{\varepsilon}_{ql} = \widehat{q}_0$ for longitudinal acoustic phonons, where $\widehat{q}_0$ is the unit vector in the direction of the wave vector q, we have

$$
\begin{aligned}
S_{kl}^0 &= \mathrm{i}\frac{1}{V} \int u^0 \cdot \widehat{q}_0 e^{-iq\cdot r} \, \mathrm{d}^3 r \\
&\cong -\frac{1}{V}\left(\frac{2FR}{\lambda + 2G}\right) \int_R^\infty \left(\frac{\cos qr}{qr} - \frac{\sin qr}{q^2 r^2}\right) \mathrm{d}r \\
&= \frac{1}{V}\left(\frac{2FR}{\lambda + 2G}\right)\frac{\sin qR}{q^2 R}.
\end{aligned}
\tag{27}
$$

Comparison of equation (26) with (27) gives the expression for J_k and the interaction energy I is given by

$$I = \langle \Psi| H_{int} |\Psi\rangle = -\rho V \sum_k \omega_k^2 S_{kl}^0 \langle \phi_k| S_{kl} |\phi_k\rangle. \tag{28}$$

When the lattice is completely relaxed, the oscillators are in their ground states and $\langle \phi_k| S_{kl} |\phi_k\rangle = S_{kl}^0$. Thus

$$I = -\rho V \sum_k \omega_k^2 (S_{kl}^0)^2 = -\frac{2\rho F^2 \mu^2}{\pi^2 (\lambda + 2G)^2}\left\{\frac{1}{2}k_D - \frac{1}{4R}\sin(2k_D R)\right\} \tag{29}$$

where μ is the speed of sound of the LA phonon, $\sqrt{(2G + \lambda)/\rho}$. In equation (29) the usual approximation was used in converting the summation over k to an integration.

Using equations (20), (25), (26), and (28) we see that the lattice energy L is given by

$$
\begin{aligned}
L &= \langle \Psi| H_{lattice} |\Psi\rangle \\
&= \sum_k \left[\hbar\omega_k\left(n_k + \frac{1}{2}\right) - \frac{J_k^2}{2\rho V \omega_k^2}\right] + \sum_k \langle \phi_k| J_k S_{kl} |\phi_k\rangle \\
&= \sum_k \frac{1}{2}\hbar\omega_k - \frac{1}{2}I
\end{aligned}
\tag{30}
$$

where we have also assumed that all the oscillators are in their ground states, $n_k = 0$. The total energy E of the system consisting of the electron and the deformable lattice is given by

$$E = K + I + L = K + \frac{1}{2}I + \sum_k \frac{1}{2}\hbar\omega_k \tag{31}$$

where K is the electronic energy $\langle \Psi| H_e |\Psi\rangle$.

Since the spatially extended state has a higher energy than the sodide anion's compact 3p state whose energy is about 1.9 eV with respect to the ground state, we expect that 1.9 eV $\leqslant K \leqslant$ 2.5 eV, where the upper bound energy 2.5 eV represents the continuum state, measured in a temperature-dependent conductivity experiment. The optical excitation was obtained with a laser pulse of 2.1 eV. Thus, it is reasonable to assume that most of the EPs have energies lower than 2.1 eV. The energy of the SES differ from that of the EP by at most the optical phonon energy. Therefore we estimate 1.9 eV $\leqslant K \leqslant$ 2.1 eV.

In an optical transition that involves a Franck–Condon transition [18], we can employ Bartram and Stoneham's criterion to determine whether the excited state de-excites

radiationlessly. For a mode with angular frequency ω the Bartram and Stoneham parameter Λ is defined as the ratio of the excited state's relaxation energy $S\hbar\omega$ to the optical absorption energy [19], where S is the Huang–Rhys factor. The parameter Λ determines the relative configuration of the ground and excited states. According to this criterion, an excited state makes a non-radiative transition if the parameter Λ is greater than 1/4 [19].

We assume that the elastic constants of the sodium cryptand sodide's excited state remain unchanged from their values in the ground state. It is also assumed that as a result of the compactness of both the ground and the sodide's 3p states the lattice is not relaxed when the electron is excited into the 3p state. In the present case, the 'absorption energy' in Bartram and Stoneham's parameter corresponds to the electronic energy K of the SES and the relaxation energy $S\hbar\omega$ corresponds to $|I/2|$ in equation (31) (see figure 3). Thus Bartram and Stoneham's parameter in this case becomes

$$\Lambda = \frac{|I|}{2K} \tag{32}$$

and we must have $\Lambda \geqslant \frac{1}{4}$, since the SES de-excites nonradiatively. (The relaxation energy can easily be several tenths of an eV [19].)
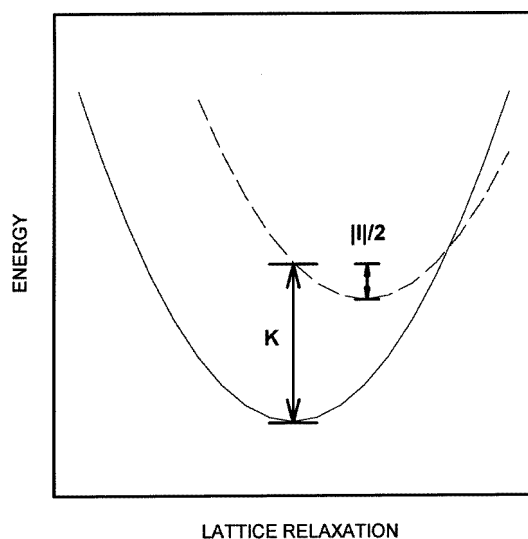

Figure 3. A configuration coordinate diagram showing the relationship between the ground state (lower curve) and the SES (upper curve). Although there is no absorption process in this diagram, the energy K of the SES relative to the ground state corresponds to the 'absorption energy' in a Franck–Condon transition. $|I/2|$ represents the relaxation energy.

To evaluate the parameter Λ, it is necessary to know about the wavefunction of the SES. At the present stage we do not have such information, but some estimation can be carried out. Let x be the probability that an electron in the SES is found in a sphere of radius $R = 7.06$ Å, and y be the probability that it is found in a spherical shell of inner radius R and outer radius $R + D$ where $D = 7.06$ Å is the cation–anion distance. Then the force $\boldsymbol{F}$ on a dipole consisting of the sodium cation at distance R and the sodide anion at $R + D$ from the origin is

$$\boldsymbol{F} = e^2 \left[\frac{1}{R^2}(1 - x) - \frac{1}{(R + D)^2}(1 - x - y) \right] \widehat{\boldsymbol{r}}_0. \tag{33}$$

Let us put $K = 2.0$ eV and $\lambda = G$. Then from equations (29), (32), and (33) we see that the speed of sound μ decreases when either y decreases or x increases. It is also a decreasing function of Λ. Therefore when $\Lambda = \frac{1}{4}$, the maximum of the speed of sound μ occurs at $y = 1$ and its value is 1.05×10^5 cm s^{-1}. Thus, we conclude that in sodium cryptand sodide the speed of sound is smaller than about 10^5 cm s^{-1}.

5. Summary

In this paper, the SES was introduced in order to explain the temperature dependence of the fluorescence intensity. The scattering of the EPs by the phonons causes the EPs to transit into the SES which does not form another exciton–polariton state. The number of EPs that make transitions into the SES depends on both the energy relaxation speed of the EPs on the LPB and the number of phonons which increases with temperature. Thus the decrease of the fluorescence intensity at a higher temperature is due to the increased scatterings of the EPs by phonons. The transition of the EPs into the SES is completed within a few ps, in agreement with the experiment.

We attempted to describe the nonradiative de-excitation process of the SES in terms of the spherically symmetric lattice relaxation induced by the diffuse wavefunction of the SES. The magnitude of the lattice relaxation was quantified by approximating the crystal as an elastic continuum. The variational principle and the continuum elasticity theory were combined to find the electron–lattice coupling that is responsible for the displacement of the lattice vibration. We see that the electron in the SES forms a polaron state with the coupling occurring between the electron and the longitudinal acoustic phonons. It is interesting to note that while the EP state arising from the coupling of the exciton and the photon is responsible for the photoluminescence in sodium cryptand sodide, the polaron state arising from the coupling of the electron and the phonon is responsible for quenching the photoluminescence. By applying Bartram and Stoneham's criterion to our case, we estimate that the speed of sound in sodium cryptand sodide should be less than about 10^5 cm s^{-1}.

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