Loosing Energy Mechanism of the Optically Excited *F* Centers in KCl

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Abstract

The loosing energy mechanism of the optically excited states (OES) of the *F* center in KCl has been investigated by the measurement of resonant secondary radiation (RSR) caused by its resonant excitation with either continuous wave (*cw*) or picosecond (*ps*) pulse laser. The sepctrum of the RSR intensity and its linear polarization are observed as a function of the wavenumber over the Stokes range. They are examined semi-classically and quantum mecahnically based on a realistic vibronic scheme. As a result, the de-excitation mechanism of the OES has been clarified from fitting analysis of the experimenal data, the lattice relaxation time, τ_l, of the OES are estimated to be in the order of 10^{-13} sec. From the time-resolved ps spectroscopy of RSR, a revised configuration coordinate scheme of de-exitaiton of the OES is proposd qualitatively.

1. Introduction

The color centers in alkali halide crystals are a typical model system for the study of defects in solids. Particularly, the *F* center has the simplest model structure amongst all other color centers. It consists of an electron trapped by an anion vacancy, that possesses attractive Coulomb potential [1]. So that it has very similar microscopic structure as a hydrogen atom. It is well known that the studies of the hydrogen atom have createed revolutionary development in the modern physics accompanied by establishment of quantum mechanics. Similarly, the studies of the *F* centers have played essentially important role in developing the physics of solids, particularly on defects in solids, since late in the last century when they were discovered.

In the present work, we describe mostly the loosing energy mechanism of the

footnote

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optically excited state (OES) of the F centers that is related closely to its optical pumping cycle. For this purpose, we should clarify the initial and final states for the lattice relaxation of the OES which are called the Franck and Condon state (FCS), and relaxed excited state (RES), respectively. In §2, we briefly chronicle the history of investigation of these two states as well as the ground state (GS) of the F center which have been done almost over a century. In § 3, we introduce a concept of resonant secondary radiation (RSR) of the F' center that is most advantageous to study the loosing energy processes of its OES[2]. Actually, the RSR occurs as a sequential series of optical processes: They are resonant Raman Scattering (RRS), hot luminescence (HL), and ordinary luminescence (OL) successively. We mention primary experimental works which had been tried by the other research groups early in the 70 s before our investigating of RSR. In § 4, we summarize our experimental works of RSR done by resonant excitation of the F centers with a continuous wave (*cw*) of Ar^+ ion laser and its cooperative dye laser. These are the first spectrum of RSR observed over the whole Stokes wavenumber (Ω) range covering from the optical absorption band to the OL band. Theoretical analysis to explain the RSR spectrum, that have been carried out by several groups in Japan, are briefly introduced. From the fitting analysis, the lattice relaxation time (τ_l) is estimated to be sub picosecond. In § 5, recent work on the time-resolved picosecond (*ps*) spectrosopy of the RSR of the F center is presented. To describe the de-excitation processes precisely, the adiabatic potential energy surfaces (APES) of the OES are plotted in the configuration coordinates. The dynamical level crossing processes that may occur in the Stokes range are also discussed. In § 6, conclusion is summarized.

2 . Historical overview of the study of the optical pumping cycle of the F center

We briefly review a history of the research of the GS, FCS, and RES of the F centers which have been done nearly over recent half century. These states appear successively during the optical pumping cycle of the F center.

In the decade of the 50 s, the GS of the F centers was investigated by means of the electron spin resonance (ESR) technique that had been developed then[3]. The work was extended to electron nuclear double resonance (ENDOR), with which the model of the F center proposed by de Boer was identified completely. Furthermore, models for several color centers proposed so far by many authors have been checked and refined.

In the decade of the 60 s, the Franck-Condon state (FCS) of the F center that is the final state for the optical absorption transition from the GS has been extensively investigated in the University of Illinois particularly by Henry, Schnatterly, and Slichter[4]. In fact, they clarified the structure of the FCS by analyzing the external perturbation effects on the absorption band of the F centers. Their method was abbreviated as HSS method that was adopted as a standard and general method to clarify the FCS as well as the optical absorption processes for all defects in condensed matters.

In the decade of the 70 s, the relaxed excited state (RES) of the F center that is the

initial state for emitting OL has been predominantly investigated[5]. The study has been started priory in 1962 by the discovery of unexpectedly long radiative lifetime (τ_r) for the F centers found firstly by Swank and Brown[6] and for the F_A centers by Spinolo and Brown[7]. In order to explain such an anomalously long τ_r , two different models were proposed . One is a large orbital $2p$-like wavefunction model[5], while another is a model proposed by Bogan and Fitchen in Cornell University early in the 70 s[8]. Actually, they carried out the precise analysis of Stark effect on the OL band of the F center. They proposed that the RES consists of $2s$ state admixed with a small fraction of energetically higher-lying $2p$ state through the electron-phonon interaction. The model is known as Bogan and Fitchen model. They showed that the RES can be described in terms of a few parameters. However, if carefully checking the validity of these fitting parameter values to experimental data, one could easily find that that were not reasonably well to describe the real structure of the RES[9-12]. The issue of a vibronic theory of the RES was highly required to improve and sophisticate Bogan and Fitchen model of the RES.

The vibronic scheme has been introduced by several theorists. Prior approach was carried out by Iida et al. in 1973[9]. Ham[10], Ham and Grevsmühl[13] formulated more rigorous type of vibronic scheme in 1974. Finally Kayanuma in Toyozawa school established it in 1976[11,14]. Parallel to this theoretical progress, the studies of external perturbation effects on the OL band of the F center had been carried out by several authors, for instance, Stark effect by us[12] that was complementary to ref, 8, uni-axial stress effect by Hetrick and Compton[15] which were refined by us[16], hydrostatic pressure effect by Asami et al.[17] and magnetic circular polarization by Baldacchini et al.[18] which was followed by us[19,20]. We have carried out the precise measurement of above-mentioned external perturbation effects using newly developed laser excitation technique then for at most eight different kinds of alkali halides, and tried to explain these experimental data consistently on the basis of the *realistic vibronic scheme* that was developed by Kayanuma[21].

As a result, by the end of the 70 s, we have achieved detailed information of both states of FCS and RES, that are the initial and final states for the loosing energy process of the OES of the F centers. This facilitates the detailed investigation of the problem of interest.

3 . Resonant secondary radiation (RSR) caused by the optically excited F centers

By the beginning of the decade of the 80 s, the investigation of the loosing energy (or de-excitation) mechanism of the OES of the F center was a sole problem left unexplored. De-exciation occurs in the Stokes wavenumber range (Ω)that covers from the FCS to the RES energetically. The process has been called nonradiative or radiationless process, since nobody except a few research group have ever observed the presence of the emitted light in this range of Ω so far. However, one may notice that the dipole transition matrix element connecting between the GS and OES still survives in the whole Stokes range. Thus, in principle, one may expect to observe the light intensity

emitted in this range. The observable light can be called HL because it woule be emitted from any levels in unthermalized OES during the de-excitation that would be characterized effectively by hot temperatures. This is our motivation to start the measurement of the HL in the Stokes range. However, the intensity of HL would be quite faint, because it is relevant to the ultra short time to stay at any levels in the OES of the F center even if it could survive dynamically. We expected to measure HL by means of a photon counting method, no matter how faint they were. The average of staying time duration is defined as the lattice relaxation time τ_l. This can be estimated from the curve fitting analysis of the HL spectrum over the whole Stokes range[2,22].

Theoretical argument of RSR, that occurs during the de-excitation process in the Stokes range, was introduced by Hizhnyakov and Tevher in 1976.[23] They postulated that successive occurrence of series of optical processes as RRS, HL, and OL can be described basically on the same physical origin in a concept of the second order radiation (luminescence). Later on, Toyozawa established a general theory of RSR in 1975[24]. Then, the RRS of the F center that had been already investigated, were unified into the RSR. Thus-developed theories of RSR belong to a category of a of a general theory. Usually, the general theory would not lead to explicit explanation of experimental data so that it would be somehow unrealistic. For the quantitative explanation of the loosing energy mechanism through the study of the RSR, *a realistic physical scheme* of the OES of the F center should be established. This theoretical improvement has been done by two theoretical groups in Japan: They are Muramatsu and Nasu[25], and Kayanuma[26]. Thus, the experimental data of the RSR obtained under *cw* excitation have been understood in a realistic vibronic scheme of the OES which includes the FCS and RES all together. Their theoretical works will be reviewed in the proceeding section.

In 1982, Mori et al. firstly reported the experimental data of HL (Ω), which were for instance plotted in Fig. 2 in Ref. 2 as a function of wavenumber Ω in the Stokes range[27]. Prior to our measurement of RSR, preliminary measurement of HL has been carried out by three different research groups. They were Fitchen and Buchenauer in Cornll University[28], Lüty school in University of Utah[29,30], and Freiberg *et al.* in Tartu University[31]. Unfortunately, they were not successful in its observation over the whole Stokes range. Their failure depends on the sample temperature of LHeT that they chose. When the colored crystals were cooled down to LHeT, a huge amount of OL due to the F_2^+ centers appeared almost in the intermediate region of the Stokes range that interrupts the measurement of HL (Ω) over the whole Stokes range. On the contrary, our measurement was done at 77 K where the OL of F_2^+ centers are thermally quenched to very faint level[32]. We will show our results in the following section.

4. RSR with *cw* laser excitation

In addition to the first observation of the HL(Ω), we have also measured the degree of linear polarization, P (Ω), of the HL (Ω). They are, for instance, plotted in Fig. 3 in ref. 2 as a function of Ω ; here the P (Ω) is defined as the difference of intesities of the

HL with parallel and perpendicular polarization with reference to the polarization of the excitation light divided by total intensity of the HL [2,27]. Both the HL(Ω) and P (Ω) were taken by excitation with a *cw* Ar^+ ion laser or its related dye laser with the excitation wavenumbers, Ω_{ex}. Two following outstanding evidences have been obtained for both quantities.

(1) The HL (Ω) specrum is decreased to vanishingly small level nearly at the onset region of the OL band.

(2) The P (Ω) spectrum holds constant value of about 40 % over a wide range of Ω. But it started to decrease to vanishingly small value nearly at the beginning of the OL band.

We have interpreted the item (1) by proposing that the HL (Ω) spectrum reveals, the loosing energy mechanism of OES. We semi-classically adopted a classical damping oscillator model with a damping constant, γ, for a phonon wave packet created after resonant excitation of phonon system coupled strongly with electron in the configuration coordinates, Q. Thus-created damping oscillator could drop down along an adiabatic potential energy surface (APES) from the FCS down to the RES with a velocity of dQ/dt to fulfil the de-exciation. As mentioned in the first paragraph in § 3, the HL intensity observed at a certain Ω is relevant to a time when the damping oscillator could stay dynamically at the temporary energy level of Ω. Thus, it is proportional to $(dQ/dt)^{-1}$. So, by adopting Franck-Condon principle, we calculated the HL (Ω) intensity as a function of Ω. From the curve-fitting analysis of thus-calculated HL (Ω) with the experimental HL (Ω) spectrum, we could estimate the value of γ, that is the inverse of τ_l defined. They are summarized in Table I for KCl, KBr and RbCl[22]. It clearly shows that they are all in ultra short of 10^{-13} sec. Such ultra fast τ_l enforces the HL intensity to reduce to extremely faint level that would be unable to observe if adopting a conventional detector with less sensitivity. This is the reason why nobody could observe the RSR light intensity in the Stokes range except a few researchers[28-31]. So that the Stokes range has been called the nonradiative or radiationless range so far.

In 1987, Kayanuma *et al.* theoretically confirmed the validity of this classical

Table I Lattice relaxation time (τ_l) of the optically excited state of the F centers. The secound row is obtained from semi-classical damping oscillator model[22]. The third is from quantum mechanical calculation[25),33)].

CRYSTALS	Semi-classical (sec)	Quantum mechanical (sec)	References
KCl		8×10^{-13}	25
	2.7×10^{-13}		22
		3×10^{-13}	33
KBr	2.8×10^{-13}		22
RbCl	3.3×10^{-13}		22

damping oscillator model for loosing energy processes[33]. Kayanuma extended Toyozawa's general theory of RSR to a strongly coupled electron-phonon system like the *F* center. He calculated the spectrum of HL (Ω) both in stationary and transient conditions[26]. From the curve-fitting of his theoretical curves with our experimental data of HL (Ω) for KCl, he estimated τ_l of 3×10^{-13} sec approximately. This gives a good coincidence with our estimated values listed in Table I. However, he mentioned that theoretical argument has still left unresolved for complete fitting with experimental values.

Item (2) is the most drastic observation for HL. This clearly shows that, after loosing a part of the polarization memory of the resonant excitation light in the whole RRS range, the remaining memory was kept almost constant over the whole Stokes range. The fact implies that above-mentioned phonon wave packet could drop down along one of the $2p$-like three APES troughs spanned by the A_{1g} mode with total symmetry, without suffering from the interaction with the T_{2g} mode phonons of non-cubic symmetry that would be negligibly small in the OES. The P (Ω) spectrum was interpreted theoretically in 1985 by Muramatsu and Nasu[26]. They calculated the P (Ω) by calculating vibronic wavefunction at any Ω on the bassis of the *realistic vibronic scheme of the RES* by Kayanuma. Actually, they treated dynamical change of P (Ω) as dynamical exchange of total angular momentum in the vibronic states at Ω. They showed fairly reasonable fitting with experimental data of P (Ω) in KCl, with choosing the lattice relaxation time of 8×10^{-13} sec. This is close to our estimated value of τ_l listed in Table I.

In 1984, Hizhnyakov derived a *general theory* of RSR[34]. His particular interest was focused on a switching off mechanism (according to his naming) that occurs in P (Ω) at a wavenumer Ω_S, say P (Ω_s), of the transition range from the multi-phonon RRS to HL. He predicted that the P (Ω_s) may show concave downward characteristic against the excitation wavenumber of Ω_{ex}. He also emphasized that, if experimental data could show such a tendency, it would be an experimental proof for the validity of his theoretical framework. Mori and Ohkura[2,22] have observed that P (Ω_{ex}: Ω_s) shows the same characteristic as his prediction, and have given a semi-classical explanation for their experimental observation. Recently, Muramatsu[35] and Muramatsu *et al.*[36] have calculated the P (Ω_{ex} : Ω_S) on the basis of *realistic vibronic scheme of the FCS* which were introduced by Muramatsu *et al.* to explain all other experimental data related to the optical absorption consistently[37]. As a result, we may state that the HL(Ω) and P(Ω) spectra observed by cw laser resonant excitation have been all explained with the idea of the loosing energy mechanism by damping oscillator model proposed.

On the other hand, in 1987, Nakamura *et al.* in Tohoku University tried to measure the RSR by means of time-resolved *ps* spectroscopy[38]. Their result of both HL(Ω) and P (Ω) spectra show the same as ours over the whole Stokes range. However, one difference found is that P (Ω) does not decrease even in the Ω range of the OL band. Difference would be intuitivey explained as the difference of excitation conditions. However, we suspected that the P (Ω) should dercrease vanishingly small at some Ω

range since the OL band has no linear polarization at all. We really want to know experimentally at which Ω the P will begin to decrease to zero level.

One of the merit of the *ps* spectroscopy is to separate HL and OL feasibly even at the OL band region with respect to the difference of their own relaxation times after resonant excitation. However, an experimental restriction does exist in the choice of the repetition rate per second (*rps*) of laser pulse, that is, the *rps* should be much less than the inverse of the radiative lifetime (τ_l) of the RES. In spite of this demand, Nakamura *et al.* adopted commercially available 80 MHz for the *rps*, that is much larger than the inverse of τ_r of 0.65 μsec. So that they violated above-mentioned condition completely.

In 1993, Akiyama and Ohkura developed a new *ps* time-resolved spectroscopy apparatus of RSR with the *rps* of 380.0 KHz. Unfortunately, They could not yet observe the decrease of the P (Ω) of HL over the Ω range observed[39]. A year later, however, we reduced the *rps* down to 253.3 KHz, and could finally observe the decrease of the P (Ω) at the higher Ω range of the OL band[40]. Thereafter, they could reproduce the data of Nakamura *et al.* with adopting *rps* of 80 MHz to our apparatus. Thus,we have confirmed that their failure really depends on their unreasonable selection of the *rps*.

5 . *ps* Time-resolved spectroscopy of RSR

In 1993, Akiyama and Ohkura [9] have illustrated the RSR signals observed by *ps* spectroscopy in a there dimensional image processing scheme through a streak camera scope (Hamamatsu Streak Scope C4334). Actually, as was typically shown in Fig. 1 in ref. 39, the RSR intensity in the *z*-axis is plotted as functions of time in the x-axis and Ω in the y-axis, respectively. Data were taken at LNT with Ω_{ex} =17,712 cm^{-1}.

In the Ω range from 16,000 to 13,000 cm^{-1}, the shapes of the RSR intensity at Ω plotted against the duration time are all the same as that of the excitation laser pulse at Ω_{ex}. This implies that the lattice relaxation time (τ_l) at any Ω in the HL range is much less than the apparent half width of excitation pulse with a resolution limit of 15 *psec*. This implication is coincident with the values of τ_l as shown in Table I . In the Ω range below 13,000 cm^{-1}, however, the shapes of the RSR intensity shows clearly antisymmetric shapes with respect to the time duration. Finally, at Ω =11,000 cm^{-1}, its intensity shows saturation behavior over relatively long time duration (until≈200 *psec*) after passing the time-response of the HL of about 30 *psec*. Thus, we may state that the RSR intensity at 200 *psec* reveals solely the OL intensity at Ω=11,000 cm^{-1}. With this information and using the de-convolution analysis mehtod of the RSR spectrum, both the HL (Ω) and OL (Ω) can be well separated in the Ω range from 13,000 to 10,000 cm^{-1} : These intensities I_{OL} and I_{HL} are plotted in Fig. 1 with broken lines and closed inverse triangles, respectively. It clearly reveals remarkable rise of OL (Ω) and continuous decrease of the HL (Ω) but keeping constant level in the OL band with decrease of Ω.

In the Ω range below 13,500 cm^{-1}, we have also observed the apparent delay in the

rise time of RSR intensity in comparison with that of the excitation pulse. From the analysis of time dependent RSR, the rise time of the OL band is estimated to be below 3 *psec*. Unfortunately, its resolution is limited by the dot width of 2.8 *psec* of the steak scope. This rise time may correspond to a net dynamical transition time from the $2p$ APES to the $2s$ APES troughs.

From the parallel and perpendicular intensities of thus-separated HL (Ω) with reference to the polarization of incident excitation pulse, one can calculate the P (Ω) spectrum which is plotted in Fig. 1 with solid lines and closed circles borderiug above and below the Ω of 13,200 cm^{-1}, respectively, as a function of Ω. It shows evidently that the P (Ω) decreased markedly down to zero in the onset region of the OL band at its high Ω side. This vanishing reduction of the P (Ω) is the first observation for *ps* spectroscopy. This behavior implies that the dynamical transition from the $2p$ to $2s$ APES troughs would undergo at their level crossing range by a way of Landau-Zener mechanism in a certain sense of adiabatic approximation. It is worthwhile to notice that it occurs near the onset of the OL band.[41] Thereafter, the thermalization occurs in the $2s$ APES where the RES is established.

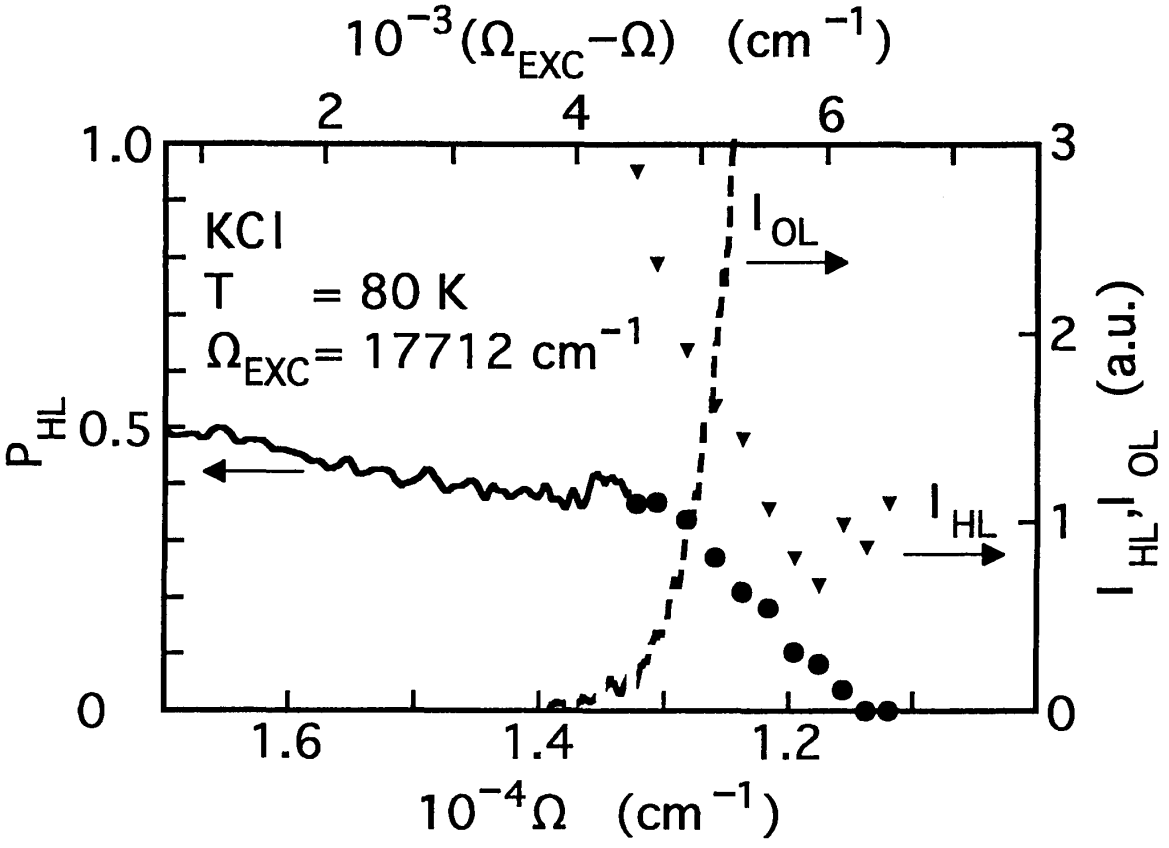

Fig. 1. The spectrum of the intensity of the luminescence (I_{HL}), and of ordinary luminescence (I_{OL}) separated from the RSR spectrum at the onset raegion of the OL band (see the text) are plotted with broken lines and closed inverse triangle as function of Ω and (Ω_{EXC}-Ω), respectively, where Ω_{EXC} is the resonant excitation wavenumber Ω of the *F* center. The linear polarization spectrum (P_{HL}) is also plotted with solid lines and closed circles. Data are taken from ref. 40.

In order to elucidate the loosing energy mechanism over the Stokes range, one must consider the detailed APES schema. They are plotted in Fig. 2 as a function of configuration (or interaction) coordinates in which the FCS and RES are depicted. From the analysis of Stark effects on the F absorption band, Grassano *et al.* have

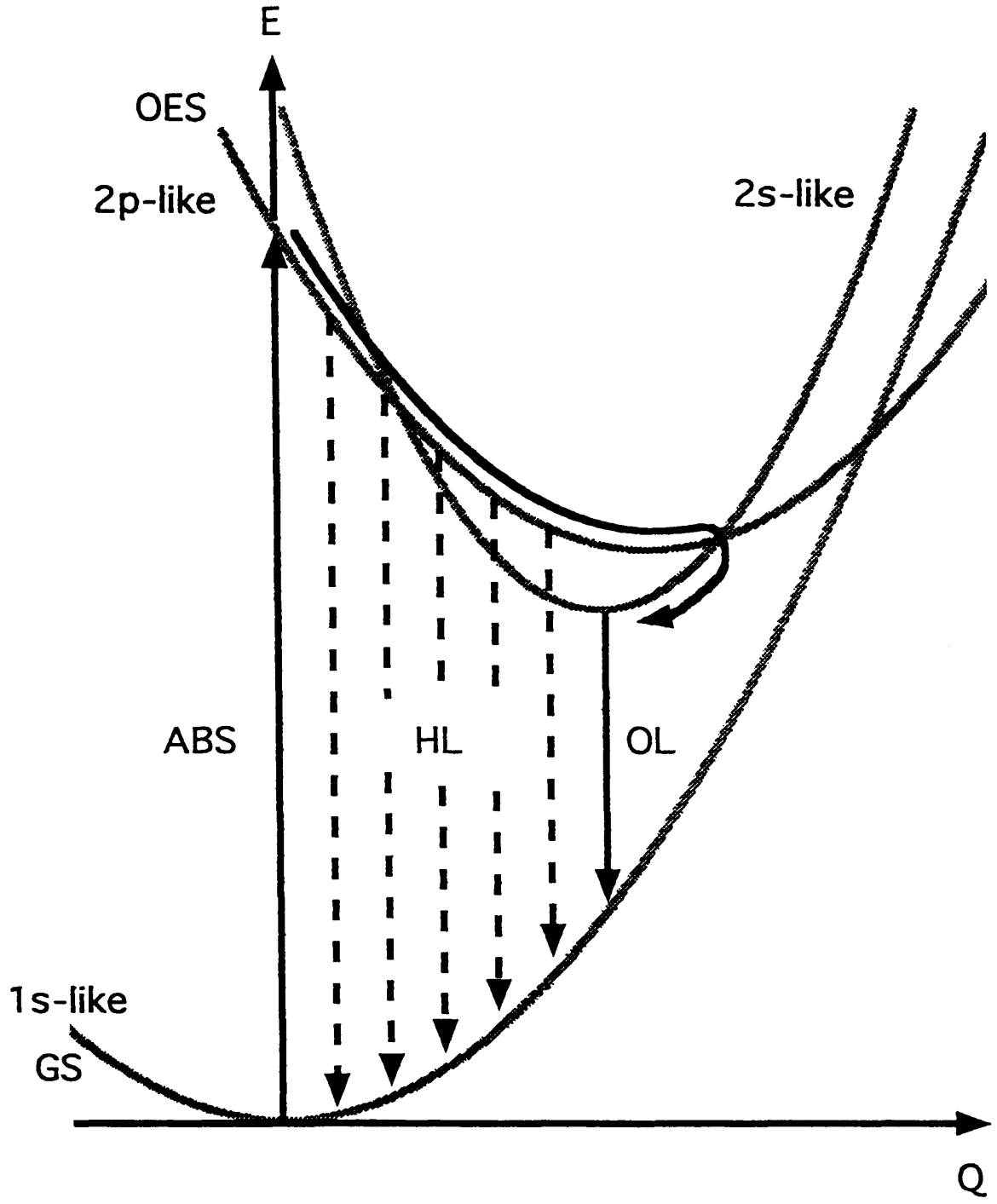

Fig. 2. Adiabatic potential energy surfaces for the GS, and optically excited state (OES) are plotted in the configuration coordinates. The latter is divided into *2s* and *2p* components. Geometrical features for both are proposed to account for the data from time-resolved *ps* spectroscopy. This figure is taken from ref. 40.

propsed that the $2s$ level should lie slightly above the $2p$ level in the FCS[42]. Recently, independen of their theoretical calculation, Muramatsu[44] also confirmed the validity of their scheme based on *the realistic vibronic scheme of the FCS*[37]. On the other hand, according to the vibronic scheme of the RES[5,8,43], the $2s$ level should tend to lie below the $2p$ levels in the OES nearly at the termiantion stage of the de-excitation process. With this information, we may roughly figure the geometrical relation of $2s$ and $2p$ APES in Fig. 2. Here, one may expect that the two steps of level crossing will occur during the de-excitation process. The dynamical ralaxation process which we have already discussed in the preceding paragraph may occur at the second level crossing near the lowest OES shown at the right-hand side in Fig. 2. Here, as the kinetic energy of the packet was alment exhausted, the dynamical transition from the $2p$ to $2s$ APES troughs would occur predominantly : This clearly causes the vanishing reduction of P (Ω) mentioned above.

On the other hand, the first level crossing would occur at the early stage of the HL range in the higher OES as shown in Fig. 2. If it occurred, the dynamical change of P (Ω) would have been observed[41] after the RRS. On the contrary, the fact that the P (Ω) keeps constant value over the whole Stokes range would be contrary from this expectation. This contradiction implies that the wave packet created in the FCS may have so large kinetic energy that it could hardly experience the dynamical interaction caused from the 2s level lying nearby. In another word, at the first level crossing, the packet could pass there so fast and non-adiabatical that there would be no chance to cause the dynamical relaxation. The checking of this non-adiabaticy condition should be left as a future problem.

6 . Conclusion

The loosing energy mechanism (de-excitation process) of the OES of the F center in KCl has been investigated experimentally and theoretically from the study of RSR obtained by two different types of laser excitation, *cw* and *ps* pulse, respectively. Two outstanding evidences observed are (1) the dependence of the HL intensity on Ω, the HL (Ω) spectrum, is continuously decreased to vanishingly small level over the whole Stokes range, and (2) the degree of linear polarization of the HL (Ω), the P (Ω) spectrum, keeps almost constant value of about 40% over the whole Stokes range before it is quenched completely in the higher energy side of the OL band.

The classical damping oscillator model is proposed for the analysis of the HL(Ω). The de-excitation mechanism of the OES of the F centers that is created just after the resonant excitation can be treated as a ultra-fast dropping down motion of the damping oscillator along the APES trough composed of $2p$-like state. The HL intensity observed at any Ω in the Stokes range is proportional to the inverse of the velocity of the damping oscillator in the ineraction coordinates, Q namely $(dQ/dt)^{-1}$, so that it can be calculated. From the curve-fitting analysis of thus-derived curves with experimental HL(Ω) spectrum, the τ_l values have been determined : They are in the order of 10^{-13} sec. The validity of this classical model mechanism has been confirmed quantum

mechanically by Kayanuma. He estimated the τ_l is in the same order of magnitude of 10^{-3} sec. Muramatsu and Nasu also estimated τ_l of the same orders of magnitude from their theoretical analysis of the P (Ω) spectrum.

In order to explain the present results consistently with the vibronic structures of the FCS and RES studied already, the APES are plotted in Fig.2 as a function of the configuration coordinates. Here, we may expect that the level crossing may occur twice times in the de-excitaion process. If the dynamical transition from the $2p$ to $2s$ APES trough could occur at the level crossing range, drastic change in the P (Ω) spectrum should be expected. Disappearance of the P (Ω) spectrum that was observed near the bottom of the $2p$-APES trough might correspond to this expectation. The first level crossing would occur at the early stage of the HL spectrum, in the higher OES according to Fig. 2. No variation of the P (Ω) spectrum in this Ω range has been observed. The fact may imply that the de-excitation would occur non-adiabatically. The detailed discussion on this problem is left as a future problem.

Both the τ_l and the dynamical transfer time from the $2p$ to $2s$ APES troughs near the level-crossing in the HL range are too ultra-short to be measured directly by using our *ps* spectroscopy apparatus. Both qunatities are less than the resolution limit of 8*psec*. Direct observation of these quantities are also left as a future work.

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