

Temperature Effects on the Energy Gap Dependence of Charge Recombination Rates of Ion Pairs Produced by Excitation of Charge-Transfer Complexes Adsorbed on Porous Glass

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The energy gap dependence of the charge recombination (CR) rate constant (k_{CR}) of geminate ion pairs produced by exciting the ground-state charge-transfer complexes adsorbed on porous glass and temperature effects on it were investigated by means of picosecond laser photolysis. At room temperature, the same energy gap dependence of k_{CR} as observed in polar solutions was found also in the adsorbed systems. This result indicates that not polar solvent dynamic motions but intramolecular high-frequency quantum modes in the ion pair predominate in the CR process of these ion pairs. At 77 K, an energy gap dependence with a somewhat steep slope was obtained. This result indicates that the intra-ion-pair reorganization with low-frequency motion that seems to be frozen at 77 K contributes to the gentle slope in the energy gap dependence at room temperature. By integrating the present results with those obtained in solutions and with theoretical investigations, the factors regulating the charge recombination dynamics of this kind of ion pair are discussed.

Introduction

Photoinduced electron transfer (ET) and related processes play fundamental and important roles in a number of photochemical reactions in the condensed phase and have been studied from various viewpoints.^{1–4} Among these investigations, much effort has been focused on the relation between the ET rate constant and the energy gap (ΔG) of the reaction in solutions.^{5–10} Theories¹ of ET assuming weak interaction between donor and acceptor predict the bell-shaped energy gap dependence of the ET rate with the maximum at $\Delta G = \lambda$. Here, λ is the reorganization energy arising from the environment and the molecules undergoing ET reaction. Hence, it is predicted by the usual theories of ET that the energy gap dependence is also affected by the properties of the solvent. The comparison of theoretical predictions with experimental results for charge separation, charge recombination, and charge shift reactions has elucidated important factors regulating the ET processes.^{1,2,5–13}

Although above predictions have been confirmed experimentally for several systems covering the normal as well as the inverted regions,^{6,7} quite different behaviors were presented for the energy gap dependence of charge recombination (CR) rate constants (k_{CR}) of the geminate ion pair produced by the photoexcitation of ground-state charge-transfer (CT) complexes in solutions with different polarities;^{8,9} (a) no or very little solvent polarity effect on the k_{CR} vs ΔG_{CR} (the energy gap for the CR reaction) relations and (b) a $\ln(k_{\text{CR}})$ vs ΔG_{CR} linear relation, $\ln(k_{\text{CR}}) = \alpha - \beta|\Delta G_{\text{CR}}|$, with a gentle slope and α and β independent of the solvents, were reported. In addition, (c) no normal region was observed in these experiments, while

ion pairs produced by ET upon encounter between donor (D) and acceptor (A) in fluorescence-quenching reactions showed a bell-shaped energy gap dependence for the same DA pairs in the same solvent.^{7,8} These experimental results showed that the change of the solvents for the same DA pair yielded almost the same universal energy gap dependence, which is a quite different behavior from that predicted by usual theories of ET.

For this particular behavior, it was proposed^{8,9} that the intramolecular high-frequency quantum modes, rather than solvent dynamic motions, predominate in the CR process of these ion pairs produced by the excitation of the ground-state CT complex. Moreover, the linear relation of $\ln(k_{\text{CR}})$ vs ΔG_{CR} was interpreted^{8,9} by analogy with the weak coupling limit in the radiationless transitions.^{14–16} Also from the theoretical viewpoint, the role of the intramolecular high-frequency quantum modes and its effect on the energy gap dependence in the ET processes have been investigated in detail recently.^{11,12}

For more directly assessing the role of dynamic motions of polar solvents from the experimental viewpoint, we have investigated the energy gap dependence of the CR process of the ion pairs produced by the excitation of the ground-state CT complex adsorbed on a porous glass where neither large intermolecular motions nor *surrounding solvents* are of importance. In the previous communication,¹⁷ we reported that the same energy gap dependence of k_{CR} as that observed in polar solutions was found also in the adsorbed systems. In the present study, the temperature effect on the energy gap dependence of k_{CR} in the porous glass systems was studied in order to elucidate in general the factors regulating the CR process of ion pairs prepared by excitation of the ground-state CT complex. In the following, we will discuss the origin of the global k_{CR} vs ΔG_{CR} relation by taking into account the experimental results reported

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recently for the CR process in the CT crystals^{18,19} as well as theoretical investigations.

Experimental Section

A porous glass plate (Corning, Vycor No. 7930, mean pore radius = 4 nm, 1 mm thickness) was washed with nitric acid at 100 °C and water, followed by heating at 400 °C for 48 h. 1,2,4,5-Tetracyanobenzene (TCNB), tetracyanoethylene (TCNE), anthracene (An), naphthalene (Np), 1-methylnaphthalene (MNp), perylene (Pe), and pyrene (Py) were purified by recrystallization and sublimation in a vacuum. Adsorption of the CT complex was performed in the following manner. The purified porous glass plate (*ca.* 1 cm × 1 cm) was put into 1,2-dichloroethane solution of the electron donor (D) and the acceptor (A) and stored at 30 °C for more than 24 h. The concentrations of D and A in the solution were on the order of 10⁻³ M, respectively. The porous glass adsorbing the CT complex was dried in a vacuum for more than 4 h.

A microcomputer-controlled picosecond laser photolysis system with a handmade repetitive mode-locked Nd³⁺:YAG laser was used for measurements.²⁰ A second-harmonic (532 nm) or third-harmonic pulse (355 nm) with 15 ps fwhm and *ca.* 0.5 mJ output power was used for the selective excitation of the CT absorption band of the sample. Monitoring white light was generated by focusing the fundamental light into a 10 cm D₂O–H₂O (3:1) cell. Two sets of the multichannel diode array (MCPD, Hamamatsu S3904-1024Q) combined with a polychromator were used for the detection of the monitoring light. The repetition rate of the excitation light was kept low (<0.3 Hz), and sample positions were replaced after several exposures. Most of the data were accumulated over five measurements.

To investigate the system with very short lifetime, a double OPA femtosecond laser system for kinetic transient absorption measurements was used. The details of the system are described elsewhere.²¹ Briefly, the output of a femtosecond titanium sapphire laser pumped by an Ar ion laser was regeneratively amplified with 1 KHz repetition rate. The amplified pulse (1 mJ/pulse energy and 110 fs fwhm) is divided into two pulses with the same energy (50%). These pulses are guided to two OPA systems, respectively. OPA output pulses are converted to the SHG, each of which covers the wavelength region between 600 and 700 nm with 5–10 mW output energy and 120 fs fwhm. One of these two pulses is used as a pump light, and the other one, which is reduced to <1/5000 output power, is utilized as a monitoring light. The intensity of the light monitoring the sample excited with a pump pulse was detected by a photodiode and sent to the microcomputer for further analysis.

For the measurements of the temperature effect, the sample cell was put in the quartz Dewar with flat windows. Temperature was monitored by a thermocouple contacted to the cell holder and was controlled by changing the flow rate of cold N₂ gas evaporated from liquid N₂. All measurements were performed under O₂-free conditions.

Results and Discussion

Steady State Absorption and Emission Spectra. Figure 1 shows ground-state absorption and fluorescence spectra of anthracene (An) coadsorbed with 1,2,4,5-tetracyanobenzene (TCNB) on a porous glass plate at 295 and 77 K, respectively. The ground-state CT absorption spectrum at 295 K shows a broad band with a maximum at 20 900 cm⁻¹ (478 nm), whose bandwidth and absorption maximum were almost the same as those observed in various solutions. These results indicate that

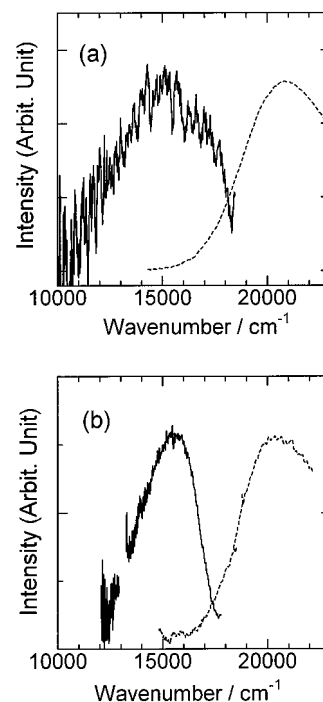


Figure 1. Ground-state absorption (dotted line) and fluorescence (solid line) spectra of anthracene (An) coadsorbed with 1,2,4,5-tetracyanobenzene (TCNB) on the porous glass: (a) at 295 K and (b) at 77 K.

the adsorption on the porous glass does not strongly affect the ground-state structure of the CT complex. Fluorescence spectra were obtained by exciting the sample with a picosecond 532 nm laser pulse and detected by the MCPD system. The spectrum was calibrated by using the standard tungsten lamp. Although the fluorescence spectrum at 295 K has rather poor S/N ratio, one can observe the broad band with a maximum at 15 000 cm⁻¹ (662 nm). The energy level of the ion pair state was estimated to be 18 000 cm⁻¹ (2.23 eV) from the midpoint of these two spectral maxima. The reorganization energy (λ) in this system was determined to be equal to 0.36 eV from the Stokes shift between the absorption maximum and the fluorescence one, provided that the Stokes shift corresponds to 2λ .

At 77 K, CT absorption and emission spectra show slightly narrower band shapes than those at 295 K. The CT absorption and emission maxima were at 20 380 cm⁻¹ (496 nm) and 15 550 cm⁻¹ (576 nm), respectively. From the midpoint of these two spectral maxima, the energy level of the ion pair was also estimated to be 18 000 cm⁻¹ (2.23 eV), indicating that the energy level is independent of the temperature. The reorganization energy (λ) at 77 K equals 0.29 eV from the Stokes shift between the absorption maximum and the fluorescence one. At both temperatures, the λ value for the porous glass system was much smaller than that in polar solutions. In addition, the temperature effect on it is also very small, indicating that an effective environmental reorganization does not take place in the present system. Nevertheless, as will be discussed later, low-frequency intermolecular vibration within the DA pair will contribute to the reorganization energy in addition to the contribution from the intramolecular high-frequency modes.

For the naphthalene (Np)–TCNB system adsorbed on porous glass at 295 K, CT absorption and emission maxima were 25 250 and 17 360 cm⁻¹, respectively. The energy gaps for the charge recombination and the reorganization energy were estimated to be 2.64 and 0.49 eV, respectively. This reorganization energy is also much smaller than those in polar solutions, leading to the conclusion that also in Np–TCNB system the effective environmental reorganization does not take place. The reor-

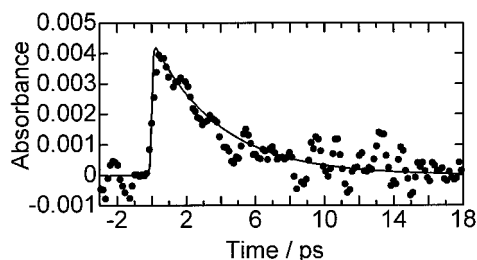


Figure 2. Time profile of transient absorbance at 680 nm of MNp-TCNE adsorbed on porous glass, excited with a femtosecond 610 nm pulse. Solid line is the curve calculated by taking into account the pulse durations and the decay time constant of 3.8 ps.

ganization energy of the Np-TCNB system is, however, slightly larger than that of the An-TCNB system. It should be noted that the tendency of the larger Stokes shift of the CT fluorescence was observed previously in the case of the larger energy gap of CR transition for the CT complex in solution.²³

By measuring the absorption and fluorescence spectra, we have tried to directly estimate the energy level of the ion pair for all the systems used here. However, because of the weak intensity of the fluorescence for the strong D-A pairs and the overlap of the locally excited absorption with the CT band for rather weak D-A systems, it was difficult to determine them except for An-TCNB and Np-TCNB systems. Hence, we estimated the energy level of the ion pair state (corresponding to $-\Delta G_{CR}$) by the following equations.

$$-\Delta G_{CR}(\text{in porous glass}) = -\Delta G_{CR}(\text{in acetonitrile}) + \Delta F \quad (1)$$

$$\Delta F = E_{IP}(\text{An-TCNB}) + \Delta G_{CR}(\text{An-TCNB in acetonitrile}) \quad (2)$$

Here, $E_{IP}(\text{An-TCNB})$ is the energy level of the ion pair estimated for the An-TCNB system from Figure 1. $|\Delta G_{CR}(\text{in acetonitrile})|$ is the energy gap for the CR in acetonitrile solution, which is conventionally estimated on the basis of oxidation and reduction potentials of D and A and the Coulombic energy.⁵ ΔF is the correction term and is usually estimated by the Born equation for solutions. In the present system, we used the experimentally obtained value for the An-TCNB system and assumed that ΔF values for all the other systems were the same as those for the An-TCNB system. It should be noticed that the energy level estimated on the basis of the above equations for Np-TCNB is 2.74 eV, which within 0.1 eV error is almost the same with that determined by direct measurement.

Dynamic Behavior at 295 K. As mentioned in the introductory section and in the previous paper,¹⁷ the excitation of the ground-state CT complex adsorbed on porous glass resulted in the formation of the transient ion pair state in the excited state, and the decay profiles of the transient ion pair states at 295 K were reproduced fairly well by the first-order decay.

In Figure 2, we show the time profile of transient absorbance of the 1-methylnaphthalene (MNp)-TCNE system adsorbed on porous glass. In this measurement, we have employed a femtosecond laser system. The pump wavelength at 610 nm corresponds to the selective excitation of the ground-state CT complex, and the probe light at 680 nm was tuned to the absorption band of the cation radical of the MNp (MNp^+).¹⁷ Since the pump wavelength selectively excites the ground-state CT complex and the transient absorption is remarkable only in the wavelength around 680 nm, the present decay is ascribed to the charge recombination (CR) process of the ion pair,

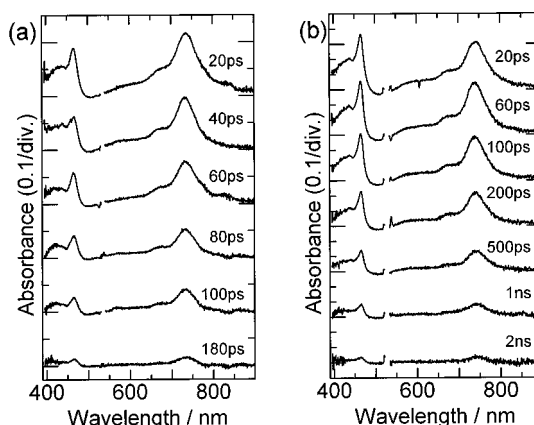


Figure 3. Transient absorption spectra of An-TCNB adsorbed on porous glass, obtained by the selective excitation of the CT absorption band with a picosecond 532 nm laser pulse: (a) at 295 K and (b) at 77 K.

($\text{MNp}^+\text{TCNE}^-$). The solid line in the figure is the result calculated by taking into account the pulse widths of the pump and probe pulses and the lifetime of the ion pair state. The observed decay profile was reproduced fairly well by the single-exponential function with the time constant of 3.8 ps. Transient absorption spectra and time profiles of other systems at 295 K were described in the previous paper.¹⁷

Temperature Effect on the Dynamic Behavior. Figure 3 shows transient absorption spectra of An-TCNB adsorbed on the porous glass at 295 and 77 K, excited with a picosecond 532 nm laser pulse. The excitation at 532 nm corresponds to the selective excitation of the ground-state CT complex. The absorption maximum at 465 nm and that at 735 nm are safely ascribed to the anion radical of TCNB (TCNB^-) and the cation radical of An (An^+) on the basis of the coincidence of peak positions and spectral band shapes of the observed spectra to the reference data.^{23,24} The sharpening of absorption bands of ions, especially for TCNB^- , was observed at 77 K. From these spectra, it can be concluded that the excitation of the ground-state CT complex results in the ion pair formation in the excited state. At other temperatures examined in the present paper, the formation of the ion pair following the excitation at the CT absorption band was also observed.

With increase in the delay time after the excitation, the ion pair state monotonously decayed at both temperatures. The relative ratio of the absorption intensities between 465 and 735 nm are constant during the decay process. Since no absorption signal was observed on and after 500 ps delay time from the excitation at 295 K, almost all deactivation of the ion pair state is ascribable to the charge recombination resulting in the ground state. Also at 77 K, almost all of the ion pair was deactivated without any appearance of new absorption bands in several nanosecond time region. At other temperatures examined here, the appearance of the ion pair after the excitation at the CT band and the deactivation due to the charge recombination were also confirmed.

Figure 4 shows the temperature dependence of the time profiles of the ion pair between An and TCNB adsorbed on porous glass. The monitoring wavelength was 464 nm. Although the decay profile at 295 K is monophasic, the deviation from the single-exponential decay profile is pronounced with decrease in temperature. The origin of this decay will be discussed later.

Figure 5 shows the temperature effect on the time profiles of transient absorbance of the Np-TCNB system adsorbed on the porous glass, excited at 355 nm and monitored at 465 nm. The

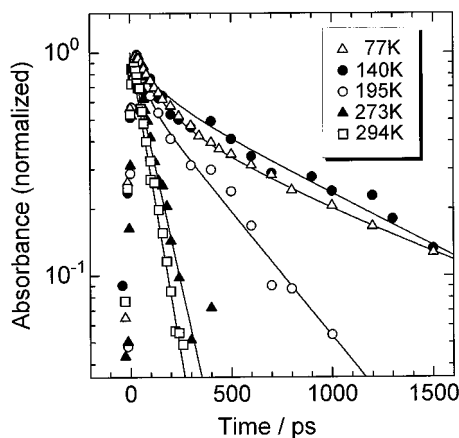


Figure 4. Time dependence of the transient absorption spectra of An-TCNB adsorbed on porous glass, obtained by the selective excitation of the CT absorption band with a picosecond 532 nm laser pulse at various temperatures. Solid lines in the figure were the results calculated by single-exponential decay or eq 3. To the nonexponential decay profiles, eq 3 was applied (see text).

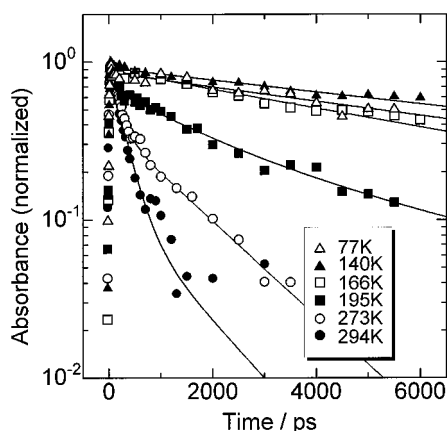


Figure 5. Time dependence of the transient absorption spectra of Np-TCNB adsorbed on porous glass, obtained by the selective excitation of the CT absorption band with a picosecond 355 nm laser pulse at various temperatures. Solid lines in the figure were the results calculated by single-exponential decay or eq 3. To the nonexponential decay profiles, eq 3 was applied (see text).

irradiation at 355 nm corresponds to the selective excitation of the ground-state CT complex. As in the An-TCNB system, the temporal evolution of the spectra showed that the ion pair decreased while keeping the relative ratio of the absorption intensities between the cation and the anion with increase in the delay time after the excitation.¹⁷ Since no appearance of a new absorption band was observed during the decay process, almost all of the deactivation of the ion pair is ascribed to the charge recombination leading to the ground state. Figure 5 indicates that a decrease in the temperature increases the decay time of the ion pair also in the Np-TCNB system.

The deviation of the decay profile from the first-order kinetics with lowering of the temperature was also observed for other ion pairs adsorbed on the porous glass. The multiphasic decay at lower temperatures may be related to the inhomogeneity of the adsorbed sites. It should, however, be noted that the ground-state CT absorption band at 77 K is narrower than that at 295 K as shown in Figure 1. Hence, the multiphasic decay cannot simply be ascribed to an increase in the distribution of the ground-state CT complexes over various DA geometries due to the surface inhomogeneity with a decrease in the temperature. Rather, dynamic processes in the excited CT complex may be responsible for this multiphasic decay.

Regarding the dynamic behavior of the excited CT complex, it was pointed out in the early stage of the investigations^{22,25,26} that the DA geometry in the excited Franck-Condon state is different from that in the fluorescent state with full charge separated structure. Actually, in glassy matrices at low temperature, this geometrical change is restricted,²⁵⁻²⁷ and as a result, the Stokes shift between the CT absorption and emission decreases, as observed in the present adsorbed system. The dynamics of the relaxation from the excited Franck-Condon state to the ion pair state with the aid of some small intracomplex geometrical change (intermolecular reorganization) including the rearrangement of the surrounding solvents (solvent reorganization) at room temperature were directly revealed by femtosecond laser photolysis.^{24,28} Recent detailed investigation using Raman, CT absorption, and emission spectroscopies also indicates such geometrical changes in excited CT complexes.²⁹

Although large reorganization of the medium is not plausible, a small change of geometry in the pair may take place in the present adsorbed system at room temperature. The low-frequency motion such as the intermolecular vibration between D and A for the typical CT complex, which promotes the DA geometrical change of the CT complex, is on the order of 100–300 cm⁻¹ in the ground state as well as in the excited state.^{29,30} Hence, the decrease in temperature may drastically affect such a geometrical change in the pair promoted by these low-frequency motions in the excited CT complex. In addition, the heterogeneity in the adsorbed sites may give rise to the distribution of the barrier height for this geometrical change. Since the deviation from the first-order decay of the observed time profiles was very small at 295 K,¹⁷ almost all of the CT complex may easily undergo the geometrical change at room temperature. With decrease in temperature, however, the intermolecular geometrical change in the pair may be restricted. Hence, it is suggested that the temporal profiles exhibit the multiphasic decay at low temperature owing to the decrease in the promoting motion and the distribution of the barrier for the geometrical change. We discuss later the importance of this intermolecular reorganization in the CR decay processes of the ion pair state by integrating the present results with other experimental as well as theoretical investigations.

In order to estimate the rate constant of charge recombination whose temporal profile is multiphasic, we analyzed the experimental results by the following procedures. First, we estimated the averaged rate of the decay such as

$$1/\langle k_{\text{CR}} \rangle = \int_0^\infty f(t) dt / f(0) \quad (3)$$

Here, $f(t)$ is the decay function and $f(0)$ is the transient absorbance at $t = 0$. For the single-exponential decay function such as $f(t) = f(0) \exp(-k_{\text{CR}}t)$, $\langle k_{\text{CR}} \rangle$ is exactly equal to k_{CR} . In the actual analysis, we tentatively fitted the observed decay profiles that show multiphasic decay with the triphasic exponential function. The solid lines in Figure 4 and 5 are the results based on the above function.

Second, we applied the Kohlraush-Williams-Watt equation for the analysis.

$$f(t) = f(0) \exp\{-(k_{\text{CR}}t)^\beta\} \quad (0 < \beta \leq 1) \quad (4)$$

This stretched exponential law is generally based on the strict physical models and mechanisms such as the serial hierarchically constrained dynamic model, defect-diffusion, and parallel relaxation with a hierarchy distribution.³¹ It should be noticed here that it is rather difficult to clearly derive the physical origin of the stretched exponential law for the present case. Moreover,

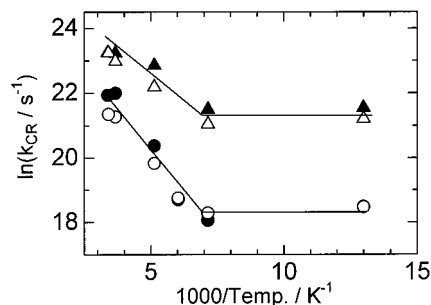


Figure 6. Temperature dependence of the CR rate constants of Np-TCNE (circles) and An-TCNB (triangles) adsorbed on porous glass. Closed marks were obtained by eq 3 and open ones by eq 4. Solid lines are to guide the eye.

the time window seems insufficient to determine whether the stretched exponential law is valid for the present case. This analysis, however, gives the degree of the deviation from the single exponential decay as the exponent of β . In addition, the obtained $\langle k_{\text{CR}} \rangle$ is the value averaged mainly over the early stages of the decay profiles. In the present case, typical β values were obtained to be 0.7–1.0.

The temperature dependence of the rate constant of the charge recombination for An-TCNB and Np-TCNB systems adsorbed on the porous glass, which was obtained by the above procedures, is plotted in Figure 6. This figure indicates that the temperature effect on the charge recombination rate may be roughly divided into two stages. First, the k_{CR} decreases with decrease in temperature. Second, k_{CR} is almost independent of the temperature below ca. 150 K. In addition, the temperature effect in the region between 293 and ca. 150 K is larger for the Np-TCNB system, which has a larger energy gap for the charge recombination. For other DA systems, the increase in the temperature effect on the CR rate constant was observed also with increase in the energy gap. The ratio, $k_{\text{CR}}(293 \text{ K})/k_{\text{CR}}(77 \text{ K})$, for each DA system is as follows: 5.3 for Pe-TCNB, 5.7 for An-TCNB, 15.6 for Py-TCNB, and 30.0 for Np-TCNB. The decrease of k_{CR} with temperature lowering will be connected with the decrease or freezing of the low-frequency motions, and the approximately constant k_{CR} below 150 K may be due to the high-frequency modes. Moreover, the tendency that the temperature effect on k_{CR} is larger for the system with larger energy gap for CR may be related also to the effect of this low-frequency motion contributing to the larger reorganization energy of the system with a larger energy gap for CR as pointed out in the first section. More detailed discussions are given in the next section.

Energy Gap Dependence of CR Rate Constants. The energy gap dependence of the CR rate constant for the present porous glass systems obtained by the above procedure is shown in Figure 7. The $-\Delta G_{\text{CR}}$ values were estimated by eqs 1 and 2, as mentioned above. The present experimental results on porous glass systems at 295 K show also the linear relation between $\ln(k_{\text{CR}})$ vs (energy gap), $\ln(k_{\text{CR}}) = \alpha - \beta|\Delta G_{\text{CR}}|$, as observed in various solutions at the same temperature.^{8,9} The dotted line is the experimentally obtained curve for the energy gap dependence of the CR rate constant of the ion pairs produced by the CT band excitation in various solutions^{8,9} at room temperature. The values of α and β in the adsorbed systems at room temperature are almost the same as those in solutions.

At 77 K, the energy gap dependence of the CR process shows a steeper slope than that at 295 K. Nevertheless, in the energy gap region examined here, also the linear relation between the energy gap and $\ln(k_{\text{CR}})$ is still observed. The steeper slope at 77 K is related to the fact that the temperature effect on the CR

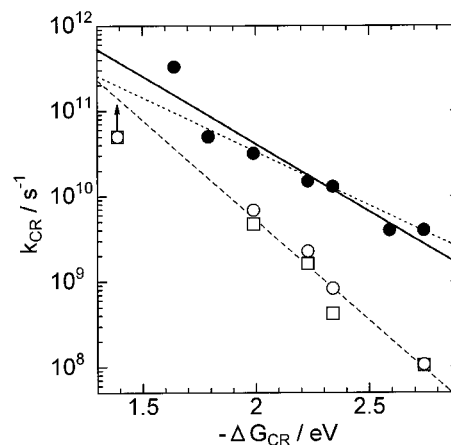


Figure 7. k_{CR} vs energy gap ($-\Delta G_{\text{CR}}$) relations of the ion pairs on porous glass produced via the excitation of the ground-state CT complex. Closed circles are experimental results at 294 K. A solid line for results at 294 K is the curve analyzed by least-squares methods on the basis of the equation $\ln(k_{\text{CR}}) = \alpha - \beta|\Delta G_{\text{CR}}|$. The dotted line is the results for solutions⁹ (see text). For the results at 77 K, open circles were obtained by eq 3 and squares by eq 4. The broken line at 77 K is the eye guide.

rate constant is larger for the ion pair with a large energy gap as discussed above.

The above described results on the k_{CR} of the adsorbed systems as well as various solutions at room temperature strongly suggest the dominant effect of the intramolecular high-frequency quantum modes and/or various intracomplex vibrational modes and a rather minor role of the medium reorganization. As conceivable from the observed relation, $\ln(k_{\text{CR}}) \propto -\beta|\Delta G_{\text{CR}}|$, this energy gap law is analogous to that of a radiationless transition³² in the weak coupling limit.^{14,15} In relation to this problem, some related theoretical studies¹² and femtosecond laser spectroscopic studies^{33,34} have been reported recently.

Qualitatively speaking, k_{CR} of the ion pair produced by the excitation of the ground-state CT complexes is determined by the electronic coupling between the ion pair and ground state and by the vibrational overlaps between the low-lying initial vibrational levels of the ion pair and isoenergetic vibrational levels of the ground state. On the basis of the theoretical treatments of the radiationless transitions in the weak coupling limit,^{14,15} an approximate equation for the energy gap dependence of k_{CR} for the low-temperature case may be expressed as follows.

$$\ln(k_{\text{CR}}) = \ln C - (\gamma/\hbar\omega_M)|\Delta G_{\text{CR}}| \quad (5a)$$

$$\gamma = \ln(|\Delta G_{\text{CR}}|/\hbar\omega_M S_M) - 1 \quad (5b)$$

Here the preexponential factor C represents mainly the contribution from the electronic coupling term connecting the ion pair and the ground state and also some additional terms. The term $-(\gamma/\hbar\omega_M)|\Delta G_{\text{CR}}|$ arises from the energy release into acceptor modes in the ion pair to ground-state transition. S_M and ω_M are average quantities for electron-vibrational coupling constants and angular frequencies of the quantum modes, respectively. Although γ contains ΔG_{CR} , its variation with the change of ΔG_{CR} is much smaller than the $|\Delta G_{\text{CR}}|$ itself in the term $-(\gamma/\hbar\omega_M)|\Delta G_{\text{CR}}|$. It should be noted here that, in general, the right-hand side of eq 5a should contain the term due to the solvent reorganization because both intramolecular and medium modes are important. In addition, intermolecular (intra-ion-pair) modes may be involved as mentioned in previous sections. Nevertheless, solvent reorganization does not seem to play an important

role in the CR process as shown in various solutions with different polarity and the present results.

The experimentally obtained relation, $\ln(k_{\text{CR}}) = \alpha - \beta|\Delta G_{\text{CR}}|$, has the same form as eq 5a with $\alpha = C$ and $\beta = (\gamma/\hbar\omega_M)$. In an extreme case of such a supermolecule composed of very strongly interacting D with low ionization potential and A with high electron affinity, the main contribution to C may be the electronic matrix element of the kinetic energy parameter for the internal conversion^{14,15,32,35} between the excited state with large CT degree and the ground state with much smaller CT degree. That is, the two electronic states are mixed by coupling to promoting vibrations that break down the orthogonality of the Born–Oppenheimer states. This is just the radiationless transition in the weak coupling limit and seems to make difficult the detection of the normal-region-like behavior even at very small $-\Delta G_{\text{CR}}$ values for these ion pairs.

On the other hand, the temperature dependence of the k_{CR} vs $|\Delta G_{\text{CR}}|$ energy gap law in the weak coupling limit can be taken into account by incorporating the factor $(\bar{n}_M + 1)$ in the electrom-vibrational coupling constant S_M in γ as follows on the basis of the previous theoretical treatments on the radiationless transition.^{14,15}

$$\gamma = \ln\{|\Delta G_{\text{CR}}|/\hbar\omega_M S_M(\bar{n}_M + 1)\} - 1 \quad (6a)$$

$$(\bar{n}_M + 1) = [1 - \exp(-\hbar\omega_M/k_B T)]^{-1} \quad (6b)$$

where \bar{n}_M is the population of the excited vibrations with frequency ω_M at thermal equilibrium.

In the case of the high-frequency modes of ω_M vibrations, the low-temperature limit in the weak coupling case as given by eqs 5a and 5b may be a satisfactory approximation. Also, at sufficiently low temperature, $(\bar{n}_M + 1)$ converges to unity and γ of eq 6a reduces to that of eq 5a. When contributions from such lower frequency modes as intermolecular (interions in the pair) vibrations become effective for the CR process, consideration of the factor of eq 6b in γ as indicated in eq 6a may be necessary at room temperature. In such a case, the factor $(\bar{n}_M + 1)$ will be distinctly larger than unity, leading to the smaller γ value compared with that at the low-temperature limit. Therefore, the thermal excitation of the low-frequency modes of the intermolecular vibrations seems to cause the more gentle slope in the k_{CR} vs $|\Delta G_{\text{CR}}|$ energy gap relation at room temperature than the low-temperature limit.

In relation to the above arguments, it is worth noting here the recent result of laser photolysis studies on the energy gap dependence of the CR process in several CT crystals.^{17,18} These papers have reported that the energy gap dependence of k_{CR} shows the linear relation between the $\ln(k_{\text{CR}})$ and ΔG_{CR} also in the crystalline phase. Moreover, recent detailed analysis of the dynamics of CR processes indicated that much steeper slope (large β) was obtained for the crystalline phases compared to those obtained in various solutions.^{8,9} Since the local intermolecular vibrations in the DA pair may be rather severely restricted in the crystalline phase, the above result indicates that the intermolecular reorganization in the DA pair plays an important role in the steepness of the slope as discussed above. At low temperature in the adsorbed systems, also the low-frequency modes may be partially or entirely frozen, which, actually, results in a rather steep slope at low temperature as shown in Figure 7.

As discussed to some extent already in the first section, it was revealed previously that the Stokes shift between the CT absorption and CT fluorescence of the DA complexes in almost nonpolar solution increased with increase of the energy gap for the CR transition.²² This result means that the reorganization

energy for the CR increases with increase of the energy gap. The same tendency has been observed also in the adsorbed state as demonstrated in the comparison of the An–TCNB system with the Np–TCNB system. In these adsorbed systems, the reorganization energies may be contributed to by the intracomplex low-frequency modes and intramolecular high-frequency ones as discussed also in the previous sections.

The intracomplex low-frequency modes may play an important role also for determining the temperature dependence of the CR transition as discussed above in terms of eqs 6a and 6b. Namely, at higher temperatures, the populations of energy levels of low-frequency modes may be broadened facilitating the vibrational overlapping of the acceptor modes,³⁵ which will lead to the enhanced tunneling to the ground state. On the other hand, at low temperatures, they may be shunk or frozen leading to the decreased tunneling probability for the CR transition. Hence, the extent of such decrease of the CR rate by temperature lowering may be more remarkable for the system with larger reorganization energy, as observed in Figures 6 and 7.

By summarizing above results and discussion, it may be concluded that for such energy gap dependence in solutions as well as in the adsorbed systems, the intramolecular high-frequency quantum modes and some low-frequency intracomplex vibrational modes predominate in the CR process of these ion pairs produced by the excitation of the ground-state CT complex. The decrease in the temperature freezes these low-frequency modes partially or entirely, and high-frequency modes seem then to be effective in promoting CR, which causes a rather steep slope in the energy gap dependence of CR in the adsorbed state at lower temperature.

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References and Notes

- (1) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265.
- (2) Mataga, N. *Pure Appl. Chem.* **1984**, *56*, 1255. (b) Mataga, N. *Pure Appl. Chem.* **1993**, *65*, 1606. (c) Mataga, N.; Hirata, Y. In *Multiphoton Processes and Spectroscopy*; Lin, S. H., Ed.; World Scientific: London, 1989; Vol. 5, p 175. (d) Mataga, N.; Miyasaka, H. *Prog. React. Kinet.* **1994**, *19*, 317.
- (3) Rips, I.; Klafter, J.; Jortner, J. In *Photochemical Energy Conversion*; Norris, J. R.; Meisel, D., Eds.; Elsevier: New York, 1988; p 1.
- (4) Barbara, P. F.; Jarzeba, W. *Adv. Photochem.* **1990**, *15*, 1.
- (5) Rehm, D.; Weller, A. (a) *Ber. Bunsen-Ges. Phys. Chem.* **1969**, *73*, 834. (b) *Isr. J. Chem.* **1990**, *15*, 1.
- (6) (a) Miller, J. R.; Calcaterra, L. T.; Closs, G. L. *J. Am. Chem. Soc.* **1984**, *106*, 3074. (b) Closs, G. L.; Miller, J. R. *Science* **1988**, *240*, 440.
- (7) (a) Mataga, N.; Kanda, Y.; Okada, T. *J. Phys. Chem.* **1986**, *90*, 3880. (b) Mataga, N.; Kanda, Y.; Asahi, T.; Miyasaka, H.; Okada, T.; Kakitani, T. *Chem. Phys.* **1988**, *127*, 239. (c) Mataga, N.; Kanda, Y.; Asahi, T.; Okada, T.; Kakitani, T. *Chem. Phys.* **1988**, *127*, 249.
- (8) (a) Asahi, T.; Mataga, N. *J. Phys. Chem.* **1989**, *93*, 6575. (b) Asahi, T.; Mataga, N. *J. Phys. Chem.* **1991**, *95*, 1956.
- (9) Asahi, T.; Mataga, N. *J. Phys. Chem.* **1991**, *95*, 1956.
- (10) Gould, I. R.; Young, R. H.; Moody, R. E.; Farid, S. *J. Phys. Chem.* **1991**, *95*, 2068.
- (11) (a) Islampour, R.; Alden, R. G.; Wu, G. Y. C.; Lin, S. H. *J. Phys. Chem.* **1993**, *97*, 6793. (b) Lin, S. H.; Alden, R. G.; Hayashi, M.; Suzuki, S.; Murchison, H. A. *J. Phys. Chem.* **1993**, *97*, 12566.
- (12) (a) Jortner, J.; Bixon, M.; Heitele, H.; Michel-Beyerle, M. E. *Chem. Phys. Lett.* **1992**, *197*, 131. (b) Bixon, M.; Jortner, J.; Cortes, J.; Heitele, H.; Michel-Beyerle, M. E. *J. Phys. Chem.* **1994**, *98*, 7289.
- (13) Tachiya, M.; Murata, S. *J. Am. Chem. Soc.* **1994**, *114*, 2434.
- (14) Englman, R.; Jortner, J. *Mol. Phys.* **1970**, *18*, 145.
- (15) Freed, K. J.; Jortner, J. *J. Chem. Phys.* **1970**, *52*, 6272.

- (16) (a) Meyer, T. J. *Prog. Inorg. Chem.* **1983**, 30, 389. (b) Chen, P.; Duesing, R.; Tapolsky, G.; Meyer, T. J. *J. Am. Chem. Soc.* **1989**, 111, 8305. (c) Chen, P.; Duesing, R.; Graff, D. K.; Meyer, T. J. *J. Phys. Chem.* **1991**, 95, 5850.
- (17) Miyasaka, H.; Kotani, S.; Itaya, A. *J. Phys. Chem.* **1995**, 99, 5757.
- (18) Hubig, S. M.; Kochi, J. K. *J. Phys. Chem.* **1995**, 99, 17578.
- (19) Asahi, T.; Matsuo, Y.; Masuhara, H.; Koshima, H. *J. Phys. Chem.* **1997**, 101, 612.
- (20) Miyasaka, H.; Moriyama, T.; Kotani, S.; Muneyasu, R.; Itaya, A. *Chem. Phys. Lett.* **1994**, 225, 315.
- (21) Schweitzer, G.; Xu, L.; Craig, B.; De Schryver, F. C. *Opt. Commun.*, in press.
- (22) Mataga, N.; Murata, Y. *J. Am. Chem. Soc.* **1969**, 91, 3144.
- (23) Shida, T. *Electronic Absorption Spectra of Radical Ions*; Elsevier: Amsterdam, 1988.
- (24) Miyasaka, H.; Ojima, S.; Mataga, N. *J. Phys. Chem.* **1989**, 93, 3380.
- (25) Egawa, K.; Nakashima, N.; Mataga, N.; Yamanaka, C. *Bull. Chem. Soc. Jpn.* **1971**, 44, 3287.
- (26) Nagakura, S. In *Excited State*; Lim, E., Ed.; Academic Press: New York, 1975; Vol. 2, p 321.
- (27) (a) Masuhara, H.; Tsujino, N.; Mataga, N. *Chem. Phys. Lett.*, **1972**, 12, 481. (b) Masuhara, H.; Mataga, N. *Chem. Phys. Lett.* **1973**, 22, 305.
- (28) Ojima, S.; Miyasaka, H.; Mataga, N. *J. Phys. Chem.* **1990**, 94, 7534.
- (29) (a) Kulinowski, K.; Gould, I. R.; Myers, A. B. *J. Phys. Chem.* **1995**, 99, 9017. (b) Kulinowski, K.; Gould, I. R.; Ferris, N. S.; Myers, A. B. *J. Phys. Chem.* **1995**, 99, 17715.
- (30) McHale, J. L.; Merriam, M. J. *J. Phys. Chem.* **1989**, 93, 526.
- (31) Klafter, J.; Shlesinger, M. F. *Proc. Natl. Sci. U.S.A.* **1986**, 83, 848.
- (32) Kubo, R.; Toyozawa, Y. *Progr. Theor. Phys.* **1955**, 13, 160.
- (33) Wynne, K.; Galli, C.; Hochstrasser, R. M., *J. Chem. Phys.* **1994**, 100, 4797.
- (34) Wynne, K.; Reid, G. D.; Hochstrasser, R. M. *J. Chem. Phys.*, to be published.
- (35) Chen, P.; Mecklenburg, S. L.; Meyer, T. J. *J. Phys. Chem.* **1993**, 97, 13126.