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Energy Transfer in Molecular Liquids

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Abstract : The existing information on the energy exchanges in molecular liquids is briefly reviewed. Main experimental methods are enumerated, and a phenomenological description of the observed material is given. The effects of various competing processes such as bond scission, conformational changes, twist-induced charge transfer, etc, are commented. Theoretical methods employed in this field, as well as difficulties inherent to them, are sketchily presented at the end.

1. INTRODUCTION

The purpose of the present paper is to review briefly the information on the energy exchanges in molecular liquids, and to transfer it from the liquid state physics to detonics. This task is difficult, experimental conditions being very different in the two fields. There is no similarity between the structure, at the atomic level, of a liquid sample in thermal equilibrium, and of a shock wave. The difficulty is further increased by the limited size of this review. It is then impossible to treat the problems in any comprehensive way ; only the most basic information can be given. Though, the resulting picture will hopefully be representative of the state of the art in the field.

2. EXPERIMENTAL METHODS

Early work on the energy transfer in molecular liquids was based on the use of classical spectroscopic techniques such as fluorescence or ultrasonic attenuation. For example, the average decay period, τ , of fluorescing material indicates that this is the order of magnitude of the lifetime of excited molecules. Various modes of deactivation of the electronically excited molecules may be studied in this way. From the other side, when absorbing an ultrasonic wave, the molecules of the liquid sample are vibrationally excited. As the absorption spectra depend on the energy relaxation rates, the latter are deducible from the experiment. A significative information has been collected in this way. Nevertheless, the real expansion of this field did not occur until the development of sensitive laser techniques. The time domain from the nano- to the femtosecond has been explored in this way.

The basic principles are as follows [1]. The system submitted to the investigation is a pure liquid, or a liquid mixture, in thermal equilibrium. A short and intense pump pulse is focused on the sample, bringing molecules to an excited vibrational or electronic level ; the saturation conditions are generally avoided. A nonequilibrium situation results ; the return of the system to the equilibrium is then monitored as a function of time. A number of methods have been invented for that purpose. (i) In a time resolved fluorescence experiment, the emitted radiation is analysed by employing devices for wave length selection, and a detection system including signal recording and data processing. Streak cameras and time-correlated single photon counting systems are of current use. (ii) In a pump-probe absorption experiment, a weak probe pulse monitors the changes in transmission, reflection or polarization after a variable delay time τ (Fig.1). For other experimental techniques, see Ref. [1].

The characteristics of the initial, pump-prepared state are as follows. The majority of degrees of freedom remain in, or close to, thermal equilibrium at room temperatures and pressures. Only some of

they are selectively excited to energies corresponding to high temperatures. For example, a 1eV electronic excitation corresponds to 11605°K, and a 1000 cm⁻¹ vibrational excitation to 1440°K. The states representative of detonics are very different. A large number of degrees of freedom are excited to high temperatures. Moreover, statistical characteristics of the matter in the shock wave front are only poorly understood. Any attempt of transferring data from molecular physics to detonics thus requires much care.

Fig.1 Picosecond pump-probe spectrometer (BS is a beam splitter, M a mirror, VD a variable delay device, FD a fixed delay device, WT a wavelength tuner and D a detector).

3. PHENOMENOLOGICAL DESCRIPTION

3.1 Generalities

Transitions between different molecular states, radiative or radiationless, are governed by selection rules. Those expressing the conservation of angular momentum, are particularly important. The overwhelming majority of liquids are formed by molecules which exist in a singlet ground state. Moreover, as spin and orbital momenta are only weakly coupled to each other, the rule of spin conservation is independently valid. Only singlet states are thus available for the absorption of light. The absorption process does not generate any significative distortion of molecular geometry (Franck-Condon principle).

3.2 Deactivation channels.

The subsequent discussion [1] is greatly facilitated by the use of the well known Jablonski diagram (Fig.2). According to the Franck-Condon principle, some vibrational excitation usually accompagnies electronic excitation. The primary relaxation process is then vibrational relaxation (VR) ; this process is very fast and is accomplished in few picosecond or less. It leads to a distribution of vibrational energy to other modes, or to a descent down the vibrational ladder of a given mode.

Fig.2 Jablonski diagram (S_0 , S_1 , S_2 , T_1 , T_2 are the singlet and triplet electronic states, IC indicates the internal conversion, ISC the intersystem crossing, F the fluorescence and Ph the phosphorescence). Straight lines represent the radiative, and wavy lines the radiationless transitions.

Once the vibrational relaxation is accomplished, the excited molecule may convert its electronic energy to vibrational energy of a lower electronic state of the same multiplicity, a process called internal conversion (IC). It is much faster for higher excited states than for the lowest excited singlet state. This fact is expressed by the Kasha rule according to which various conversion processes usually start from the vibrationally relaxed lowest excited state of a given multiplicity.

One of these processes is the radiationless transition from the lowest excited singlet to the corresponding triplet state, a process called intersystem crossing (ISC). Since it is forbidden, comparatively low rates are usually observed. Other processes are fluorescence, a radiative transition between two singlet states, and phosphorescence, a radiationless depopulation of the lowest triplet to the ground state. Characteristic relaxation times of all those processes are collected in Table I.

3.3 Competing processes

3.3.1 Bond scission.

Energy exchanges between molecules are often complicated by the presence of various competing processes. One of them is the rupture of a chemical bond A-B, producing either two oppositely charged ions $A^+ + B^-$ or two neutral radicals $A + B$. In favorable conditions, this process may be studied in real time conditions. For example, the reaction $I-CN \rightarrow I + CN$ was examined by setting up an experiment, in which ICN was first excited from the ground to the first excited repulsive state and next, after a time delay τ , from this state to another repulsive state (Fig.3). Knowing the R-dependence of the energy of the two repulsive states, the τ dependent separation of the fragments I and CN may be examined. This experiment was realized in the gas phase [2], but data are also available for liquids.

Fig. 3 Schematic presentation of the experiment permitting a real time study of dynamics of the ICN dissociation.

3.3.2 Conformational changes.

Geometrical changes may occur via rotation of a part of a molecule with respect to the remaining part. The spectral effect depends on the viscosity of the solvent [1]. If the isomerisation barrier height and the solvent viscosity are both low, a multiexponential decay of fluorescence is observed. Another observation is the conversion of the molecule, excited by the light absorption to a Franck-Condon state, to a local energy minimum of the first excited singlet state. Other spectral effects are described in the same reference.

3.3.3 Photoejection of electrons.

First reported in 1942, this process has frequently been observed in rigid solutions, but is also present in the liquid phase [3]. Photoionisation takes place either immediately after absorption, or after some delay ; there may be a barrier to the electron loss due to the resonance effects. Photoionisation can be monophotonic, biphotonic, or involve intermediate states between successive ionisations. Typical questions to be answered concern the rate of autoionisation, the nature of the intermediate states and the final fate of the resulting radical cation and of the electron. A number of systems have been investigated from this point of view.

3.3.4 Twist-induced charge transfer (TICT).

Subsequent to an electronic excitation, the TICT occurs in molecules composed of electron donor and acceptor subgroups. It is favored by appropriate conformation changes [4]. For example, a twisted configuration in which the two parts of the bichromophoric molecule are orbitally decoupled, is often representative. Arguments for the existence of the twisted configuration come mainly from the characteristic solvent dependence of the fluorescence, and from theoretical considerations. Although extensively studied, the detailed mechanism of the TICT is not yet entirely understood.

3.3.5 Solvatochromism

Solutions submitted to pico- or femtosecond light pulses often exhibit a time dependent fluorescence [5]. The origin of this effect is the variation of the electronic distribution of the dissolved molecule when it is electronically excited, and the subsequent reorganisation of the solvent around it. The experimentally measured quantity is the spectral response function

$$S(t) = \frac{\omega_p(\tau) - \omega_p(\infty)}{\omega_p(0) - \omega_p(\infty)} \quad (1)$$

where $\omega_p(0)$, $\omega_p(\tau)$ and $\omega_p(\infty)$ indicate the peak frequencies of the fluorescent light immediately after the excitation, τ seconds after excitation and at very long times, respectively. In practice, some care must be exercised in determining $\omega_p(0)$ and $\omega_p(\infty)$. This experiment permits to explore the poorly known excited state charge distributions.

Table I
Representative lifetimes

Vibrational relaxation	$1 - 10^3$ ps
Internal conversion	$10^1 - 10^5$ ps
Intersystem crossing	10^6 ps
Fluorescence	$10^2 - 10^6$ ps
Phosphorescence	$1 - 10^2$ sec

4. THEORY

4.1 Semi-classical approach

Any theory of the energy transfer in liquids requires the knowledge of the electronic distributions inside a molecule, as well as that of molecules in the liquid sample. It thus associates two disciplines of a very different origin. Quantum chemistry permits the study of the electronic structure of molecules as well as that of intermolecular forces. The latter are most often considered to be pair additive, which reduces the N-molecule electronic problem to its 2-molecule analogue. Statistical mechanics, in its classical form, permits to study the motions of N molecules of the liquid sample, coupled under the influence of these forces. According to a well known rule, the classical approach is valid whenever the inequality $\hbar\omega/k_B T \ll 1$, where $\hbar\omega$ is a representative molecular energy, holds true.

The electronic problem is generally treated in the clamped nuclei, or Born-Oppenheimer, approximation. The currently employed methods are the self-consistent field (SCF) and configuration interaction (CI) methods [6]. The maximal size of the basic set of atomic orbitals is of the order of a few thousands, whatever method is used. If a precise determination of molecular properties is required, the molecule should not contain more than 15 atoms of the second row of the periodic system. In other cases, compromises are necessary ; a number of semi-empirical methods have been invented for that purpose. As far as the density functional method is concerned, see below.

The statistical part of calculation may conveniently be realized by applying the molecular dynamics or Monte Carlo methods [7]. The procedure consists in substituting to the real system a system of reduced dimensions. The latter contains, typically, 10^2 to 10^3 molecules. In the molecular dynamics method, the Newton equations of motion are solved numerically, by the help of a computer. Alternatively, in the Monte Carlo method, the configuration integral is calculated by a judicious choice of configurations representative of the system ; here again, a computer must be employed. The calculations are often large-scale calculations, and parallel computers may be necessary.

4.2 Quantum mechanical approach

The semi-classical theory just described is inappropriate whenever some nonelectronic degrees of freedom are quantum mechanical, e.g. the proton degrees of freedom in a proton transfer reaction. Even if this is not the case, fully quantum mechanical simulations may be preferable, e.g. in calculating intermolecular potentials in thermally inaccessible regions. Quantum numerical methods are actually under development, following the initial work by Car and Parinello [8]. The procedure is based on the density functional theory, and involves energy minimization procedures such as simulated annealing. Several versions of this method exist at the present time. Although not yet applied to problems covered in this paper, quantum simulations will certainly play a major role in the future of this field.

4.3 Applications

Theoretical methods sketched above permit, in principle, to study energy exchanges in liquids. At first sight, the situation seems much alike that currently encountered in the liquid state physics. Unfortunately, the present problem is in reality much more difficult. The first difficulty is that several electronic states, both singlet and triplet, are involved in calculations. Energies, charge distributions and intermolecular forces must thus be evaluated for each of them. As they are much less known than for the ground electronic state, the experimental control is fragmentary. The second problem is that energy transfer processes are often relatively long ; compare with Table I. As it is difficult, at the present time, to perform molecular simulation runs much longer than 10^3 ps, it is impossible to follow an internal conversion process over a time interval as long as 10^5 ps ! Brownian dynamics, in which the true intermolecular forces are replaced by an effective stochastic force, permits to prolongate the calculations to a certain extent, but not as much as desirable. Another possibility is to consider the Heller theory of the internal conversion in free molecules [9] ; this theory employs the overlap correlation functions. In spite of these difficulties, a number of problems have been treated successfully by the existing theory. Two of them are illustrated below.

The first example of a succesful application of the theory is the calculation of the vibrational relaxation time T in liquids. The starting point is the well known Landau-Teller formula for the transition rates

$$T_{ij}^{-1} = \frac{2\hbar^2}{1 + \exp(-\beta\hbar\omega_{ij})} \int_{-\infty}^{\infty} dt \exp(i\omega_{ij}t) \langle V_{ij}(0)V_{ji}(t) \rangle \quad (2)$$

where $\hbar\omega_{ij}$ is the energy separation of the vibrational states i,j and $V_{ij}(t)$ the matrix element of the intermolecular potential between them. The latter is calculated, in principle, by employing quantum chemical methods, but empirical potentials are used too. The correlation function $\langle V_{ij}(0)V_{ji}(t) \rangle$ is then evaluated by performing a classical molecular dynamics simulation of the liquid sample. A number of systems have recently been treated in this way [10], e.g. the mixtures $\text{CH}_3\text{Cl}/\text{H}_2\text{O}$, $\text{I}_2/\text{H}_2\text{O}$ and the pure water.

The second, and the last, example concerns the solvatochromic effect. One generally assumes a linear solvation response, which permits to replace the spectral response function $S(\tau)$ by a simpler objet, the classical time correlation function

$$C(\tau) = \frac{\langle (\omega(\tau) - \langle \omega \rangle) (\omega(0) - \langle \omega \rangle) \rangle}{\langle (\omega(0) - \langle \omega \rangle) (\omega(0) - \langle \omega \rangle) \rangle} \quad (3)$$

where $\hbar\omega(\tau)$ is the fluctuating energy difference of the two electronic states ; the average is taken over the ground electronic state distributions [11]. The above simplification, which makes the calculation of averages in the excited electronic state unnecessary, has been controlled by several authors. It was found satisfactory even for jump as large as a full electronic charge on the solute molecule. A good agreement between theory and experiment has been reported.

5. DISCUSSION

It results from the above discussion, that a large body of information is actually available on the energy exchanges in molecular liquids. Experimental techniques exist to study the underlying molecular dynamics up to the femtosecond time scales. Moreover, theoretical methods are powerful enough to analyse an important fraction of the experimental material. Unfortunately, the number of theoreticians working in the field is relatively limited ; this field certainly merits more attention.

The situation is more uncertain as far as direct numerical simulations of detonations are concerned ; see e.g. Ref.[12]. As the structure of the shock wave is virtually unknown at the atomic level, numerical simulations are highly desirable. In fact, a significative progress has been accomplished in this domain the last decade. New computer architectures and new numerical algorithms have been developped ; the systems submitted to the investigation are more realistic and include more spatial dimensions and chemical complexity. Nevertheless, a computer simulation always remains, to a certain extent, an experiment. The experience has convinced the liquid state physicists that a long time is necessary before the quality of simulations can be assessed with certainty. This will no doubt be the conclusion of experts in this field too!

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