ULTRA-FAST CHEMICAL PHENOMENA: A FRONTIER OF PHYSICAL CHEMISTRY*

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The field of ultra-fast chemistry has been a subject of tremendous activity in the recent years. This article briefly discusses some of the problems investigated recently. The understanding that has emerged from these studies can have important consequence in many branches of chemistry.

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Introduction

There are many chemical reactions that occur with great rapidity. It is only after the availability of ultra-short laser pulses and after the perfection of the associated detection techniques that the study of these processes has become possible. A large number of elementary chemical processes such as isomerization reaction, bond dissociation and formation, vibrational energy relaxation, electron transfer reactions, solvation dynamics, orientational relaxation and many others have been studied in the last decade[1-12]. It is important to realize that the underlying physical and chemical phenomena in different time scales are often profoundly different. In many cases, the availability of shorter time scales meant more accurate measurement thatn was hitherto possible, often leading to new understanding. In some other cases, completely new phenomena could be studied. In Fig. 1, a schematic illustration of the rapid availability of increasingly small time scales is provided. In the same figure, we have also shown the chemical phenomenon which became accessible for experimental study as the time resolution improved.

In this article, we shall briefly touch upon a few of the chemical processes which have been studied intensely in the last few years. The emphasis here is entirely on the phenomena and their understanding-technical details (both experimental and theoretical) will be omitted. The list of

references is not exhaustive. There are several reviews[1-8] and books[9-10,12] that have appeared in the last 5-6 years which contain the details and in addition, provide useful starting point for the non-expert.

Solvation Dynamics in Dipolar Liquids

The solvation of chemical and biological molecules in polar and non-polar liquids is an important phenomenon which controls both chemical and biological activity of many molecules in solution. By solvation one usually means the energetic and the structural changes which accompany the incorporation of a polar or non-polar solute molecule in a solvent. Since the common chemical solvents are liquids of very high density, the effects of a foreign solute on the structure and dynamics of the solvent are usually significant. As these changes occur within the liquid and are inherently microscopic in origin, the study of these processes is rather difficult. Much of the study of solvation dynamics has been carried out with well-known dye molecules (such as nile red, coumarin) which serve as excellent probes because these molecules have large excess polar stabilization energy in the excited state as they often undergo a large increase in the dipole moment on excitation, or sometimes may even photo-ionize. Therefore, the optical excitation prepares the molecule in the Franck-Condon state which is of much higher energy than the minimum of the potential energy in the excited state surface. This situation is shown in Fig. 2. Subsequent to the excitation, the solvent molecules rearrange and reorient themselves to stabilize the
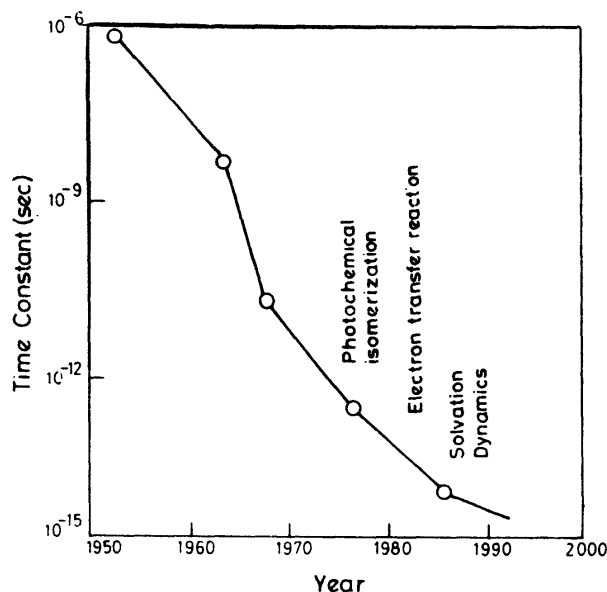
Fig 1 A schematic diagram to illustrate the evolution of progressively smaller time scales which became available in the study of chemical dynamics. Some of the processes which became possible to study have also been shown here.

new charge distribution in the excited state. The resultant change in energy is of course the solvation energy of the solute. The second reason for the choice of dye molecules as suitable probes is that they often have easily detectable fluorescence with long life times, one can easily study the time dependence of the Stokes shift of this fluorescence as solvation energy of the dye molecules evolves. This time dependence is described by the solvation time correlation function which is defined as[1-6,13]

$$S(t)= \frac{E_{solv}(t) - E_{solv}(\infty)}{E_{solv}(0) - E_{solv}(\infty)} \qquad ...(1)$$

where $E_{solv}(t)$ is the solvation energy of the newly created ion at time t. This function is defined such that it decays from unity at the initial time (t=0) to zero in the long time. The solvation dynamics is reflected in the red shift of the fluorescence spectrum and this experimental procedure is known as the time dependent fluorescence Stokes shift (TDFSS). One may expect that TDFSS may strongly depend on the nature of the solute probe which can complicate the study of solvation dynamics. Fortunately, one finds that $S(t)$ is largely probe independent, for reasons which are only partly understood, to be discussed later. The second reason for the great interest in solvation dynamics
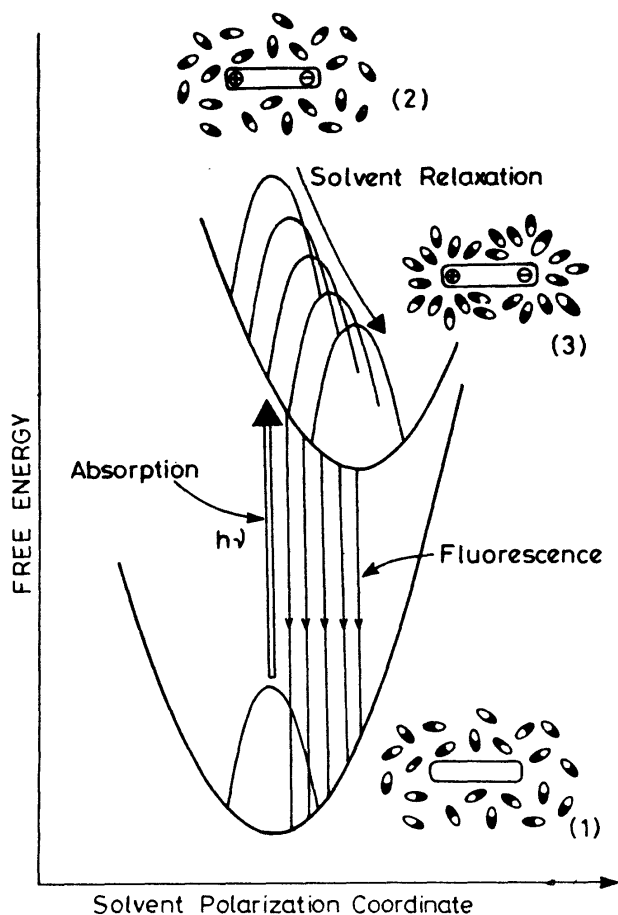

Fig 2 A schematic illustration of the physical process involved in the experimental study of solvation dynamics. The initial state (marked by 1) is a non-polar ground state. Laser excitation prepares it instantaneously in a charge-transfer (CT) state, which, however, is a highly non-equilibrium state because at time t=0, the solvent molecules are still in the Franck-Condon state of the ground state. This is the state (2). Subsequent solvation of the CT state brings the system to the final equilibrium which is detected by the time dependent fluorescence Stokes shift.

was the realization that it can significantly influence many chemical reactions, especially electron and proton transfers in polar liquids. Yet another reason is that the standard continuum model (SCM) theories predicted that $S(t)$ would decay at a rate much faster than the rotational (and, of course, translational) relaxation. Thus, for water SCM predicted that the decay time would be about 250 fs[3,13] which was startling even in the later eighties!

Over the last decade, $S(t)$ has been measured for a large number of polar molecules in different solvents. In the first phase (1986-1990), the

experiments were done with time resolution only in the picosecond range. The solvation time correlation function was found to be non-exponential and differed from the predictions of the continuum models. During this period, an old comment of Onsager[14] became the topic of much discussion and we briefly discuss it here. In the Banff Conference on the "Solvated Electron" in 1976, Onsager made the interesting comment that the polarization structure of an electron should form from outside in. That is, the molecules far from the electron should rearrange first, while the nearest-neighbour molecules relax at the last. This suggestion came to be known as Onsager's "inverse snow-ball picture". This also suggests that the solvation energy relaxation would be intrinsically non-exponential, as many, length dependent, time scales are involved. Initial theoretical studies[15] supported this picture. However, it was argued later that the contribution of solvent translational modes may lead to the break-down of the inverse-snow ball picture[16]. More recently, it has been argued again that the Onsager picture may after-all be correct for electron, but not for ions[17,18]. The latest suggestion is that the electron being a very light particle will travel a long distance before it settles down in an existing trap. The dipolar molecules further from the electron can relax but the ones close to it must wait[18].

The most exciting experimental work on solvation dynamics has, however, taken place in the last six years only and the results appear to have far-reaching consequences. The first study was the solvation dynamics of a dye, LDS-50, in acetonitrile reported from Fleming's laboratory at the University of Chicago[19]. This landmark experiment showed that solvation dynamics is biphasic with an ultra-fast Gaussian component which decays with 80% of the total solvation energy within 200 fs. This is followed by a slow exponential-like decay with a time constant about 1 ps. This result was found to be in agreement with both computer simulation[20,21] and theoretical studies[22]. An even more interesting study has been reported recently on the solvation dynamics in water[11]. Here the initial Gaussian component decays with a time constant of value less than 54 fs while the long time decay can be described as bi-exponential with time constants equal to 240 fs and 860 fs. In Fig. 3, the solvation time correlation function in water is shown. What is also interesting is the agreement of the long time components with the earlier experimental results of Barbara et al.[3] who could not detect the ultra-fast component because of limited time resolution. The solvation time correlation in methanol also contains an ultra-fast Gaussian component with a time constant of about 70 fs. However, the relative weight of this part is somewhat less (about 30%) although still significant.

What is the origin of such ultra-fast solvation in water, acetonitrile and methanol? These three liquids are quite different from each other and it is instructive to compare their dynamical features before we comment on the physical origin. Water, because of its small molecular weight and the extensive hydrogen bond network, has well-defined high frequency librational modes. However, the single particle orientation of water molecules is rather slow, with a correlation time of about 9 ps, due to the same hydrogen bonding. Acetonitrile, on the other hand, has fewer high frequency librations, but orients very fast, with a correlation time of 0.3 ps. Methanol is again different. Because of chain-like hydrogen bond character, it has certain degree of high frequency libration, slow over all rotation but very fast rotation around the C—OH bond which gives rise to a very fast polar response. All these details seem to be important in solvation dynamics[25]. Theoretical studies indicate[22-25] that nearly all of the natural fast dynamics of the system couple in different ways with the long wavelength polarization fluctuation to give rise to the ultra-fast component. This is because the main contribution to ion solvation energy comes from the long wavelength part of the polarization which is created in the liquid by the ion. Now, the force constant for the longitudinal polarization fluctuation is rather large in a strongly polar liquid. Thus, the thermodynamic driving force to make ion solvation very fast exists in all strongly polar liquids. However, for solvation to be really fast, the liquid itself must be able to respond in the ultra-fast time scale. This is where water and acetonitrile (and to smaller extent methanol and perhaps formamide) are exceptional. Water, due to its high frequency librations and inter-molecular vibrational modes, and acetonitrile, due to its fast rotational motion, can respond at a very high speed. The explanation given above is borne out by
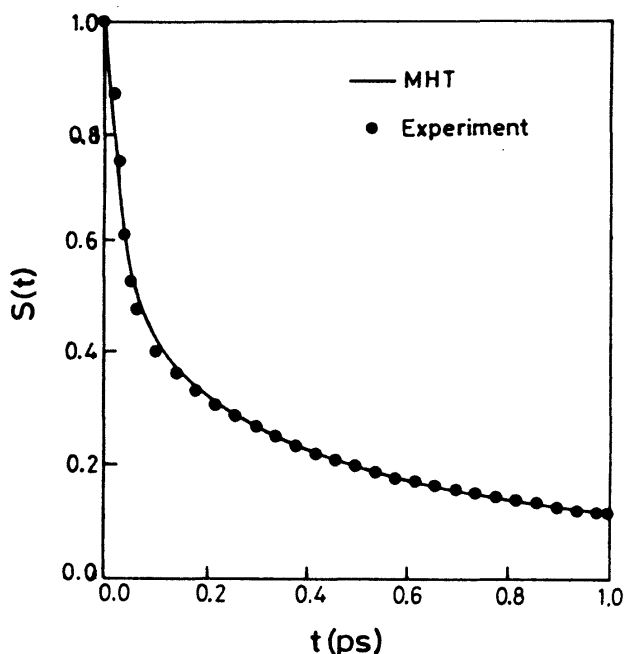
Fig 3 Solvation dynamics in water of an ionic probe in water. The black dots are the experimental results[11] and the solid line is the theoretical prediction[21].

microscopic theory as shown in Fig. 3. Another important point to note is that the relative insensitivity of solvation dynamics to the details of probe-solvent interaction seems to agree with the above suggestion that the initial part of solvation dynamics is dominated by a collective mode.

Actually, even in these liquids, all is not ultra-fast. Just as the rotation of water molecules is rather slow, so also the response to perturbations that vary on molecular length scales. These responses are also probed in many chemical processes, even in water. As discussed above, several rather unconnected (both microscopic and macroscopic) factors combine to give rise to the dominance of the ultra-fast component in the solvation dynamics in water and acetonitrile.

Electron Transfer Reactions

Electron transfer reactions have been studied extensively both in chemistry and biology. The initial studies were motivated by the desire to understand acid-base equilibrium and organic reactions which involve electron transfer as a key step. With the advent of laser it is now possible to study many kinds of electron transfer reactions, especially those occurring in the excited state, for the first time. The reason is that many of these reactions were found to proceed at exceedingly fast speed, often with time constants in the sub-picosecond range. Well-known examples are electron transfer in photosynthetic reaction center, fluorescence quenching in excited betaines and ion pair formation in various charge transfer complexes. We address below only the recent advances in understanding solvent effects in ultra-fast electron transfer reactions in solution.

The key to the great success of the Marcus theory[26] lies in the choice of the reaction coordinate. The motion of the system on the reaction potential energy surface along this coordinate takes the system from the reactant surface minimum to the product surface minimum. In conventional chemical picture, this coordinate is usually some distance or angle and its nature is clear from the beginning. The situation is different for the electron transfer reaction. In this case often no chemical bond is broken or formed. The major part of the activation energy comes from the interaction between the reaction system and the dipolar liquid and not from any intra-molecular potential. Thus the reaction coordinate is collective in origin. In the Marcus theory the reaction coordinate is essentially the solvation energy difference between the reactant and the product. However, in order to specify the nature of any electron transfer reaction we must know the nature of interaction between the reactant and the product surfaces. Interestingly, this interaction itself is determined by the nature of the Born-Oppenheimer surfaces as a function of the nuclear coordinates. Thus, in order to understand electron transfer reaction one must consider the potential energy surface as function of both the reaction coordinate and the nuclear coordinate. If reactant and the product surfaces interact very weakly, then the reaction can be considered as a transfer of the electron from the former to the latter at the crossing point and the reaction is termed "non-adiabatic". On the other hand, if the two surfaces interact strongly near the crossing, then the electron transfer occurs on one surface (which is given by a combination of the two parent surfaces according to the rules of quantum mechanics) and the reaction is termed "adiabatic". The experimental situation often lies between these two broad classifications and is termed loosely as "weakly adiabatic" or even "weakly non-adiabatic".

Recent studies[27-33] have critically examined the dynamic effects of solvent on various electron transfer reactions. One is particularly interested to know what effects the newly discovered ultra-fast solvation could have on electron transfer reactions. The answer depends on the "adiabaticity" of the reaction. For non-adiabatic reactions even the ultra-fast polar response was found to be not fast enough to seriously affect electron transfer. The situation is rather different for weakly adiabatic electron transfer. Here the first and foremost effect is that the rate of barrier crossing increases by almost an order of magnitude over the old estimates that ignored the ultra-fast solvation effects[31-33]. This is true not only for water, but also for the other two ultra-fast solvents, acetonitrile and methanol. For acetonitrile, some additional interesting features appear. For this solvent, the reactive friction (which arises from coupling between the electronic charge and the solvent) becomes so small that the electron transfer is controlled not by the rate of barrier crossing, but rather by the rate of energy diffusion to the barrier from the reactant well. Electron transfers in water and methanol are predicted to be in the normal regime. In fact, it is rather ironic that ultra-fast solvation in water implies that this solvent will be able to respond very fast to chemical changes during a reaction which, in turn, will not show any dynamic solvent effects[32-33].

Marcus theory predicts a parabolic dependence of reaction rate on the free energy of the electron transfer reaction. Although this dependence was predicted in 1956, its verification had to wait till the 1984 landmark experiment of Miller et al.[34]. These authors measured the rate of electron transfer across a bridge of organic groups of varying length. Subsequently, several confirmations of the parabolic dependence has been reported[35]. However, there are also several recent studies of ultra-fast electron transfer which found interesting breakdown of the Marcus parabolic dependence[36-40], due to various reasons. One such example is shown in Fig. 5 where the rate of charge recombination (CR) of newly formed contact ion pair (CIP) is plotted against the free energy of reaction. The rate increases in the normal region with decrease in the free energy gap. Tachiya and Murata[40] has recently provided an elegant explanation of this non-Marcus energy gap

dependence by invoking the interplay between relaxation and electron transfer. A more detailed theoretical work by our group[41] has shown that the above interplay can give rise to highly non-exponential decay of the reactant population. Another reason of non-Marcus energy dependence is the involvement of high frequency modes of the product state which often serve as the accepting modes to accelerate electron transfer[37-39]. This mechanism is particularly useful when the electron transfer is in the Marcus inverted regime and results in the absence of the decrease of the rate as the free energy change between the reactant and the product is made larger (i.e. G is negative and large). This mechanism of non-Marcus energy gap dependence seems to be responsible for the large electron transfer rate observed recently in betaines[38].

Actually the back-electron transfer reaction in the excited betaines presents a very interesting example where the quantum effects, ultrafast solvation dynamics and vibrational relaxation all combine to give rise to rather exotic behaviour[42,8]. It has been pointed out[42] that in this case even a small ultrafast component in the solvation dynamics can accelerate the rate to a great extent. This is possible because the Franck-Condon active reaction channels are rather far from the initially excited state—the ultra-fast component brings the reactant to the region of efficient reaction[8].

Isomerization Dynamics

These are very important chemical reactions. There are several reasons why these reactions often proceed at a very high speed. First, no chemical bond is broken or formed. The barrier is often rather small, only a few kcal/mole[43]. Moreover, there are several important reactions which proceed in the absence of any activation barrier. The examples are the cis → trans isomerization of excited stilbene and also the isomerization of triphenyl methane dyes, such as malachite green[43]. These reactions are naturally very fast. There are some cases also where the barrier is significant. In other words, the isomerization reactions span a diverse range in kinetic behaviour. Because of the simplicity of these reactions, they serve as the testing grounds for the theoretical models of solvent effects. We shall discuss here two

important and recent theoretical developments which were initially motivated by experimental results on ultra-fast isomerization reactions in solution, but led to far-reaching consequences.

Before 1980, the effects of solvent viscosity on isomerization reaction was explained by using the well-known Kramers' theory[44]. This theory assumes that a chemical reaction can be viewed as the passage of a Brownian particle over an activation barrier. At large solvent viscosities, this theory predicts that the rate is inversely proportional to the viscosity. This is a straight-forward consequence of modelling the reaction as a Brownian motion. Initial experiments seemed to have supported this. Detail experimental studies could be undertaken only after picosecond laser became available in the early eighties. The new experimental results clearly indicated that for fast isomerization reactions (with lifetimes in the picosecond and even in the subpicosecond range) in solution, Kramers' theory was inadequate to explain the viscosity dependence—the observed viscosity dependence was much weaker than the inverse dependence predicted by Kramers' theory[45-47]. This started a flurry of theoretical activity[48-51]. Interestingly, the work that proved to be the most useful in this stage was published only a few years ago by Grote and Hynes[49]. The understanding that has emerged is the following. In cis ↔ trans isomerization reactions, the two potential energy minima are often separated by a dihedral angle which is between 90 and 180. This gives rise to a sharp barrier when the activation energy barrier is somewhat larger than 10 kcal/mole. A sharp activation barrier implies that the reactant spends very little time in the barrier region, and, therefore, probes only the high frequency part of the solvent frictional response. The relation between the barrier height and the barrier curvature has been illustrated in Reference 43. This is to be contrasted with the Kramers' theory which assumes a slow diffusive motion along the reaction coordinate across the barrier. For a sharp barrier only the former picture is valid. Since at large viscosities the high frequency frictional response of the liquid gets decoupled from the macroscopic i.e. zero frequency) viscosity, the reaction rate also gets decoupled from viscosity and this shows up as a weak dependence of the reaction rate on the solvent

viscosity. This rather elegant explanation is also known as the non-Markovian effect in barrier crossing.

Another class of isomerization reaction has drawn attention in the recent years[43,52-54]. This is the zero barrier reaction limit. As already mentioned, several important photochemical reactions fall in this limit. Consider that a molecule is optically excited and that in the excited state there is a photochemical funnel at the minimum of the excited state surface. The motion that takes the system from its initial state to the final state is the reactive motion. The situation is depicted in group (as in the case of TPM dyes). In this case the rate of the reaction can be very high and dependent on the solvent viscosity. For cis ↔ trans isomerization of stilbene in hexane, the isomerization rate seems to be as high as 10^{13} sec^{-1}[53,54]. This is one of the fastest rate measured in the condensed phase. The decay of population on the excited state can often be measured by studying the disappearance of fluorescence from the excited state or by the recovery of the ground state population. An important characteristic of this type of reaction is that the time dependence of the excited state population is highly non-exponential. Another important hall-mark of barrierless reactions is the fractional viscosity dependence of the rate. The reason for the fractional viscosity dependence here is rather different from that in the high barrier reaction and is often due to the multi-dimensional nature of the reaction potential energy surface, the second dimension may be a solvent mode or an intramolecular vibrational mode.

The theoretical studies of barrierless reactions are mostly based on a stochastic approach where a Smoluchowski or a Fokker-Planck equation is used to describe the motion on the reaction potential energy surface with a coordinate dependent sink term to account for the decay from the photochemical funnel. This approach[43] seems to have been fairly successful in describing the experimental results.

Effects of Ultra-fast Solvation on Ionic Mobility

The anomalous properties of the limiting ionic conductance of an electrolyte solution has drawn attention of both physicists and chemists for more than a century[55]. There are two important anomalous properties. The first one is the non-

monotonic ion size dependence of the conductivity for small cations and the second is the concentration dependence. An example of the non-monotonic inverse size dependence of the limiting conductivity of small ions is shown (in liquid methanol) in Fig. 4. A quantitative understanding of such non-monotonic ion size dependance in various electrolyte solution has proven to be very difficult.

The discovery of the ultrafast solvent response to the creation of a new charge in water, acetonitrile and methanol led to a new thinking about the role of solvent dynamics in the ionic mobility. The ultrafast solvation of ion is quite relevant here because the friction acting on a moving ion in a dipolar solvent is dominated by polar forces and this part of friction, known as dielectric friction, is distinct from the collisional or hydrodynamic friction. This dielectric friction is expected to be dominated by the same polar forces responsible for the ultrafast solvation. Recent theoretical work showed that the ultrafast solvent forces indeed play a very important role. This is shown in Fig. 4 where both the theoretical prediction and the experimental results are shown. In the same figure the effects of ultrafast solvation on ionic mobility are also shown. When the ultra-fast components are absent, the friction on the ion is much larger, and as a result, the ionic conductance is much smaller. This is an interesting example where an intrinsically fast dynamics control an intrinsically slow process. The details of the theory and calculations are available in Refs. 55 and 56.

Conclusion

Advancement of ultra-fast laser spectroscopy in the last decade has led to many fascinating discoveries which have helped in solving several long standing puzzles in chemistry and biology. For example, one was puzzled by the absence of dynamic solvent effects on various charge transfer reactions in water. The paradox was partly due to the known result that the dielectric relaxation in water is about 9 ps which is quite long. Only recently it was discovered that solvation dynamics in water is more than two orders of magnitude faster. This explains why we do not see the above mentioned solvent dynamic effects in water. Similarly, the recent understanding of electron transfer reactions,
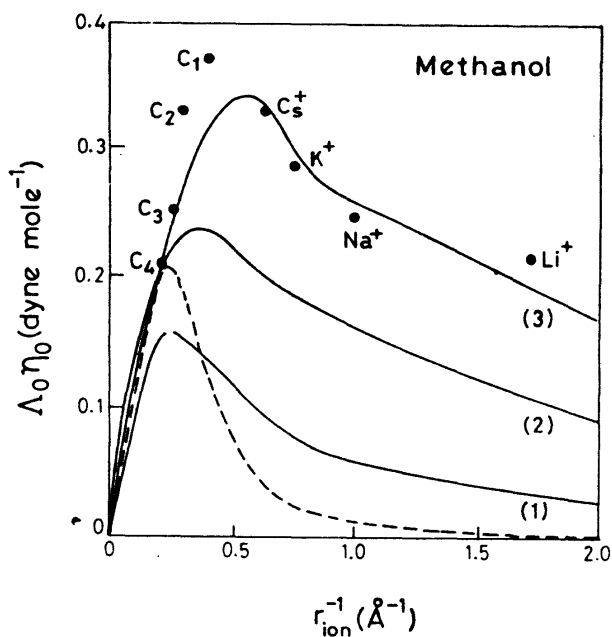

Fig 4 The effects of ultra-fast solvation on the limiting ionic conductivity of rigid cations in methanol. The solid dots are the experimental results. The solid line is the prediction of the full theoretical calculation. The other two lines show the decrease in ionic conductivity as the ultrafast components are progressively removed from the relaxation spectrum.

especially the involvement of the high frequency vibrational modes, has also emerged only in the last five years and again the impetus came from the discovery of novel aspects by using ultra-fast spectroscopy. A third example comes from the old field of ionic mobility where anomalous ion size dependence was a puzzle for a long time. It seems now clear that the ultra-fast solvation plays an important role in this problem too. With the availabilty of femtosecond lasers in many laboratories around the world, we can look forward to many more such interesting discoveries in the near future.

Acknowledgements

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