Picosecond Recombination Dynamics of Electrons in Ionic Liquids

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We report picosecond transient optical-absorption decays for electrons localized in F-center analogs in molten KCl and KBr. Absorption decays were recorded for 750 ps after electron-hole generation by a 266-nm ultraviolet pulse. The recombination process is analyzed in terms of reactions involving the anionic hole centers X_2^- and X_3^- where $X=$Cl or Br. The results confirm by direct real-time measurement that F-center electrons are sufficiently mobile to account for the electronic conductivity observed in dilute metal–molten-salt solutions. This demonstrates the necessary presence of a new polaronlike transport mechanism involving diffusive modes of ionic motion.

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Low concentrations of electrons in molten alkali halides provide particularly simple systems for the study of electron localization and transport in disordered media. Electrons introduced by interband excitation, electrolytic injection, or addition of small amounts of metal to the salt find themselves in a structure lacking long-range order but exhibiting a high degree of short-range chemical order. The latter is a consequence of the strong, unscreened Coulomb interactions present in these systems. A variety of experiments and calculations have now confirmed an early suggestion by Pitzer[1] that electrons in molten alkali halides form localized states analogous to F centers in alkali halide crystals.[2] Strong optical-absorption bands[3-6] in the red or near-infrared range are attributed to electronic excitation to the first excited state in the potential well provided by the coordinating shell of positive ions.[7]

Although the static structure of the localized electronic states in molten alkali halides is represented quite well by the F-center model, the dynamics of these states are less clear. The electrons are "localized" in the sense that electron-ion correlation times derived from NMR studies[8,9] are roughly 1000 times longer than typical of metals, yet some of the electrons, at least, are sufficiently mobile to provide substantial electronic conductivity in dilute metal-salt solutions.[10] Average mobilities determined from the conductivity are on the order of 0.1 $\text{cm}^2/\text{V s}$, exceeding ionic mobilities by about 2 orders of magnitude. Because the optical transition energies and, hence, the binding energies in the static liquid structure greatly exceed thermal energies, such rapid transport of F-center electrons inevitably requires substantial help from ionic motions. Such a mechanism may be viewed as analogous to polaron motion in solids, but it is likely to involve diffusive as well as vibrational motions. Alternatively, existing data also permit a heterogeneous transport model in which the optical bands result from a subset of electrons in relatively stable (nanosecond) F-center complexes while the conductivity is provided by the remainder in delocalized states.

In this paper we describe optical transient absorption experiments that provide the first submicrosecond real-time observations of electron dynamics in molten salts.[11] We have recorded the decay of absorption at 1064 nm for 750 ps after creation of F centers in molten KCl and KBr by ultraviolet (266 nm) pulses. The feasibility of this type of experiment had previously been indicated by the work of Williams, Bradford, and Faust[12] who observed reduced transmission at 532 nm in molten KCl 46 ps after excitation. However, their probe wavelength was far from the center of the F band and they did not investigate the time dependence of the induced absorption. We find substantially more rapid recombination in KBr than in KCl and we were unable to observe transient absorption in KI and CsI. We present an analysis of the recombination process that reflects the chemistry of the anion species (hole centers), explaining this trend and showing that the optically absorbing localized states are sufficiently mobile to provide the observed electronic conductivity.

The experiments were carried out by use of a pulsed yttrium-aluminum-garnet laser system providing pulses of 30–50-ps widths at a repetition rate of 10 Hz. After twice doubling the frequency of the 1064-nm fundamental we obtained 50–100 μJ of excitation pulse power at 266 nm. A pyroelectric detector measured the intensity of the delayed 1064-nm probe pulse and the signal was normalized by a reference signal to correct for drifts in the laser output level. We made an additional correction for baseline variations along the optical delay line. Our samples were contained in cells made of fused quartz with 1-mm walls and 1-mm optical path length. We made measurements using cells sealed under vacuum as well as some that were open to the atmosphere and we found no significant difference in the transient absorption signals. The necessary high-temperature environment was provided by an electrically heated furnace contained in a heavy nickel cylinder for homogenization of the temperature. The light beams passed through open ports in the furnace and nickel cylinder so that no windows were encountered other than the sample cells themselves.

A transient absorption signal for KCl at 800 °C is shown in Fig. 1 together with the pulse autocorrelation. An absorbance change $\{\Delta A = -\ln[I(t)/I(0)]\}$ of roughly 0.6 develops in a time comparable with the pulse width indicating that the absorbing species form in less than a few tens of picoseconds. Measurement at different excitation intensities showed that the absorbance change is roughly linear in the intensity. This indication that the excitation is predominantly a single-phonon process is expected since the excitation wavelength lies in the broad tail of the fundamental interband absorption edge. In solid alkali halides, in contrast, the 266-nm excitation energy lies below the band edge and creation of F centers necessarily requires two-photon absorption.[12] We estimated the initial concentration of absorbing species n_0 by assuming an effective absorption depth of 0.1 mm and taking the oscillator strength from studies of dilute K-KCl solutions.[6] The result, $n_0 = 8 \times 10^{18}$ e/cm^3, agrees within about a factor of 3 with an estimate based on the number of photons in the excitation pulse. We consider this level of agreement satisfactory in view of the difficulty of estimating the volume of excitation.

Our results for KBr at 750 °C are presented in Fig. 2 for two levels of ultraviolet intensity. It is clearly evident that the recombination process is substantially more rapid in KBr than in KCl (Fig. 1) and that the process is faster when the excitation intensity is higher. This latter observation demonstrates that recombination is nongeminate and suggests a bimolecular process with the formal expression

$$e^- + X^0 \xrightarrow{k} X^- \tag{1}$$

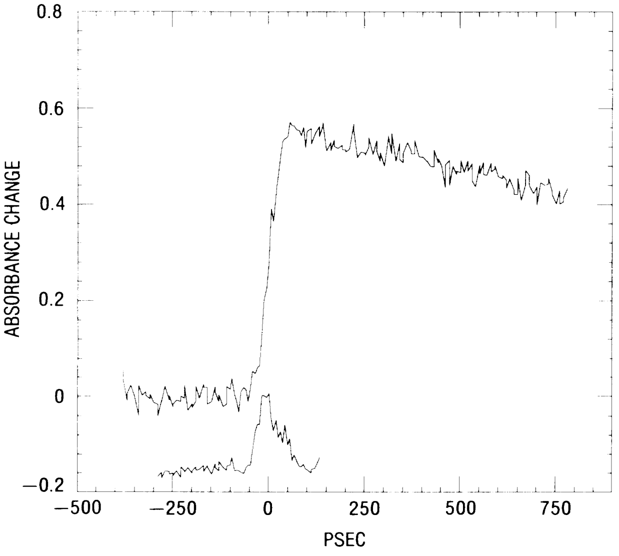

FIG. 1. Upper trace: 1064-nm transient absorption signal (absorbance change) from molten KCl at 800 °C. Lower trace: Pulse autocorrelation.

and rate constant k. Our inability to observe a transient absorption signal in the molten iodides is consistent with a trend toward progressively faster recombination in the series chloride, bromide, and iodide.

The absorption decays show qualitatively that in liquid KBr, at least, F-center electrons are relatively mobile. After excitation, half of the electrons are able to find recombination centers, at an average distance of about 50 Å, within 200 ps. Thus we find no evidence for stable, optically absorbing complexes in KBr. However, in order to relate the observations quantitatively to electronic motion and to understand the variations of the rates among different salts, we must consider the recombination process in more detail.

The simplest form of nongeminate recombination is described by Eq. (1) with $n(t) = [X^0]_t$. This leads to decay of the electron concentration according to

$$n(t) = n_0/(1 + kn_0 t). \tag{2}$$

A nonlinear least-squares fit of the KCl data in Fig. 1 gives a decay half-life $(kn_0)^{-1} = 2340 \pm 120$ ps or, for

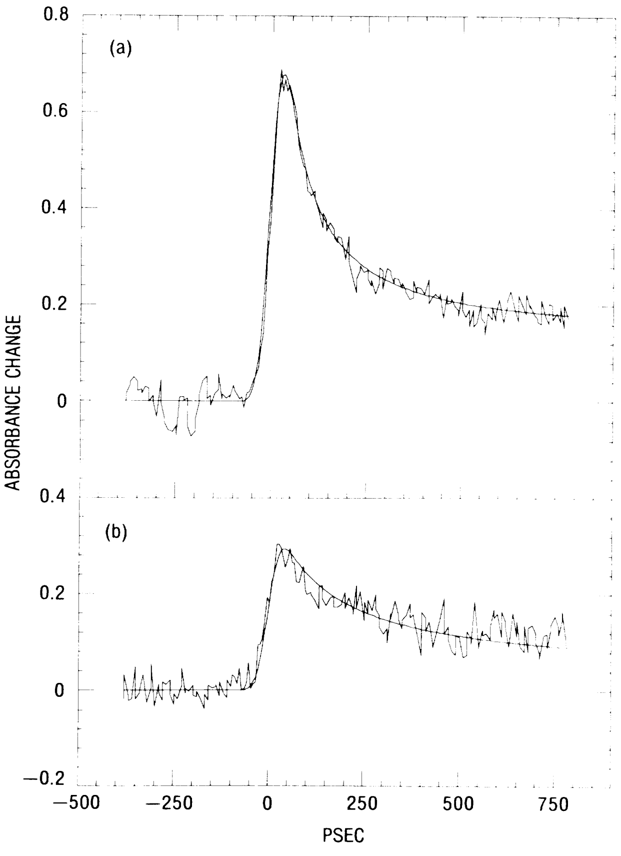

FIG. 2. Transient absorption signals from molten KBr at 750 °C for (a) higher and (b) lower excitation pulse intensities. Solid lines are electron concentrations obtained by numerical solutions of Eqs. (7) and (8) and convoluted with the pulse width.

$n_0 = 8\times10^{18}$ e/cm^3, a rate constant $(5.4\pm0.3)\times10^{-11}$ cm^3/s.

Our attempts to fit Eq. (2) to the KBr data gave unsatisfactory results. The observed decays systematically decrease more rapidly at short times than the "best fit" curves and they exhibit a long-time "tail" not predicted by Eq. (2). We suggest that the explanation is related to additional reactions involving the recombination centers:

$$X^0 + X^- \rightarrow X_2^- \tag{3}$$

and

$$2X_2^- \xrightarrow{k_i} X_3^- + X^-. \tag{4}$$

Reaction (3) describes formation of the liquid-state analog of the V_K center, a well-known polaron formed by holes in alkali halide crystals. The formation of X_2^- by reaction (3) can be expected to be very rapid on our time scale because little translation motion of the hole (neutral halogen) is required, i.e., for low concentrations of holes, a halide ion X^- is always nearby. Reaction (4) is well known from studies of excess halogen in alkali halide melts[9,13] where it tends strongly to the right-hand side. Once formed, the dimers X_2^- are depleted by reaction (4) in competition with the direct recombination process

$$e^- + X_2^- \xrightarrow{k_e} 2X^-. \tag{5}$$

After depletion of the dimer concentration, electrons can recombine only vie the much slower third-order process

$$2e^- + X_3^- \rightarrow 3X^- \tag{6}$$

or its equivalent. Electron pulse experiments indicate, in fact, that F-center absorption persists for 1–2 μs.[11]

We have analyzed our data for KBr using a simple model based on reactions (4) and (5). We assume that all neutral halogens are converted rapidly to dimers by reaction (3) and that reactions (4) and (5) run to completion. Thus we neglect the small equilibrium concentration of dimers associated with reaction (4). The concentrations of electrons, dimers, and trimers then obey the following set of coupled differential equations:

$$dn/dt = -k_e n[X_2^-], \tag{7}$$

$$d[X_2^-]/dt = -k_i[X_2^-]^2 - k_e n[X_2^-], \tag{8}$$

$$d[X_3^-]/dt = \tfrac{1}{2}k_i[X_2^-]^2. \tag{9}$$

We solved these equations numerically and adjusted the three parameters n_0, k_e, and k_i for the best fit to the KBr data. The qualities of the fits were tested by comparison of the residuals with those of least-squares fits by the analytic form $n(t) = A/(1+Bt)+C$, equivalent to Eq. (2) with an additive constant. The results shown in Fig. 2 correspond to values of the rate constants $k_e = 1.2\times10^{-9}$ cm^3/s and $k_i = 0.25\times10^{-9}$ cm^3/s for both decays and to values of the initial concentrations of 1.6×10^{19} cm^{-3} and 0.5×10^{19} cm^{-3}, respectively, for Figs. 2(a) and 2(b). Concentrations were estimated from the initial absorbance with use of the molar extinction coefficient[6] for electrons in KCl since the corresponding value for KBr is not available. In Fig. 3, we show the evolution of the concentrations of electrons, dimers, and trimers corresponding to the parameters obtained from a fit to the data of Fig. 2(a). These curves show the expected depletion of the dimer population and the constant (in our model) concentrations of electrons and trimers at long times.

The rate constant k_e for reaction (5) is related to the diffusion coefficient for electrons, D_e, through a collision frequency

$$\nu_{\text{coll}} = 6D_e n_0^{2/3} \tag{10}$$

and activation energy E^*

$$k_e n_0 = \nu_{\text{coll}} \exp(-E^*/k_B T). \tag{11}$$

By assuming that $E^* = 0$, we can obtain a lower limit on D_e from values of k_e and n_0. The result for KBr is $D_e \gtrsim 5\times10^{-4}$ cm^2/s or roughly ten times the diffusion coefficient for single ions. Turning the argument around, we assume that D_e for the F-center electrons is the same as the average mobility, estimated from the conductivity, and now ask what must be the activation energy. Thus taking $D_e = 6\times10^{-3}$ cm^2/s, we find $E^*(\text{KBr}) = 0.22$ eV. A similar analysis for KCl yields $E^*(\text{KCl}) = 0.68$ eV. These are reasonable values for E^* which should be roughly the difference between the change of Coulomb energy on adding an electron to the dimer and the electron affinity of the dimer. The difference in the rate of decay in this interpretation is thus due to the higher activation energy for KCl relative to KBr rather than to

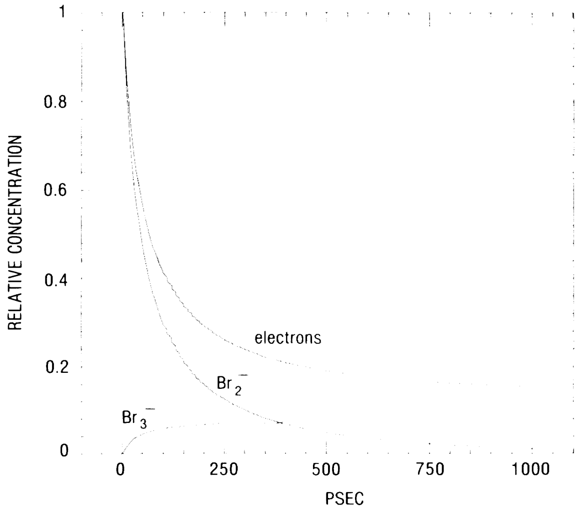

FIG. 3. Relative concentrations of electrons, dimers (Br_2^-), and trimers (Br_3^-) corresponding to parameters of the fit shown in Fig. 2(a) for molten KBr at 750 °C.

any significant difference in the electron mobility. We note that if E^* for the iodides is of order 0.1 eV, Eq. (11) predicts a decay time $k_e n_0$ of about 10 ps for an initial electron concentration of 1×10^{19} e/cm^2. Such a rapid decay would explain our inability to observe a transient absorption signal in molten iodides.

In summary, we have described a first picosecond optical study of electron recombination dynamics in ionic liquids. We conclude that electrons "localized" in F-center analogs are significantly more mobile than the surrounding ions and, for reasonable values of the recombination activation energies, the inferred electron diffusion rates are consistent with the electrical conductivity. This result necessitates a mechanism for electron transport in which ionic motion assists the electrons to escape from the F-center potential well, i.e., polaron transport. A conventional vibrational model of polaron transport as applied to solids, however, is unlikely to be appropriate in ionic liquids. The fact that electron-ion correlation times obtained from NMR (~ 1 ps) are comparable with the time scale for ionic diffusion implies, instead, that diffusive modes play an important role in this process. A transport mechanism of this character has recently been observed in simulations by Selloni *et al.*,[14] who combine a molecular-dynamics description of the liquid structure with quantum treatment of the electronic state. Their results show F-center electrons jumping to a new location after 2–3 ps as a result of ionic motions. This simulated behavior is completely consistent with our observations.

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