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# RADICAL CATIONS IN RADIATION CHEMISTRY OF LIQUID HYDROCARBONS

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# RADICAL CATIONS IN RADIATION CHEMISTRY OF LIQUID HYDROCARBONS*

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**ABSTRACT.** The state of knowledge concerning radical cations in liquid alkanes is discussed with particular emphasis on those which exhibit high mobility. Uncertainty has existed in the interpretation of previous results with respect to the nature and reactivity of high mobility ions, especially for cyclohexane. Recent time-resolved studies on pulse radiolysis/transient absorption, photoconductivity, and magnetic resonance in these systems have led us to propose new mechanisms for the high mobility ions. In decalins, scavenging of these ions by solutes is a pseudo-first-order reaction. In cyclohexane, the behavior is more complex and is indicative of the involvement of two species. This bimodality is rationalized in terms of a dynamic equilibrium between two conformers of the solvent radical cation. Several experimental tests supporting these views include a recent study on two-color laser photoionization in cyclohexane.

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The interaction of fast electrons or UV photons with matter results in excitation and ionization of molecules. Electron-hole pairs are produced; these charges are the first observable transients in addition to excited molecules. The medium determines the distance distribution of electron-hole pairs by controlling the rate of thermalization, which typically occurs with rate constant of ~ 1 eV/ps. During this stage, the mobilities of charge carriers are ~ 1-10 $cm^2/Vs$. In liquid alkanes, the thermalization distance is ~ 5-7 nm which is shorter than the Onsager radius (20-30 nm). Hence, few charged species escape the mutual Coulombic field (< 5-10 %). After thermalization, the solvated electron and its partner recombine, transform, or react with the medium (the solvent) and the solutes. As a rule, the mobility of thermalized electrons is at least an order of magnitude higher than the mobility of self-trapped holes (solvent radical cations). Unless the electrons are scavenged by solute, most of the radical ion pairs recombine within 100 ps after their formation. In the presence of electron scavengers, this recombination is slowed down and geminate ions can be observed. Of course, scavenging does not change the yield of free ions; these ions can be detected many microseconds after the ionization event.

At the present time, the reactions of thermalized (solvated) electrons are known in much detail. Our understanding of radical cations and their chemistry lags far behind. While low-temperature matrix-isolation studies helped to characterize the structure and electronic properties of various radical cations,[1] only time-resolved studies can unravel their chemistry in liquids.

Recent studies in our group have focused on solvent radical cations in alkanes. In particular, we studied cycloalkanes (cyclohexane and *cis*- and *trans*-decalin) which yield high mobility ions (HMI). HMI are ions whose migration is much faster than the rate of molecular diffusion. Such a situation is possible if the hole migrates by hopping between the neighboring molecules. In solids, hopping is the main mechanism of charge transfer. In liquids, molecular diffusion is usually faster, and the phenomenon of HMI is rare. Long-lived HMI can be detected by transient microwave and dc conductivity. Naturally, liquids yielding HMI are the ones in which the hole transport is most efficient. The study of this extreme case illuminates the role of charge transfer in radiation chemistry of nonpolar liquids in general.

To study short-lived solvent radical cations in alkanes, various fast detection techniques have been employed. Because the holes in cycloalkanes are very mobile, they can be studied in ways that are not possible for other ions. In our work, this advantage is fully exploited. We will first discuss the detection techniques that were used. Then, we will summarize our recent studies on HMI and, more generally, the fate of solvent holes in liquid alkanes.

## Observation of solvent radical cations in alkanes

*Transient absorption.* The fastest of the detection techniques is transient absorption. It provides a sensitive means of detection of solvent radical ions generated by pulse radiolysis. In our studies, we used 10-30 ps pulses of 10-20 MeV electrons from the Argonne Chemistry Division linear accelerator. Doses as high as 100 Gy per pulse can be achieved, which typically yields a transient absorbance of $10^{-3}$-$10^{-2}$.

In order to extend the lifetime of geminate ions, the alkane solutions were saturated with a gaseous electron scavenger, such as $N_2O$, which also serves as a quencher of excited molecules formed on recombination of electron-hole pairs. In spite of that, in the first nanosecond after the radiolytic pulse the absorption signal from the excited states overlaps with the signal from the solvent holes. Typically, both of these species have broad featureless UV-VIS spectra which can be distinguished only on the basis of the decay kinetics. The same problem exists at later times, as many long-lived secondary ions are present in the radiolysate. Ion-molecule and charge-transfer reactions in spurs further complicate the kinetics. In the studies of long-lived HMI, the decay kinetics are shortened due to their reactions with radiolytic products generated by the same pulse.

Because of these complications, most of what is known about the kinetics of solvent holes comes from scavenging experiments. Aromatic molecules (Ar) whose radical cations ($Ar^{\bullet+}$) yield well-characterized, narrow-line VIS spectra are added to the solution, and the formation kinetics of $Ar^{\bullet+}$ formed upon electron transfer to the solvent hole is studied. We used this approach to estimate the lifetime of the precursor of $Ar^{\bullet+}$.

*FDMR.* The lifetimes of solvent radical cations in liquids are short, and magnetic resonance experiments using conventional EPR are not possible. Fluorescence-Detected Magnetic Resonance (FDMR) is a spectroscopy in which microwave (μw) -induced spin transitions are observed through the change in the yield of singlet luminescence generated in recombination of radical ion pairs or trapped electrons and holes.[2,3] In order to observe FDMR, a resonant μw field is applied to induce spin transitions between the middle ($T_0$) and the upper and lower triplet sublevels of radical ion pairs. These triplet states are decoupled in the strong magnetic field of the spectrometer. Only the $T_0$ state is close in energy to the singlet state (S). The S and $T_0$ states are rapidly interconverted by the nuclear hyperfine interaction (hfi) in radical ions. Shortly after the generation of the pair the S state and the $T_0$ state become equally populated (~10-50 ns). The μw-induced spin transitions deplete the $T_0$ state and shift the singlet-triplet equilibrium towards the triplet manifold. Consequently, the μw field decreases singlet recombination and the luminescence yield. Importantly, cross-recombination (which yields statistical distribution of singlet and triplet random pairs) does not contribute to FDMR; i.e., only geminate pairs are observed.

In our laboratory, we have developed *time-resolved pulsed* FDMR.[3,4] With this technique, radical ion pairs are generated by 5-10 ns pulses of 3 MeV electrons, and the decay kinetics of luminescence is studied as a function of the pulsed μw field. The FDMR signals can be observed as early as 30 ns after the formation of electron-hole pairs. Only localized electronic states can be studied by FDMR. To obtain a high yield of photoluminescence, aromatic solutes are added to scavenge thermalized electrons and holes ($h^+$). Since electrons are scavenged more rapidly, most of the FDMR signal comes from the [$Ar^{\bullet -}$ $h^+$] pairs. By using deuterated solutes whose radical anions exhibit narrow EPR lines, it is possible to resolve the hyperfine structure of the holes in much detail.

FDMR experiments on neat alkanes indicate that the solvent radical cations are short-lived, as they readily undergo proton-transfer reactions. Such reactions were often observed by EPR in low-temperature hydrocarbons. In addition to proton transfer, other types of reactions involving radical cations were observed using FDMR. A partial list of these reactions includes fast rearrangements, fragmentation, loss of $H_2$ and formation of an olefin ion, aggregation of olefin ions with olefins, (resonant) charge transfer, etc. (see Figure 1).

To retard some of these reactions, we found it necessary to dilute the alkane of interest with a solvent of higher ionization potential (IP). In dilute solution, the radical cation of the alkane with the lower IP becomes isolated, and the ion-molecule reactions with like molecules are inhibited. This strategy worked in most cases, but there were notable exceptions. For cyclohexane and *trans*-decalin, we were not able to stabilize the radical cations even in dilute cold solutions ($T > 190$ K). This is surprising, since in *n*-hexane solution the radical cation of *cis*-decalin can be observed even at room temperature.[4]

*Transient conductivity.* Transient conductivity is specific to charged species. This technique exists in two varieties. With μw conductivity, the ions are detected by absorption of μw power. The signal is a product of concentration and mobility of the ions being detected. With direct current (dc) conductivity, an electric field is applied and the displacement current induced by the drift of ions is measured. The dc conductivity is a more complex quantity than μw conductivity due to the effects of geminate recombination on the charge distribution.[5] At the present time, these effects are well understood[6] and the analysis of dc conductivity is as straightforward as that of the μw conductivity.

In our studies, we champion the use of dc conductivity because with this technique very low concentrations of ions (~ $10^{-9}$ mol $dm^{-3}$) can be routinely measured. This sensitivity allowed us to complement the μw conductivity - pulse radiolysis studies carried out by the Delft group[7,8] with studies on multiphoton laser ionization.[5] In a typical photolytic experiment, a beam of a few to several hundred mJ/$cm^2$ of 4 eV or 5 eV photons from an excimer laser passes through the sample between planar electrodes (~ 8kV/cm). The displacement current is amplified and averaged using a digital signal analyzer; the rise time of the measuring system is on the order of a nanosecond. Currently, we are using a second (probe) pulse of 2.3 eV photons to study the ionization mechanism in further detail.

The conductivity signal from thermalized electrons is always stronger than the signal from molecular ions. Therefore, electron scavengers must be added in order to measure conductivity of ions. With transient conductivity, it is impossible to distinguish between the molecular cations and anions, or different cations, if these species have similar mobilities. Only in the situation where the hole has high mobility (as in cycloalkanes) does the transient conductivity provide a means of selective observation of solvent radical cations.

## HMI in cycloalkanes

With transient conductivity, HMI in cycloalkanes can be observed for hundreds of nanoseconds. These HMI are very mobile (~ $10^{-2}$ $cm^2/Vs$) and reactive. The formation rate of $Ar^{\bullet +}$ determined by transient absorption spectroscopy is in excess of $10^{11}$ $mol^{-1}$ $dm^3$ $s^{-1}$. Similar scavenging constants were obtained for HMI in μw conductivity experiments.[7,8] These results imply that HMI are indeed the solvent radical cations involved in rapid resonant charge transfer.[9,10,11] However, our FDMR results indicate that the holes are too short-lived to be the HMI detected in conductivity experiments.[4,12] This led us to speculate on other mechanisms of long-term charge transport such as fast proton hopping.[13,14]

Recently, we have undertaken an extensive series of experiments in order to resolve this conundrum.[15,16,17] In order to explain the apparent dichotomy in the HMI lifetimes in cyclohexane as measured by different techniques, we postulate an equilibrium between conformer/isomer radical cations. Before we discuss the recent findings, we digress to examine prior results on laser-induced conductivity and FDMR.

*a) HMI studied by transient dc photoconductivity.* An example of the signals obtained by the dc conductivity method is shown in Figure 2.[18] The results from several systems are normalized so that the free ion levels are all at about 0.6 nS $cm^{-1}$. From these results one can see qualitatively the large signals from HMI in cyclohexane and decalin systems in comparison with *n*-hexane, where the signal in the 40 ns to 2 μs regime is much smaller. The HMI decay mainly by reaction with impurities and have half-times of ≈500 ns in cyclohexane and 1-5 μs in decalins.

The dependence of the conductivity on the photon flux can be used to determine the photon order of ionization. Results on the dc conductivity in liquid cycloalkanes, with and without aromatic and electron-scavenging solutes, were used to determine the yields of thermalized electrons, HMI, and normally-diffusing ions.[18] For neat cyclohexane and *trans*-decalin, we found that two 5 eV photons and three 4 eV photons are needed for ionization. For anthracene solutions in cyclohexane, three 4 eV or 5 eV photons are required to produce HMI, but only two such photons are needed to ionize the aromatic solute. The latter observation means that $Ar^{\bullet +}$ produced by two-photon ionization absorbs a third photon, promoting charge transfer to the solvent. Our experiments indicate that a substantial fraction of HMI produced from Ar•$^+$ escapes scavenging by the resulting geminate aromatic molecule, presumably due to the long thermalization distance of the solvent hole (we are investigating this mechanism further by using a second laser pulse (different wavelength and delayed with respect to the first) to excite Ar•$^+$, thereby causing an increase in the conductivity from HMI). Importantly, the decay kinetics of HMI do not change if one uses deuterated solutes. Since resonant proton transfer exhibits large isotope effects, this observation suggests that the mobile charge carrier is not the proton.

In decalins, whose IP is lower than that of cyclohexane (9.24 eV *(trans)* and 9.26 eV *(cis)* vs 9.88 eV, respectively),[19] solvent ionization can be two-photon even in the presence of a light-absorbing aromatic solute. In decalin solutions with added benzene, two-photon excitation of benzene with 5 eV photons results in the formation of HMI with 100% efficiency. The IP of benzene is less than 10 meV higher than that of *trans*-decalin.[19] Toluene, which has a lower IP of 8.82 eV, does not yield HMI in a two-photon process. These energetics suggest that in decalins, HMI are solvent radical cations. In both cycloalkanes, HMI were found to react with oxygen with a rate of (2-3)x$10^8$ mol$^{-1}$ dm$^3$ s$^{-1}$. This reaction cannot be charge transfer or proton transfer. The H atom transfer is exothermic only if the HMI is a solvent radical cation.

Conductivity signals such as those shown in Figure 3 were used to estimate the fraction of the cations which initially have high mobility.[18] The conclusion was reached that only 35% of the cations in cyclohexane photoionization have high mobility. A more accurate analysis of the conductivity signals has been done in more recent work.[15] In this we suggest an equilibrium mechanism to explain the behavior of HMI in cyclohexane, and the results of the analysis indicate that more than 70% of the cations produced by photoionization of neat cyclohexane have high mobility. Similar experiments using radiolysis indicate that less than 50% of the cations have high mobility.

*b) Time-resolved pulsed FDMR studies.* FDMR can contribute to the studies on HMI in alkanes in three ways. First, by using FDMR one can identify the hole as a radical cation with known EPR structure. Second, by following the spectral changes on addition of solutes one can demonstrate fast scavenging of mobile holes. Third, by studying the FDMR lineshape one can observe the spectral diffusion due to the hopping of electron spin between molecules with different orientations of nuclear spins in protons. For simplicity, assume that in the absence of hopping the EPR spectrum of the hole is an inhomogeneously broadened singlet with the spectral width of $\Delta$. Then, the appearance of spectral diffusion in the EPR spectrum would depend on the hopping rate ($\tau_h^{-1}$) *versus* the rate of spin transitions induced by hfi of the electron spin with protons ($\sim \Delta$). If the hopping rate is high ($\Delta\tau_h \ll 1$), then the electron spin does not interact with protons and the EPR line collapses to a narrow line. These structureless lines are easy to confuse with FDMR signals from aromatic, impurity, and secondary ions. In the opposite limit, $\Delta\tau_h >> 1$, the electron spin interacts with many protons on the timescale of μw-induced transitions; these interactions result in the broadening of the resonance line. One would expect that by lowering the temperature (increasing $\tau_h$) it would be possible to observe a gradual change from the narrowing to the broadening regime.

It is our belief that the hopping due to resonant charge transfer occurs in all hydrocarbons. However, for the hopping at 300 K to be faster than molecular diffusion it must occur with $\tau_h < 1$ ps. Since the typical $\Delta$ is ~ 1 GHz, the FDMR from HMI cannot be observed, even if these HMI are long-lived. To make the FDMR detection of alkane holes even more problematic, in many hydrocarbons the lifetime of the solvent holes is short (1-30 ns). The solvent holes are either too short-lived or hop too fast to be detected by FDMR reliably.

In principle, the hopping rate can be reduced by cooling of the liquid or dilution with an "inert" solvent with high IP (whose holes transfer charge to the molecules of the studied hydrocarbon). The problem is that in liquid alkanes which yield HMI the hopping is not thermally activated, so the anticipated reduction in the hopping rate occurs only below the glass transition or melting point, i.e., when the holes are deeply trapped. As for dilution, it is difficult to completely rule out reaction with the solvent.

In the past we combined both of these strategies (dilution *and* cooling) in order to resolve the resonance lines of alkane radical cations, with some success. Cooled *n*-pentane and *n*-hexane were used as solvents. The resolved FDMR spectra of methylcyclohexane$^{\bullet+}$ and *cis*-decalin$^{\bullet+}$ (which exhibit high-mobility at 300 K) can be obtained in this fashion, while *trans*-decalin$^{\bullet+}$ can be observed only in the solid.[4] In neat hydrocarbons, the holes of methylcyclohexane and *cis*-decalin are much less mobile than the holes of cyclohexane and *trans*-decalin. Hence, more dilute solutions must be used for the latter two alkanes in order to slow down the hopping. The solvent radical cations in *n*-alkanes rapidly fragment yielding $H_2$ and olefin radical cations. Though some of these olefin ions have higher IP than decalins, it seems very likely that these ions do not transfer charge to decalins. Indeed, from the conductivity studies, it is known that HMI in neat decalins are *scavenged* by olefins.[8] Thus, precisely for those cycloalkanes which exhibit the lowest $\tau_h$, it is difficult to generate sufficient concentration of the holes in dilute *n*-alkane solutions.

We conclude, that *direct* FDMR evidence of the existence of long-lived HMI in liquid alkanes is lacking. Still there is a possibility of indirect detection. FDMR observation of rapid hole scavenging was reported for a viscous alkane, squalane, in which the short-lived hole (~ 25 ns) diffuses 4 times faster than molecular ions.[20] Since the scavenging kinetics is much easier to study by using transient absorption spectroscopy,[21] the use of FDMR is hardly justified.

However, time-resolved FDMR is indispensable in the studies of recombination dynamics in frozen molecular solids, such as alkane glasses. At very low temperature (4-50 K) the primary holes are stable, the hopping is slow, and the FDMR spectra positively identify the holes as alkane radical cations. No dilution is needed to observe the holes below 100 K. Since at cryogenic temperatures the thermally-activated diffusion is stalled, the charges migrate by tunneling between the nearest trapping sites. On the timescale of our time-resolved FDMR experiments (< 5 μs after the radiolytic pulse) the electrons are not fully thermalized, residing in shallow traps at the tail of the conduction band. These band-tail electrons have large localization radii (0.2-0.5 nm) and the recombination kinetics is dominated by their long-range tunneling to deeper traps (such as the solute molecules, defects, and holes). The hopping of holes adds marginally to the overall recombination kinetics. By observation of spectral diffusion in the FDMR signals from the holes, it is possible to estimate the residence time $\tau_h$ of the hole on a single molecule. These times vary between $10^{-5}$-$10^{-7}$ s. The hopping can be observed both in vitreous and microcrystalline solids. It seems that it comprises the rule, like the related process in semiconductors.

From the general studies of hopping in disordered systems, one would expect that in frozen alkanes the holes hop only to the lower-energy sites, in descending order. Subtle differences between conformers (on the order of 100 μeV) can direct such transfers. Another view of the hole is that of a massive small polaron strongly coupled to the lattice. The mobility of such polarons is expected to be temperature-independent below 20-30 K, in agreement with experiment. Both of these concepts suggest that the hopping must be faster in polycrystalline solids in which the neighboring alkane molecules and the corresponding trapping sites have close geometries. Supporting this view, the maximum hopping rates were observed in crystalline short-chain paraffins, whereas vitreous cycloalkanes (e.g., decalins and methylcyclohexane) exhibit fairly low hopping rates. This situation is opposite to that observed in the liquid: normal alkanes, due to their pronounced conformational isomerism, exhibit much slower hopping rates than conformationally-frozen cycloalkanes. Further FDMR experiments, especially at very low temperatures, are needed to elucidate the exact mechanisms of hole transport.

## Recent time-resolved studies and the equilibrium mechanism

*Cyclohexane.* The study of transient absorption kinetics in radiolysis of $N_2O$-saturated cyclohexane was carried out in the 0.5-100 ns time regime.[16] The absorption spectra indicate that there are at least three cations present. Only one of them exhibits high mobility behavior; scavenging of the HMI with ethanol and triethylamine proceeds with rate constants of $9 \times 10^{10}$ $mol^{-1}$ $dm^3$ $s^{-1}$ and $2.3 \times 10^{11}$ $mol^{-1}$ $dm^3$ $s^{-1}$, respectively. The spectrum of this HMI is similar to the spectrum of the radical cation of cyclohexane observed in low-temperature matrices. This ion could not be observed after about 50 ns. With added pyrene and perylene we observed fast growth in absorption from $Ar^{\bullet+}$. We found no indication that proton adducts or other solute cations (e.g., alkylbenzonium ions) were formed rapidly. Comparison with results using Monte Carlo methods yields a scavenging constant $k_{HM}$ of 4 x $10^{11}$ $mol^{-1}$ $dm^3$ $s^{-1}$ and a lifetime of 30 ns for the precursor of $Ar^{\bullet +}$. The other two ions exhibit scavenging rate constants with ethanol and triethylamine of $10^{10}$ $mol^{-1}$ $dm^3$ $s^{-1}$. The short lifetime of HMI in neat cyclohexane cannot be explained by reactions with radiolytic products or by some other homogeneous reaction. In order to accommodate these results with those of conductivity experiments we propose a mechanism where the mobile radical cation is in equilibrium with a normally-diffusing ion.

We consider that only HMI is initially formed and before the equilibrium is established, in about 30 ns, fast scavenging is observed. This is consistent with the formation kinetics of $Ar^{\bullet +}$ in the time region <100 ns. After the equilibrium is established, over several tens of nanoseconds, the effective scavenging constant $k_{eff} = (K \times k_{ND}+k_{HM})/(K+1)$, where K is the equilibrium constant and $k_{ND}$ is the rate constant for scavenging of normally-diffusing cations. With $k_{eff} = 1.4 \times 10^{11}$ $mol^{-1}$ $dm^3$ $s^{-1}$, one obtains K ~ 2. Such an equilibrium can be ascribed to electron transfer between the chair and twist/boat conformers:

$$c\text{-}C_6H_{12}^{\bullet +}\ (\text{chair}) + c\text{-}C_6H_{12}\ (\text{twist}) \rightleftharpoons c\text{-}C_6H_{12}\ (\text{chair}) + c\text{-}C_6H_{12}^{\bullet +}\ (\text{twist}) \qquad (1)$$

For cyclohexane, the ring inversion time is ~ 10 μs at 25°C. On the timescale of our experiments, liquid cyclohexane can be considered as a mixture of two forms with the concentration of twist/boat form being ~ $10^{-4}$ mol $dm^{-3}$. Ionization produces the majority of radical cations in the chair form surrounded by molecules in the same conformation. This arrangement is favorable for extremely rapid resonant charge transfer. Eventually the chair-form radical cation encounters a molecule in the twist/boat form having lower IP and gets trapped. The reverse transfer is endothermic and slow. With the above stated concentration of twist/boat forms one obtains the 25-30 ns lifetime of the chair-form radical cation, consistent with the experimental observations.

Photoconductivity experiments clearly demonstrate the bimodality of the scavenging kinetics for cyclohexane. At very early times, the scavenging of HMI is faster than at later times. The demonstration of such behavior in single-pulse laser experiments is rather involved because one needs to take into account geminate reactions of HMI, their homogeneous neutralization, and transformation to normally diffusing ions upon scavenging.[15] A two-color laser experiment provides a simpler way to demonstrate the bimodality.[22]

In these experiments, we study dc conductivity in $8 \times 10^{-6}$ $mol^{-1}$ $dm^3$ $s^{-1}$ triphenylene in $CO_2$ saturated cyclohexane. The radical cation of triphenylene absorbs strongly at 532 nm. A 20-50 mJ pulse of 2.3 eV photons is delayed by 0.5-5 μs relative to the 5 eV excimer-laser pulse used to ionize the aromatic solute (and, to some degree, the solvent). Over this period of time, the lowest singlet excited state of the aromatic solute decays and HMI is scavenged by impurity. Experiments with added oxygen show that the triplet state of the aromatic is not important. Following the excitation with two 2.3 eV photons, $Ar^{\bullet +}$ captures the electron from the solvent valence band and yields a hole with excess energy ~ 2 eV. Upon thermalization, the solvent hole is sufficiently separated from the aromatic molecule to escape the reverse charge transfer. Soon after the formation of HMI the geminate stage is over (< 1 ns), and HMI decays in homogeneous reactions with anions and scavengers. The decay kinetics of HMI were obtained by subtracting the traces obtained with and without the second laser pulse. An example of such a difference trace is shown in Figure 4. The prominent feature of these kinetics is the bi-exponential decay of HMI. Approximately one-half of the signal decays with a lifetime ~ 30 ns, while the other half decays with the lifetime ~ 200-250 ns. Thus the model involving conformers provides a good explanation for the observed behavior of HMI in cyclohexane.

*Decalins.* The conformer-equilibrium mechanism suggests that in systems where the conformational dynamics is frozen simpler behavior should occur. This was explored in decalins where all molecules are in the same conformation.[15] We found that in decalins and their mixtures, the scavenging of the conductivity signal from HMI is a pseudo-first order reaction (Figure 5). A single long-lived HMI is needed to account for these scavenging kinetics. Transient absorption spectroscopy in pulse radiolysis of decalins also indicates the formation of HMI (Figure 6).[17] Perylene transfers an electron to these ions with a rate constant of $8.5 \times 10^{10}$ $mol^{-1}$ $dm^3$ $s^{-1}$ which is an order of magnitude faster than scavenging of normally diffusing ions. The lifetime of the mobile solvent ion was determined as ~ 150 ns which is compatible with the lifetime of HMI observed in the dc photoconductivity experiments, if one takes into account reactions of HMI with radiolytic products.

Nevertheless, one needs to invoke an equilibrium model to explain dc photoconductivity in the mixtures of *trans-* and *cis-* isomers.[15] The mobility of HMI in these mixtures linearly increases with the fraction of *trans*-decalin. Exponential decay kinetics of HMI seem to indicate that only one form of radical cation is prevalent. In the gas phase, the IP of *trans*-decalin is lower by 20 MeV than the IP of *cis*-decalin, so the former ion is probably more stable in the liquid mixture. If so, then the scavenging constants would always scale with the mobility of *trans*-decalin$^{\bullet +}$. Experimentally, for some solutes the scavenging rate decreases with the fraction of *trans*-decalin. This peculiarity can be explained if one assumes a reversible charge transfer:

$$\textit{cis}\text{-decalin} + \textit{trans}\text{-decalin}^{\bullet +} \rightleftharpoons \textit{cis}\text{-decalin}^{\bullet +} + \textit{trans}\text{-decalin} \qquad (2)$$

Because of the high concentration (> 0.1 mol $dm^{-3}$) of isomers of *cis*-decalin present in "pure" *trans*-decalin and *vice versa*, equilibrium (2) is established in less than 1 ns; i.e., in our conductivity experiments, the HMI always behaves like a single species.[15] To account for the observed dependence of mobility on the fraction of *trans*-decalin, the difference in the activation energies of the forward and backward electron transfers ( ~ 40 MeV) must be independent of the composition of the mixture.

*Magnetic resonance in HMI.* We no longer doubt that mobile solvent holes in cycloalkanes are long-lived. It is, however, necessary to postulate that these holes exist in more than one form and that there is an equilibrium between these forms.

This conclusion implies that the FDMR signals from radical cations of cyclohexane and *trans*-decalin were not missed because of their short lifetime. In neat cycloalkanes and their $10^{-3}$-$10^{-2}$ mol dm$^{-3}$ solutions in high-IP solvents, the observation of FDMR might be precluded by rapid resonant charge transfer. Still, FDMR must be observed in dilute solutions provided that the solute transfers electron to the solvent hole before its fragmentation. This was expected to occur in solutions of *trans*-decalin in cyclohexane. Still, no signal from *trans*-decalin$^{\bullet+}$ was observed. It seems that at room temperature even isolated *trans*-decalin$^{\bullet+}$ yields no discernible EPR signal. To explain this behavior, one needs to postulate very rapid phase relaxation in this ion or fast chemical reaction with the solvent. This is a remaining puzzle.

## Concluding remarks

In conclusion, we address the intriguing question as to why the rapidly migrating solvent radical cations are observed for a relatively small group of alkanes. In frozen alkanes, the spectral diffusion due to slow hole hopping is observed in almost any system. In liquid alkanes, only structurally frozen alkanes can exhibit high hole mobility and only when the radical cations are long-lived can one observe them by conductivity techniques. Conformational isomerism of alkane molecules seem to be the major factor in slowing down the rate of the resonant charge transfer. For typical alkane solvents that are not conformationally constrained, resonant charge transfer is not much faster than the rate of molecular diffusion.

To observe HMI behavior in typical solvents, one needs to retard diffusion by lowering temperature and/or by increasing viscosity. HMI in methylcyclohexane at low temperatures were examined by Bühler and coworkers.[23] Recently, we showed that in the viscous solvent squalane one can separate faster hole transfer from slower molecular diffusion.[20,21] This HMI is short-lived and cannot be observed using transient dc conductivity. In view of these findings, we believe that resonant charge transfer occurs in all liquid hydrocarbons but can be characterized only in the few examples discussed. Thermalization of the holes seem to be a multi-stage, slow process.

Our studies illustrate the complexity of radical cation chemistry even in the simplest of radiolytic systems. This chemistry is difficult to generalize since the intricate details of structure have substantial consequences on the longevity of ions and their transformations. While the overall picture might be relatively clear, there are numerous pitfalls waiting for the unwary. The situation with HMI is a good illustration of this maxim.

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## Figure Captions

Figure 1. Reaction scheme for radical cations.

Figure 2. Typical data on transient dc photoconductivity from $SF_6$-saturated cyclohexane, n-hexane, and *trans*-decalin.[16] The curves were obtained using the 0.25 $J/cm^2$ flux of 4 eV photons from a XeCl excimer laser (10 ns pulse). The curves are normalized so that the free ion levels match that for $10^{-6}$ mol $dm^{-3}$ pyrene in cyclohexane. The solid lines represent second-order fits to the free ion decays.

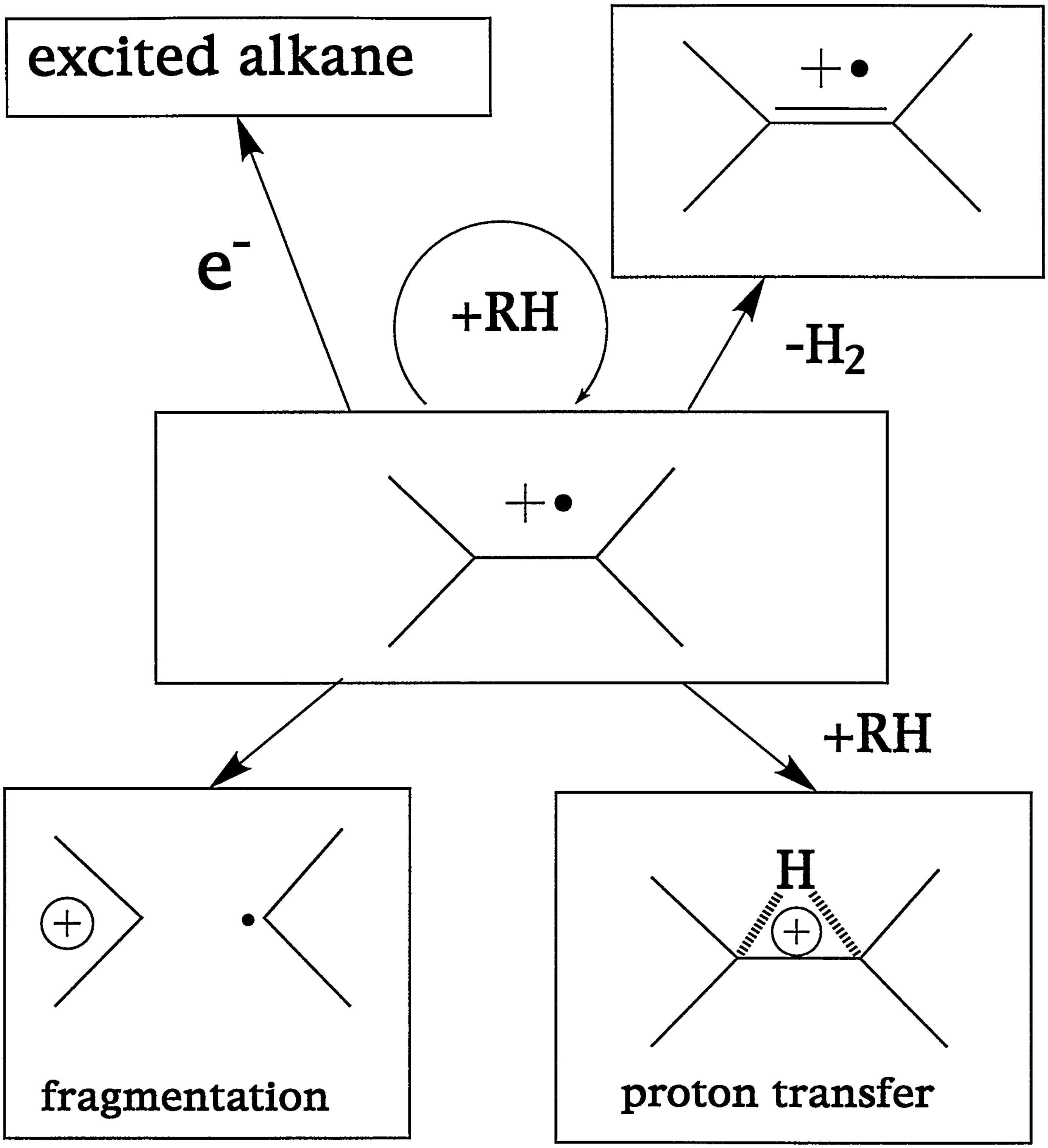
Figure 3. An example of photon flux dependence studied by transient dc conductivity. Intensity dependence of ionization in cyclohexane at 248 nm (5 eV). The upper trace is for Ar-saturated solution and the middle and lowest traces are for $SF_6$-saturated solutions. For the upper traces the signal is mainly from solvated electron, with a negligible contribution from cations; the middle set is the signal from HMI (the free ion signal at 2 μs has been subtracted). For the upper and middle traces, the open symbols represent the observed signals at 50 ns after the laser pulse, and the filled symbols represent these signals corrected for second-order neutralization, which becomes appreciable at the higher light intensities. The circles are for runs where the cross-sectional area of the laser beam was 0.3 $cm^2$; the squares and triangles are for runs where the area was 0.14 $cm^2$. Data for the free ions (lowest traces) were obtained by a fitting procedure *(open symbols)* and measurement at 2 μs *(filled symbols)*. The curves are calculated as described in Reference 18 for a two-photon ionization process.

Figure 4. Production of HMI in cyclohexane by two-photon laser excitation of tripenylene radical cation.[22] *Dots:* Increment in the dc conductivity caused by 532 nm (2.3 eV), 40 mJ pulse from a Nd:YAG laser applied 270 ns after 248 nm (5 eV), 10 mJ pulse from a KrF excimer laser. *Solid curve:* biexponential fit with with $\tau_{fast}$=32 ns and $\tau_{slow}$=210 ns. The *dashed curve* is the slow component.

Figure 5. Pseudo-first-order scavenging of HMI in decalin.[15] Scavenging kinetics of HMI in $CO_2$-saturated decalin mixture (1:3 *trans/cis* decalin). *Dots:* decay kinetics of transient dc conductivity in 248 nm laser photolysis of the decalin mixture containing (i) no, (ii) $10^{-5}$, (iii) $2x10^{-5}$, (iv) $10^{-4}$, and (v) $2x10^{-4}$ mol $dm^{-3}$ cyclohexene. *Solid lines:* best-fit kinetics obtained using a model of a single HMI.

Figure 6. Formation of perylene radical cation in the pulse radiolysis of decalin solutions, from Reference 16. Formation of perylene$^{\bullet+}$ in the $N_2O$-saturated decalin solution (63 *cis-* : 37 *trans*-decalin mixture) with (a) no and (b) 0.1 mol $dm^{-3}$ toluene. Concentrations of perylene are given in the units of $10^{-4}$ mol $dm^{-3}$: for (a) (i) 5.5 (ii) 2.8 (iii) 1.25 (iv) 0.44; for (b) (i) 5.7

(ii) 2.5 (iii) 1.1. Short time scale kinetics in (a) *(solid dots)* were obtained with 30 ps electron pulses, all other kinetics were obtained with 4 ns pulses (6-8 krad/pulse). Solid lines in (a) are a Monte-Carlo simulation for a HMI that lives 150 ns. Solid lines in (b) represent a simulation using the continuum-diffusion model (compare with the broken curves calculated with the Monte-Carlo model). The discrepancy at t>0.5 μs is due to homogeneous recombination, which was not included in the calculation.



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Radical Cations in Radiation Chemistry of Liquid Hydrocarbons

Figure 1.

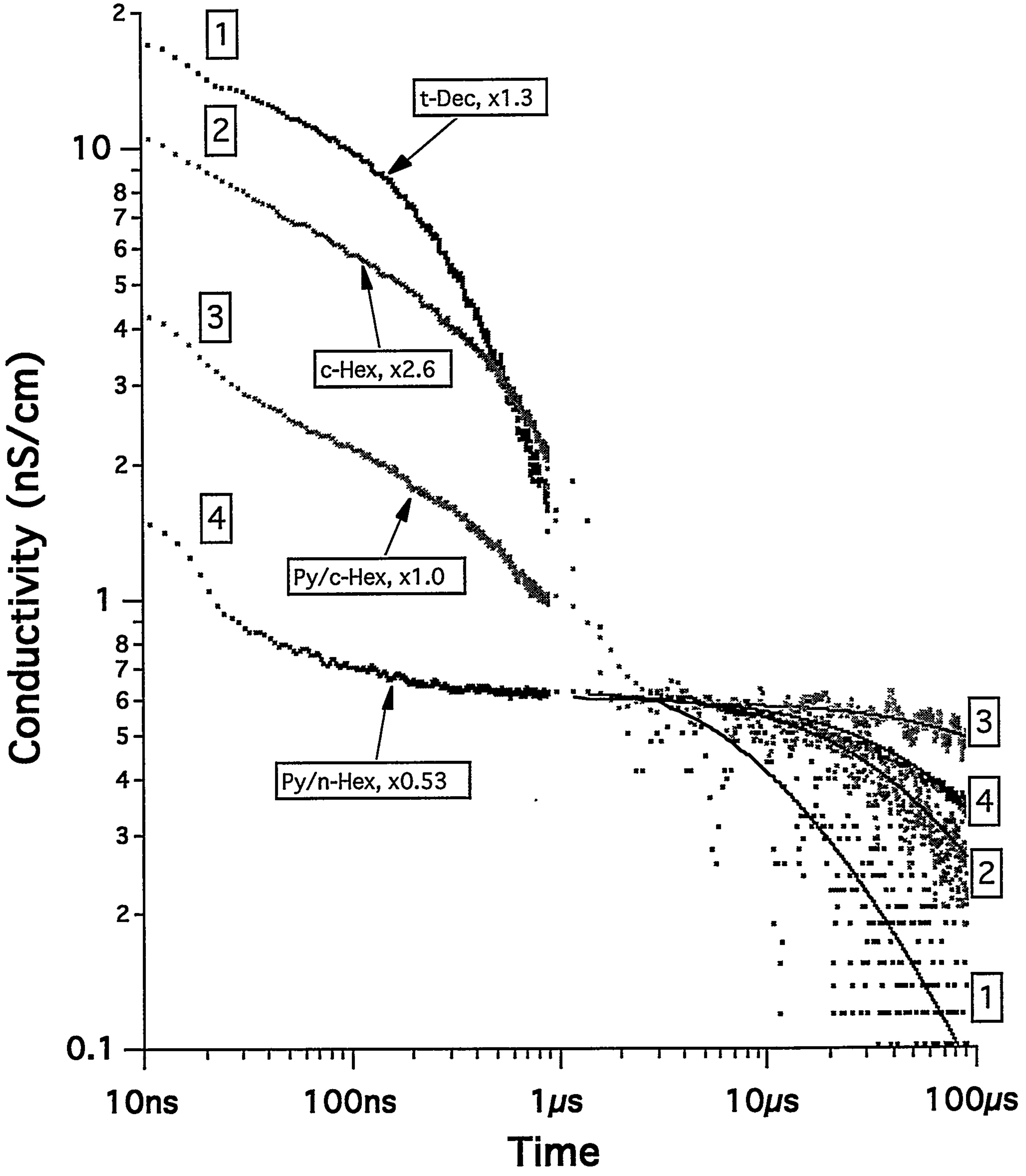

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Figure 2

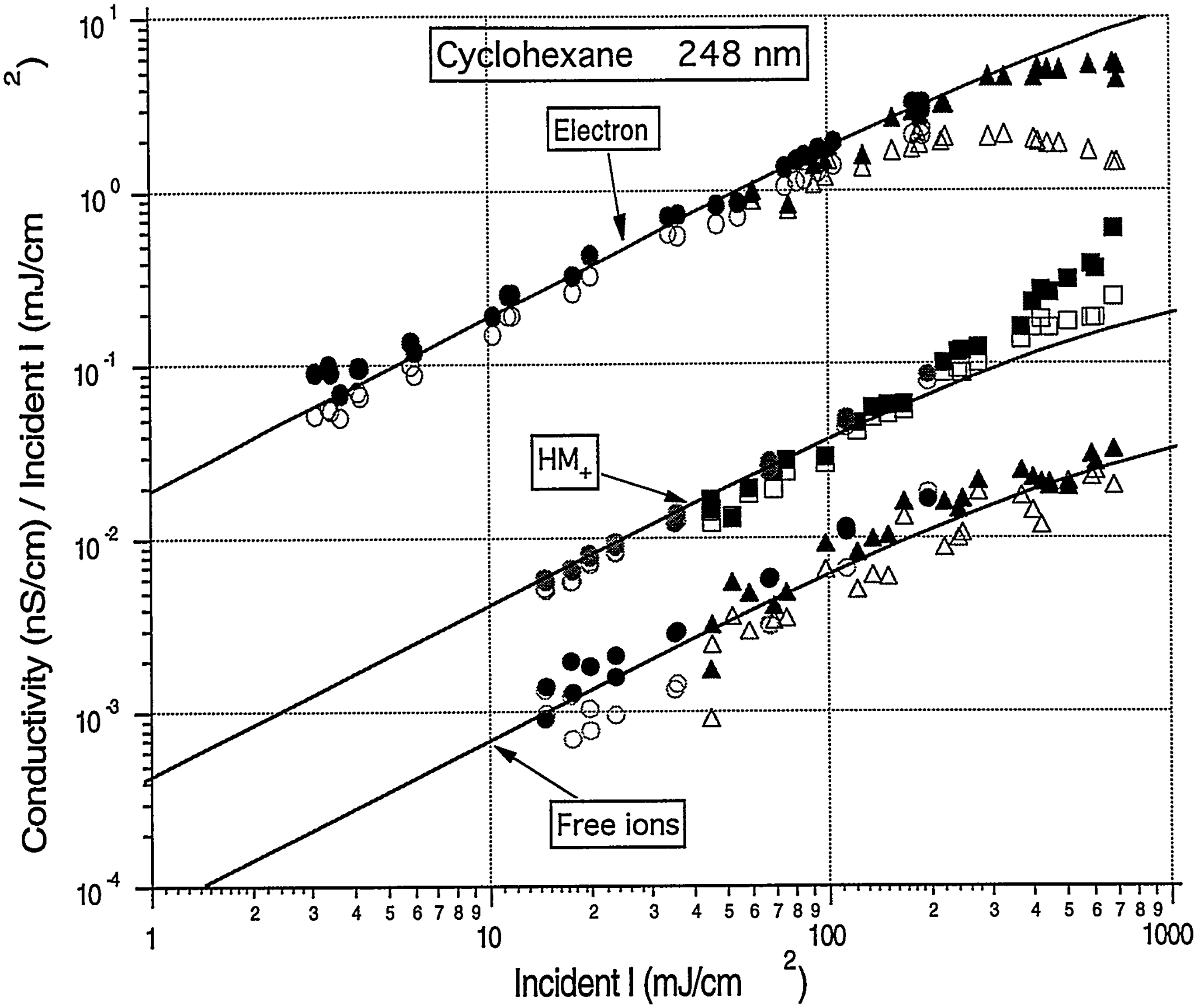

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Figure 3

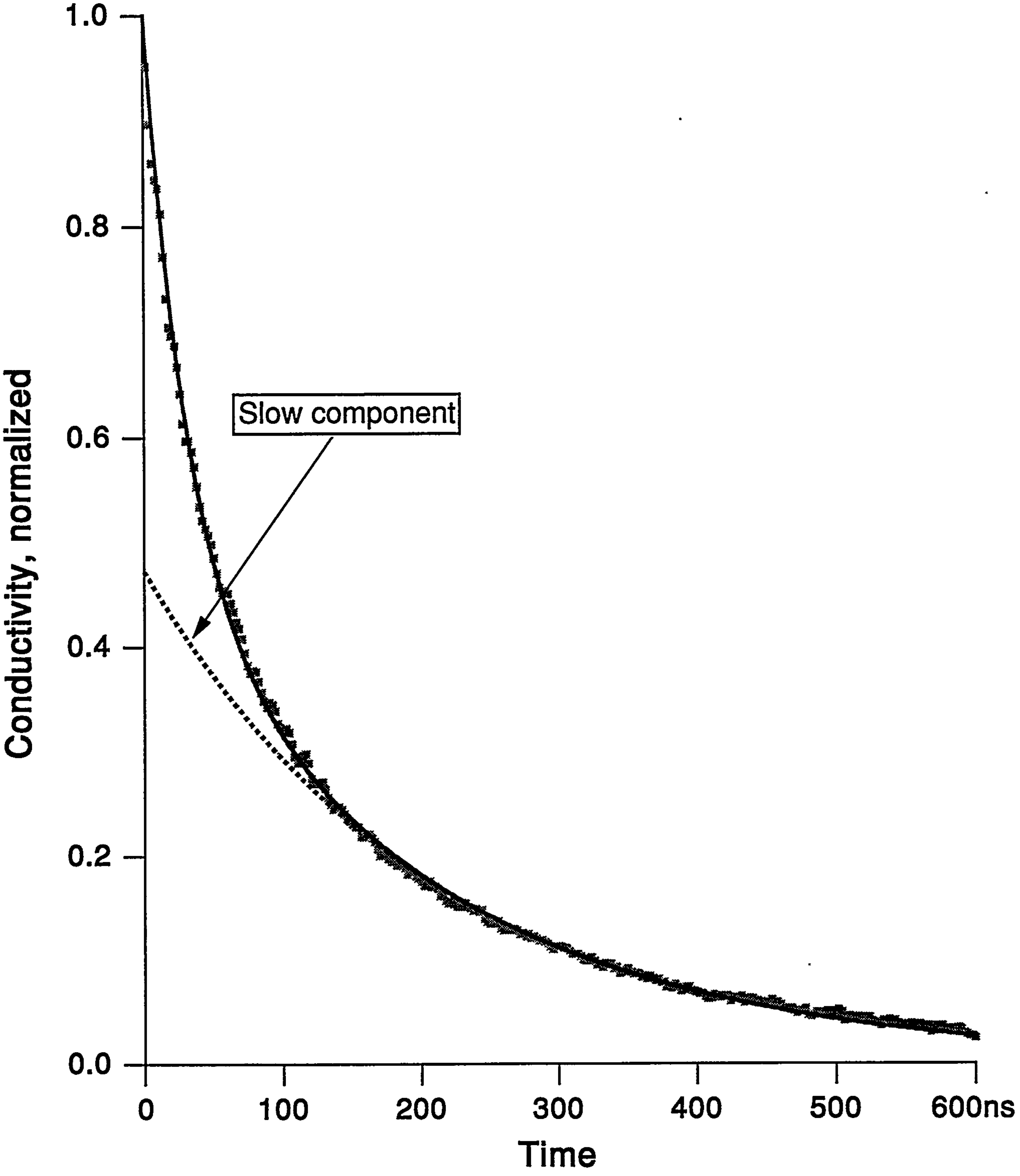
1.0
0.8
0.6
0.4
0.2
0.0
Conductivity, normalized
Slow component
0
100
200
300
400
500
600ns
Time

Figure 4

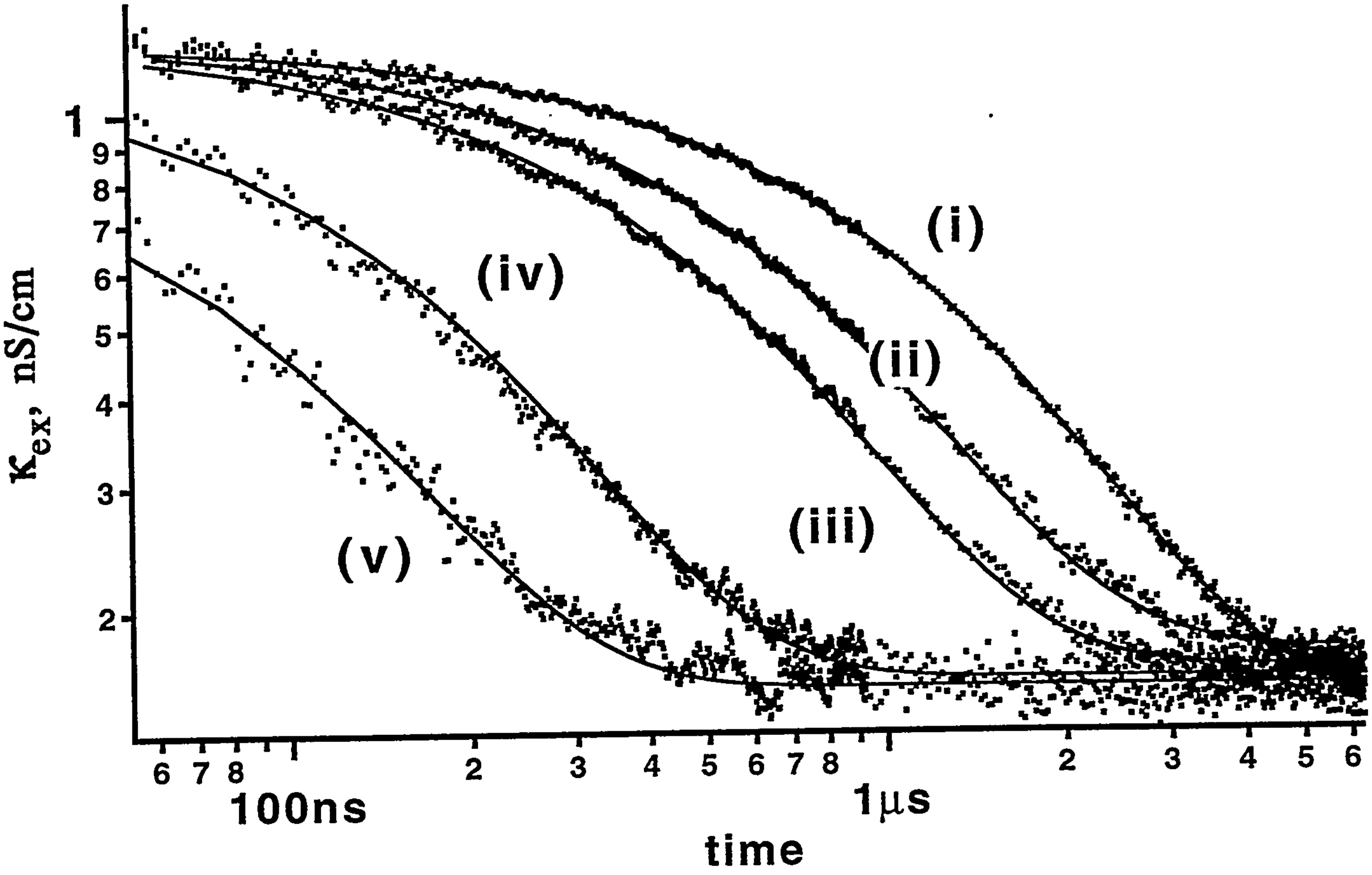

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Figure 5

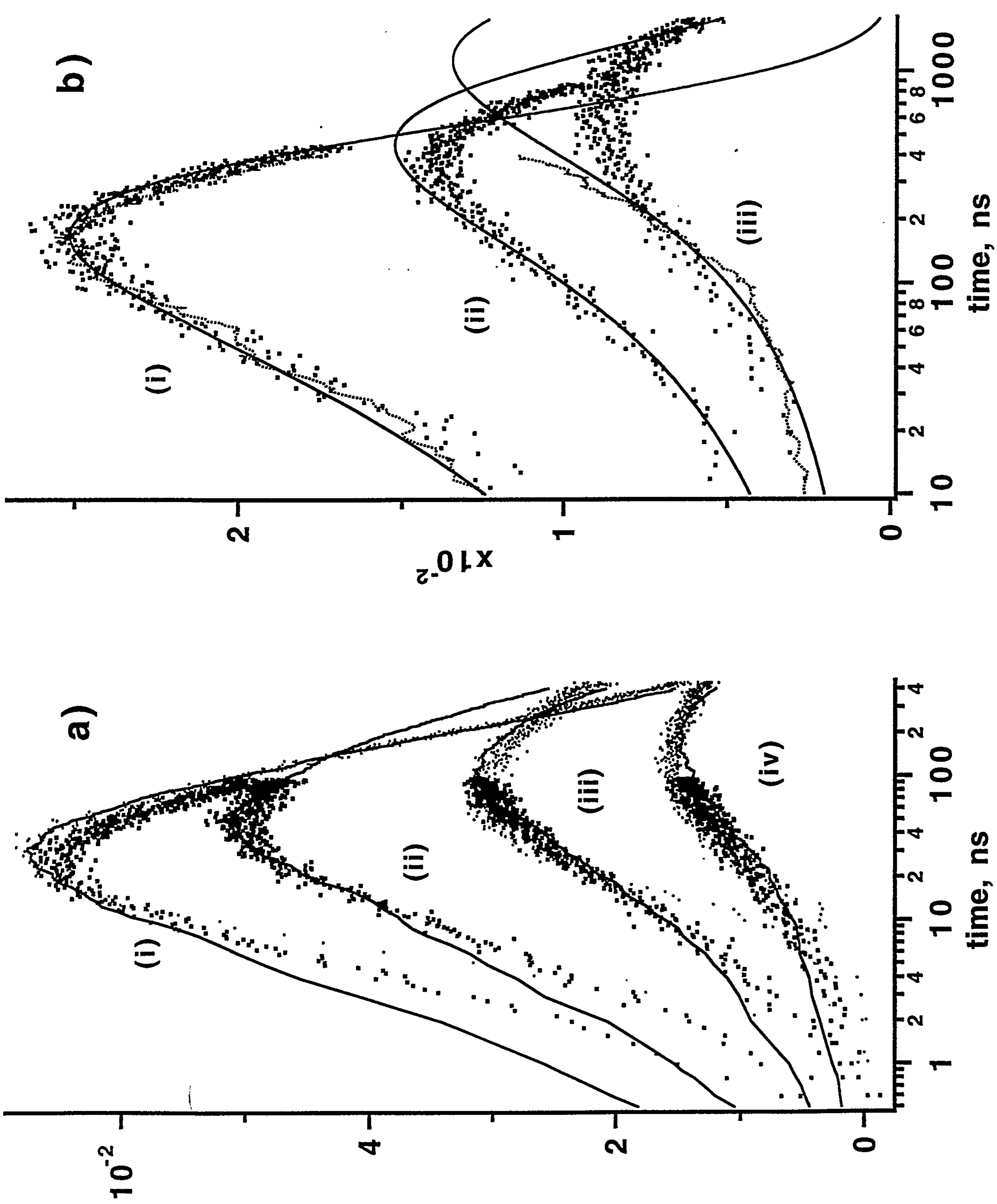
a)
absorbance
6x10$^{-2}$
4
2
0
(i)
(ii)
(iii)
(iv)
1
2
4
10
2
4
100
2
4
time, ns
b)
x10$^{-2}$
2
1
0
(i)
(ii)
(iii)
10
2
4
6
8
100
2
4
6
8
1000
time, ns

Figure 6