

# A classical molecular dynamics study of recombination reactions in a microporous solid

Francesco Delogu, Pierfranco Demontis,<sup>a)</sup> Giuseppe B. Suffritti, and Antonio Tilocca  
*Dipartimento di Chimica, Università degli Studi di Sassari, Via Vienna 2, I-07100 Sassari, Italy*

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Classical molecular dynamics calculations have been applied to the study of the recombination reaction of photodissociated radical species. Within a simplified reaction scheme it has been possible to get qualitative information about the influence of the environment. A comparison has been made between reactions in a liquid solvent and in a complex structured environment, such as a microporous silicate. Marked differences in the recombination yield and in the energy relaxation mechanism have been observed. © 1998 American Institute of Physics. [S0021-9606(98)50331-5]

## INTRODUCTION

The phenomena involved when chemical species subject to a chemical “driving force” react in a condensed phase environment are far from a detailed comprehension. In this field, computer experiments<sup>1-4</sup> seem suitable today for such detailed investigations, although they suffer considerable limits. The difficulties in developing and then applying these schemes are due, from a theoretical point of view, to the complex features of a chemical reaction and, from a practical one, to the available computing resources which prevent completely “ab initio” quantum mechanical calculations. On the other hand, although first-principles calculations<sup>5,6</sup> represent the most powerful and adequate tool, it is now well accepted that a starting point for an understanding of the intimate reaction mechanism can be achieved through classical<sup>7,8</sup> molecular dynamics (MD) simulations (so long as quantum effects are negligible), or with its semiclassical extensions,<sup>9</sup> which allow for the possibility of nonadiabatic transitions between coupled electronic states. The ability of these techniques to throw light on the microscopic details of the dynamical evolution of complex systems of atoms or molecules<sup>10-12</sup> makes them extremely useful for the analysis of condensed matter behavior. In particular, classical MD simulations have been used profitably to investigate the role played by the solvent molecules in the reaction mechanism and their influence on the stabilization of the reaction products, allowing new insight into the intimate solvent-solute interactions. At the same time, a full account of important phenomena like the caging and energy exchange processes involving a solute molecule and the solvent environment remains a difficult challenge, especially when the analysis has to be extended to a number of reactant molecules embedded in solvent cages. In fact their cooperative behavior is responsible for any encounter between the species, and it exerts a relevant influence upon the microscopic mechanism of the reaction.<sup>13,14</sup> The present work concerns the study of the geminate recombination reaction of two photodissociated atoms occurring in two different environments: a liquid one (tetrachloromethane, represented as spherical structureless

particles), and a solid one (a zeolite, that is a microporous crystalline silicate<sup>15</sup>). Zeolites are routinely used as heterogeneous catalysts in a very diverse range of catalytic reactions. Two fundamental considerations play a major role in understanding their catalytic activity: the first concerns the basic reaction mechanism, and the second, the way in which the products are controlled by the geometry and topology of the microporous crystal structure. The “molecular” dimensions of the zeolite micropores, consisting of a tridimensional network of interconnected channels and cavities, allow the selective adsorption and diffusion of chemical species;<sup>16</sup> in this respect a zeolite can be considered as a nonconventional solvent. We stress that notwithstanding the many experimental and theoretical efforts<sup>17</sup> in the understanding of the basic reaction mechanisms in zeolites, a detailed knowledge of the microscopic steps involved in the catalytic process is still lacking. Therefore we chose to model a simple radicalic reaction because many useful data can be obtained with a simple model potential. Moreover, radical species have a key role in heterogeneous catalysis, so they are a suitable starting point to investigate microscopic reaction dynamics in zeolites.

In this work we are not concerned by the determination of the detailed dynamics of the dissociation-recombination process, but the effectiveness of a microporous crystalline environment in promoting atom recombination is tested in comparison with a dense liquid solvent. The results regarding the reaction in the liquid phase are used mostly as a reference: the main purpose is to gain information about the zeolite action and, from this perspective, the comparison between the two environments is especially useful. Silicalite is the zeolite considered here. The masses and the potential parameters adopted to model the interaction between radicals correspond to the ground state of the iodine molecule: the participation of excited electronic states in the recombination is not considered. Inclusion of the curve-crossing dynamics into the simulation would be necessary in order to predict details of the recombination process, as it is well known that the iodine geminate recombination results from multiple crossings of excited electronic surfaces.<sup>18</sup> Recently, methods for incorporating electronic transitions in molecular dynam-

<sup>a)</sup>Electronic mail: demontis@ssmain.uniss.it

ics simulations have been developed,<sup>19</sup> but they are demanding of computer resources, and we preferred to model the recombination as occurring on a single electronic surface. This strong simplification allows much longer simulation times, which are required to reach the main purpose of our study. Indeed, the dissociation-recombination process is used here only as a “probe” to explore the diverse behavior of the two media, without considering the exact reaction mechanism. In other words, we are not interested in modeling the specific iodine recombination reaction, as we are well aware that the real process is much more complex than the model adopted. However, usually MD simulations effectively reproduce energy transfer and solvent caging effects, and also with a simplified model, reasonable predictions on the time scales for geminate recombination should arise. In fact, the calculated recombination times are in good agreement with experimental and theoretical data on the iodine recombination;<sup>20–31</sup> therefore, in the following, we will refer to the reacting species as “iodine,” in spite of the above-mentioned limitations.

The anisotropic structure of the silicalite, and the isotropic one of a liquid solvent embedding the solute molecules in more compact cages, can offer different structural environments to the recombination and, once it has occurred, to the energy relaxation<sup>31–39</sup> processes. Since primary recombination produces a nascent molecule near the dissociation limit, the effectiveness of vibrational relaxation in each environment plays a crucial role in the success of the reaction. The deactivation of the vibrationally “hot” molecule occurs on two different collisional pathways: inside the zeolite, the excess vibrational energy of the molecule can be transferred to the vibrational internal modes of the framework, while the adopted structureless model for the liquid solvent allows for vibrational to translational energy transfers only. The coupling between the vibrational modes could probably lead to a faster relaxation of the excited molecule inside the zeolite. However, previous works<sup>25,31</sup> showed that the V-T mechanism may be competitive with V-V energy transfer in the vibrational deactivation of an excited iodine molecule in liquid solvents. In particular, V-T transfer seems to dominate when the excited molecule moves in the upper half of the Morse well (i.e., during the more crucial step of the overall recombination process). Harris and coworkers<sup>29</sup> did not find evidence of resonant energy transfer to solvent vibrational modes in polyatomic chlorinated solvents. The present study of the recombination process in the two environments, with the choice of a structureless model of CCl<sub>4</sub>, entails a direct comparison of the effectiveness of the two energy-transfer mechanisms: in each environment a different relaxation mechanism is active. Other effects, like the different masses and density of the two media could also play an important role in the relaxation phenomenon, and they will be thoroughly examined.

## METHOD

In both liquid and silicate cases, a total of 200 MD trajectories were analyzed. All simulations have been carried out in the microcanonical (NVE) ensemble. In all cases, periodic boundary conditions were applied, and each trajectory

TABLE I. Potential parameters used.

Lennard-Jones <sup>a</sup> interactions		
Interaction	$\sigma$ (Å)	$\epsilon$ (kJ·mol <sup>-1</sup> )
I-CCl <sub>4</sub>	4.645	2.489
CCl <sub>4</sub> -CCl <sub>4</sub>	5.27	3.101
I-O	3.2745	1.737
Morse potential <sup>b</sup> parameters		
$r_{\text{eq}} = 2.666$ Å		
$D = 148.703$ kJ·mol <sup>-1</sup>		
$\beta = 1.867$ Å <sup>-1</sup>		
Harmonic potential <sup>c</sup> parameters (zeolite atoms)		
$k_{\text{Si-O}} = 2092$ kJ·mol <sup>-1</sup> ·Å <sup>-2</sup> ; $r_{\text{eq,Si-O}} = 1.605$ Å		
$k_{\text{O-O}} = 430.952$ kJ·mol <sup>-1</sup> ·Å <sup>-2</sup> ; $r_{\text{eq,O-O}} = 2.618$ Å		

$${}^a V(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right].$$

$${}^b V(r) = D \left\{ \left[ 1 - \exp[-\beta(r - r_{\text{eq}})] \right]^2 - 1 \right\}.$$

$${}^c V(r) = 1/2k(r - r_{\text{eq}})^2.$$

started with the dissociation of a stable iodine molecule in an equilibrated environment. In a real experiment the adsorption of light can produce, instantaneously on the time scale of diffusion, reactive intermediates whose chemical evolution is completely determined by their mobility in the surrounding environment. In the case considered here, dissociation takes place when the I<sub>2</sub>-CCl<sub>4</sub> solution is irradiated with a 5300 Å wavelength. Therefore, at the beginning of each simulation, dissociation was induced by attributing to each iodine atom a kinetic energy corresponding to 0.5  $h\nu$  (equal to 112.9 kJ/mol) along the axis of the molecule. After the initial dissociation, each trajectory was followed for a maximum of 60 ps. Recombination was considered to have occurred when the I-I distance fell below an empirical inner cutoff, provided that no further dissociation was observed. By direct inspection of the trajectories, a value of 4.30 Å has been assigned to the inner cutoff: indeed, once the dissociated atoms reached this distance, successful stabilization of the formed molecule was found to be very probable. In some cases, collision-induced recrossings of the critical distance were observed. Such multiple-collision events could lead eventually to a definitive separation or to a final recombination. In most cases, after the initial dissociation, the radicals lost a great part of the excess energy and thermalized before recombining. Therefore, energy requirements (i.e., internal energy below the dissociation limit) were usually satisfied.

An outer cutoff of 13 Å was also imposed: when the atoms reached this distance the probability of a later encounter on the 60 ps time scale was very low, then the trajectory was terminated.

Table I reports the adopted potentials with the corresponding parameters. The radicals always interacted via a Morse potential describing the *X* electronic ground state of the iodine molecule.<sup>40</sup> The iodine and oxygen atoms of the zeolite structure interacted via a Lennard-Jones (LJ) potential whose parameters are the same as Xe-O.<sup>41</sup> From these values, using the zeolite oxygen LJ parameters,<sup>42</sup> the combining rules<sup>7</sup> give  $\sigma_{\text{I-I}} = 4.02$  Å and  $\epsilon_{\text{I-I}} = 1.998$  kJ/mol. These parameters were used to obtain the reported I-CCl<sub>4</sub> parameters

(the source of the LJ parameters for the tetrachloromethane is Ref. 43). I-Si interactions were neglected, as usual in MD simulations of zeolites, because they are well shielded by the more polarizable oxygen atoms covering the surface of the channels. Reference 44 is the source of the O-O and Si-O interaction parameters for our zeolite harmonic model which enables a complete flexibility of the silicate framework. For later analysis the number of iodine-solvent atoms collisions, along with their duration and the energy exchanged during each contact, were recorded.

### Liquid case

A cubic simulation box containing 256 particles, with a side of 34.487 Å, reproducing the liquid density of the tetrachloromethane at 300 K, was used. At the beginning of each trajectory, a diatomic molecule was created in the liquid equilibrated configuration by randomly substituting two nearest neighbor tetrachloromethane molecules with two iodine atoms. Then the two atoms were approached along the axis of the molecule at the equilibrium bond length and the system was equilibrated for 1000 time steps (each time step being equal to 10 fs), with the interaction force between the iodine atoms described by the Morse potential. After this initial equilibration, dissociation was induced and the trajectory followed for a further 60 ps (or until the outer cutoff was reached).

### Zeolite case

Silicalite is the all silica analog of the synthetic zeolite catalyst ZSM-5. Its structure is shown in Fig. 1. Two different channel systems made of ten oxygen rings (with connecting Si atoms) with diameter of about 5.5 Å, are the main feature of its framework topology. Straight channels run parallel to [010] direction, while sinusoidal channels have an average direction along [100]. The channels' intersections, which allow three-dimensional motion of sorbed molecules, are elongated cavities of about 9 Å in diameter. We represented silicalite crystal structure, according to x-ray diffractions studies,<sup>45</sup> in the *Pnma* space group (orthorhombic), with unit cell lattice parameters  $\mathbf{a}=20.022$ ,  $\mathbf{b}=19.899$ ,  $\mathbf{c}=13.383$  Å.

The simulation box consisted of  $2 \times 2 \times 2$  crystallographic cells, resulting in 2304 framework atoms (768 Si and 1536 O). The box volume was 42 696.2 Å<sup>3</sup>, which is close to the volume of the simulation box in the liquid case (41 017.2 Å<sup>3</sup>).

In order to represent the motion of the silicate framework, we proposed<sup>44</sup> a model potential consisting of a network of neutral atoms (Si and O), the nearest neighbors being connected by harmonic springs. This mechanical flexibility, which reasonably simulates the vibrations of the framework, acts as an effective heat bath allowing for the energy relaxation of the reacting molecules. The reliability of this simple phenomenological model was tested by several authors<sup>46-48</sup> with satisfactory results.

A time step of 1 fs was used, insuring energy fluctuations lower than 0.1%. The time step was shorter than in the liquid case, in order to accurately describe the fast vibrational motion of the framework atoms. In the zeolite case,

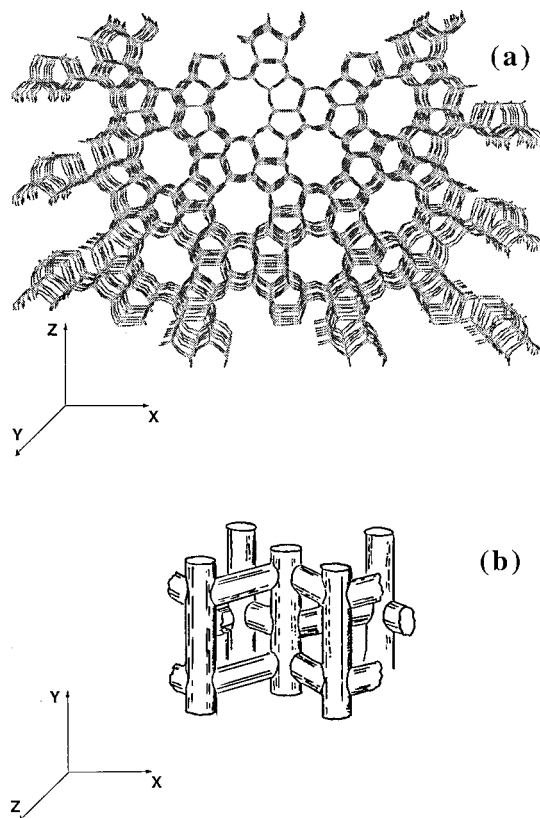


FIG. 1. (a) Structure of the straight channels of zeolite silicalite. (b) Schematic representation of channel geometry in silicalite; channels are represented as smooth pipes.

the initial relaxed system was created by introducing a stable iodine molecule in a channel of the silicate framework and then equilibrating the configuration for 200 ps. In each trajectory the molecule was allowed to diffuse for a 10 ps interval, at the end of which all information useful for the next trajectory was recorded; then dissociation was induced and the dynamical evolution of the system was followed. The next trajectory was started from the previously stored configuration, so that the initial iodine molecule moved inside the channels of the silicalite, independently of any dissociation, exploring a great part of the available void space. In this way, it has been possible to carry out the dissociation and to follow the dynamics in different regions of the silicalite with completely equilibrated configurations.

### RESULTS AND DISCUSSION

Table II reports the percentage of reactive events observed during the 200 trajectories in both solvents. Four different kind of events have been recorded:

- recombination takes place at the first encounter between the atoms;
- recombination occurs after several collisions;
- after some ineffective collisions, the molecule finally dissociates;
- no collision occurs.

The average time between the initial dissociation and the first encounter and that between the dissociation and the final recombination are also reported. The liquid solvent shows a

TABLE II. Reactive events (averaged over 200 trajectories).

	CCl <sub>4</sub>	Silicalite
Simple recombination reactions	59.5%	26.5%
Recombinations after collisions <sup>a</sup>	19%	8.5%
Collisions without reaction <sup>b</sup>	2%	5%
No collision	19.5%	60%
Mean first collision time (ps)	2.2±0.4	1.6±0.2
Mean reaction time (ps)	2.6±0.4	4.0±0.8

<sup>a</sup>Trajectories in which, after multiple collisions, a final recombination is observed.

<sup>b</sup>Trajectories which, after multiple collisional events, end in a dissociation.

greater efficiency in promoting recombination: in almost 80% of the trajectories the two iodine atoms recombine, and the small difference between the mean times of first collision and recombination indicates that almost all the first encounters are effective to promote recombination. In silicalite the encounter between atoms after the initial dissociation is less probable and, when it occurs, it appears to lead to the reaction less effectively than in the liquid phase. Indeed, the time between the first collision and the final recombination is considerably larger than in CCl<sub>4</sub>; moreover, if we analyze only the trajectories showing at least one encounter, in silicalite the fraction of ineffective (dissociative) encounters is much larger than in the liquid solvent (12.5% vs 2.5%).

The different structural organization of the two media is obviously involved in the observed differences. In dense solvents, the dissociating atoms may be trapped in a cage of surrounding molecules, increasing the primary recombination yield; at the same time, the cage hinders the encounter of atoms which have escaped from it. This last effect leads to a time scale of tens of picoseconds for secondary recombination; actually, none of the observed reactive trajectories shows such a behavior: i.e., all the recombinations observed in the liquid involve atoms which never completely escaped from the first solvent cage. In silicalite, the adsorbed molecule does not suffer any liquidlike caging and explores, driven by the surface oxygen atoms' force field, channels and cavities with a relevant free volume available. In such a situation the dissociation will cause, in most cases, the iodine atoms to depart more easily away from each other, leading to a lower recombination probability; moreover, the higher fraction of ineffective encounters and the considerable time between the first encounter and the final recombination seem to show that the stabilization of the newly formed molecule is slower in silicalite.

The average recombination times are 2.6 in CCl<sub>4</sub> and 4 ps in silicalite; due to the previously mentioned limitations of the model (in particular, the absence of internal degrees of freedom for CCl<sub>4</sub>, and the exclusion of excited state dynamics), a meaningful comparison could be made with previous work regarding the iodine dissociation-recombination in liquid xenon, whose mass and size are similar to CCl<sub>4</sub>. The MD simulations of Ref. 31, which consider only a single repulsive surface coupled to the ground state, lead to geminate recombination times of 2.5-4 ps at the various densities con-

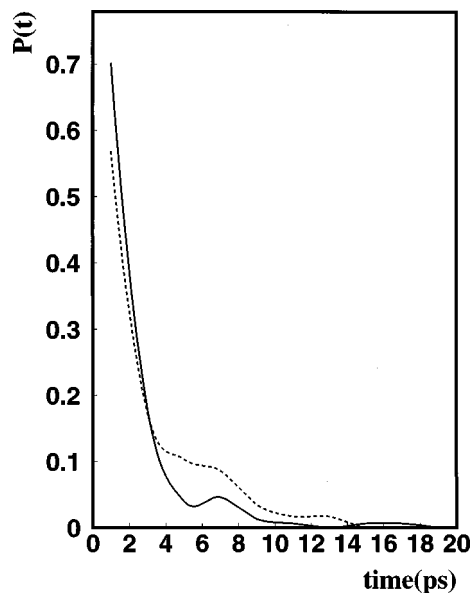


FIG. 2. Distribution functions of the final recombination times (dashed line: silicalite; continuous line: tetrachloromethane).

sidered. This is in agreement with previous simulations on similar systems,<sup>21-24</sup> as well as with our results. Moreover, the agreement with experimental results<sup>29,30</sup> is connected to the observation that the curve-crossing process (i.e., the jump from a repulsive unbound surface or an excited bound to the ground state, preceding the recombination) is very fast in the system considered here; for this reason, MD simulations could adequately predict recombination times without explicitly including surface-hopping models, as in the present study. The inclusion of all electronically excited states in the simulation could probably slow down the recombination: the occasional trapping of the molecule in an excited bound electronic state may slow the recombination rate down by a factor of five.<sup>18</sup> The simulation data should therefore be considered as lower bounds to the values of geminate recombination times.

The distributions of the observed recombination times are shown in Fig. 2 for both liquid and zeolitic cases. It is interesting to notice the similarity of the curves obtained in the two phases. A high probability of recombination in the first 2 ps after the initial dissociation and then a regular decrease to very small values are observed, the two cases differing only in the rate of occurrence of such a decrease, which is slower in the silicalite. This feature agrees with the previous observations: several collisions are often needed to form the molecular species in silicalite.

In order to better understand this point, further investigations on the energy relaxation processes have been carried out. Two distinct cases have to be considered: the first concerning the iodine atoms immediately after the dissociative event, the second the molecule formed after the recombination. In the first case, while in the zeolite the dissociated species retain a great part of their high initial kinetic energy, in the liquid the two dissociating atoms spend a part of it in deforming the surrounding solvent cage. This is shown in Figs. 3 and 4, where the kinetic energy of the two atoms, in

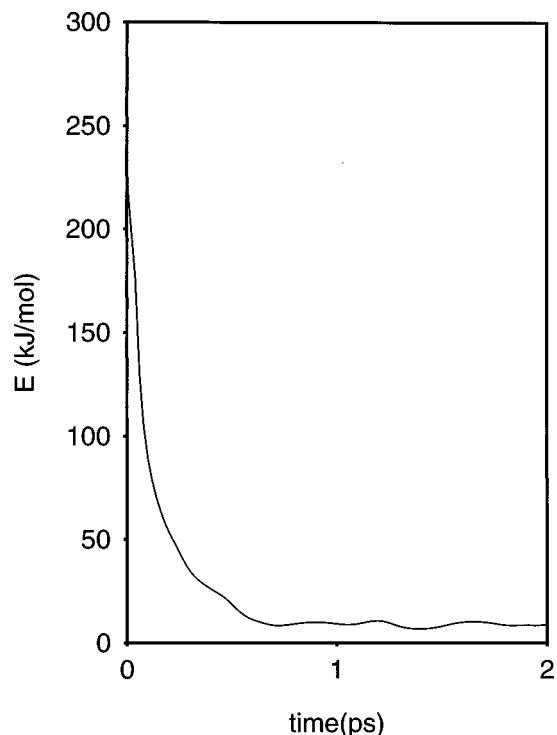


FIG. 3. Trend of the kinetic energy of iodine atoms in the first 2 ps following the dissociation in tetrachloromethane.

the first 2 ps after the dissociation, has been reported for tetrachloromethane and silicalite cases, respectively. A greater decrease of the kinetic energy curve is recorded in the liquid case. On the contrary, when the atoms have recombined, the silicalite appears to be more efficient in the dissipation of the excess vibrational energy of the molecule. This is shown in Figs. 5 and 6, reporting the vibrational energy of the molecule for  $\text{CCl}_4$  and silicalite, respectively, averaged over all the trajectories which lead to simple recombinations.

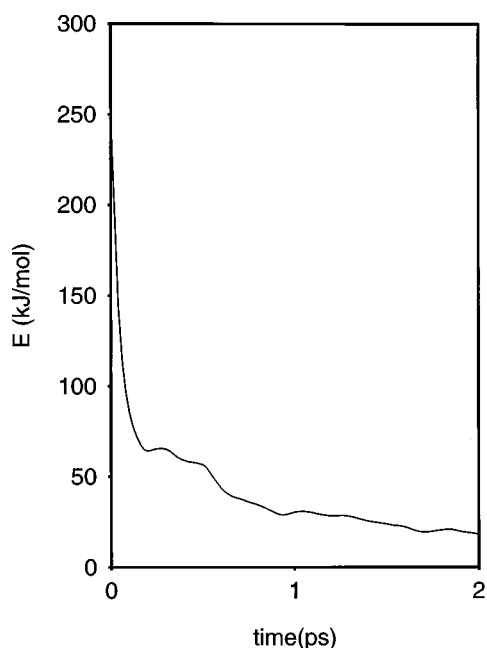


FIG. 4. The same as in Fig. 3 in silicalite.

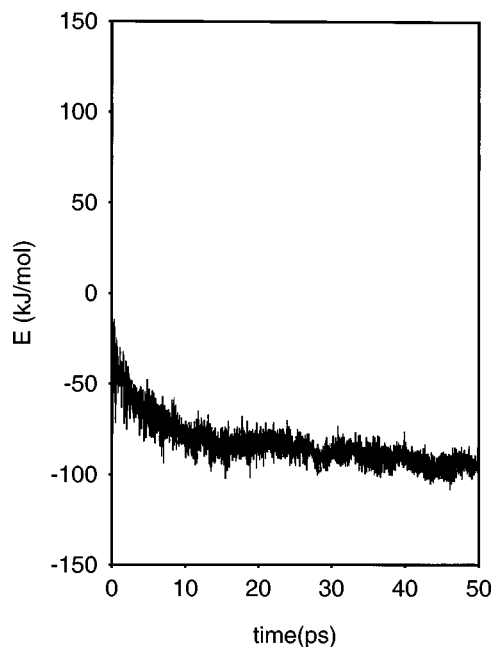


FIG. 5. Evolution of the vibrational energy of the iodine molecule in the first 50 ps after recombination in tetrachloromethane.

Note that the initial energies are similar in Figs. 5 and 6, but if we considered in the average *all* the reactive events, the initial vibrational energy in silicalite would be considerably higher (in that case, we would obtain an initial internal energy of  $-1.2$  in silicalite and of  $-8.8 \text{ kJ} \cdot \text{mol}^{-1}$  in the liquid); obviously, in order to obtain a meaningful relaxation curve, only those trajectories in which the molecule remains bound for a long time after the first encounter, i.e., the “simple reactions,” should be averaged. Larger fluctuations are recorded in the molecular vibrational energy for the liquid case. We further discuss this point below.

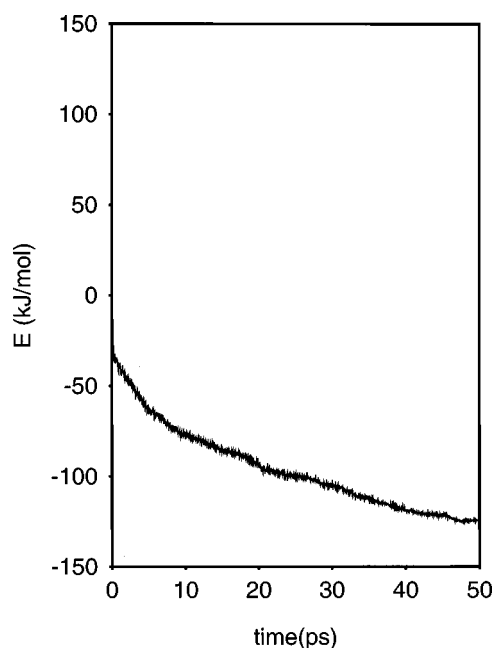


FIG. 6. The same as in Fig. 5 in silicalite.

TABLE III. Collision frequency, energy and duration.

	I-CCl <sub>4</sub>	I <sub>2</sub> -CCl <sub>4</sub>	I-O <sub>zeo</sub>	I <sub>2</sub> -O <sub>zeo</sub>
Collision frequency (ps <sup>-1</sup> )	9.6±0.4	6.4±0.5	13.1±0.6	9.1±0.8
Energy loss per collision (kJ·mol <sup>-1</sup> )	30.7±1.7	0.9±1.1	20.0±1.2	5.0±1.0
Duration of a collision (fs)	176.1±2.3	131.0±5.0	96.0±4.0	67.0±4.0

Also, the role of iodine-solvent collisions has been investigated. When the potential energy of interaction reached a positive value, a collision was recorded. Table III reports the results for the free atom-solvent and molecule-solvent collisions. In the first case the kinetic energy loss of the photodissociated radicals, and in the second case the vibrational energy loss of the molecule, have been averaged over all collisions with the solvent atoms.

When a single, highly energetic atom is considered, tetrachloromethane shows the better dissipative process. It is characterized by a lower number of collisions in the unit time, but also by a greater efficiency in the energy transfer process, together with a longer duration of the single collisions (columns 1 and 3 of Table III). Conversely, after the recombination the opposite happens. Now (columns 2 and 4 of Table III) a greater efficiency in the excess energy dissipation pertains to the silicate framework, again with a greater frequency and a lower duration of collisions but with a difference of almost one order of magnitude in the energy lost by the oscillator *per collision*.

The liquid solvent seems to better absorb the dissociation of the two atoms: the kinetic energy relaxation of the dissociated radicals is favored by the similarity of the colliding masses; the radicals dissipate their high kinetic energy through a direct transfer to translational solvent motion, and this mechanism seems to be very effective in the liquid.

Conversely, after the reaction, the energy transfer process between the silicate framework and the vibrationally excited molecule appears more efficient, notwithstanding the short duration of the collisions. It is well known that resonance between vibrational levels can significantly enhance the rate of energy transfer. Actually, the infrared (IR) spectrum of silicalite, as reproduced by the adopted harmonic model (Fig. 7), shows a broad band at frequencies just above the vibrational frequency of the iodine oscillator (214 cm<sup>-1</sup>). Therefore, the vibrational coupling between the oscillator and the zeolite framework is likely to favor the deactivation of the newly formed molecule. This phenomenon was thoroughly studied in a previous work.<sup>48</sup> In the power spectrum of the structureless CCl<sub>4</sub>, only “translational” frequencies below 100 cm<sup>-1</sup> are present (Fig. 8). It should be pointed out that, near the dissociation limit, the frequency of the “hot” molecule is significantly lower than its resonant “ground state” value ( $\omega \sim \omega_0/4$ , where  $\omega_0$  is the equilibrium frequency<sup>25</sup>). Therefore the frequency mismatch between the anharmonic oscillator and the silicalite internal modes might reduce the vibrational coupling immediately after the dissociation, i.e., in the upper half of the Morse well. After this

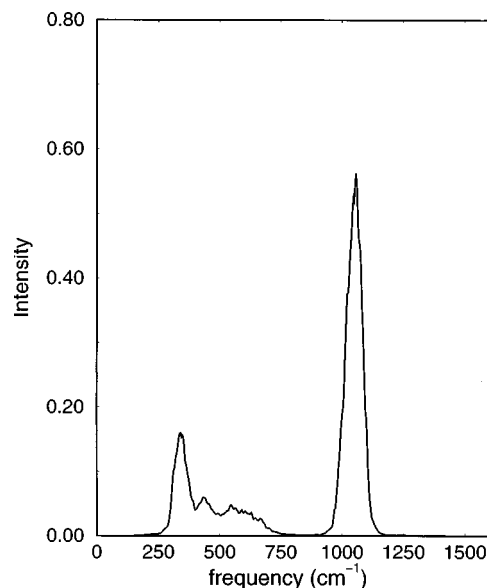


FIG. 7. Computed vibrational spectrum of silicalite (harmonic model).

initial period, the oscillator and zeolite vibrational frequencies tune into resonance, and the V-V transfer becomes finally predominant. This frequency mismatch was the explanation of the slow vibrational relaxation of iodine in flexible CCl<sub>4</sub> in the work of Nesbitt and Hynes,<sup>25</sup> where it was shown that the V-T deactivation route dominates in the first stages of the relaxation. However, in the present (zeolite) case the V-V transfer is always very effective: clearly in a detailed explanation of this phenomenon other effects than just the frequency overlap should be considered.

The energy relaxation channels have been further analyzed in terms of energy exchange between the oscillator internal modes. The total energy of the molecule was separated into translational, rotational and vibrational parts according to the following expressions:

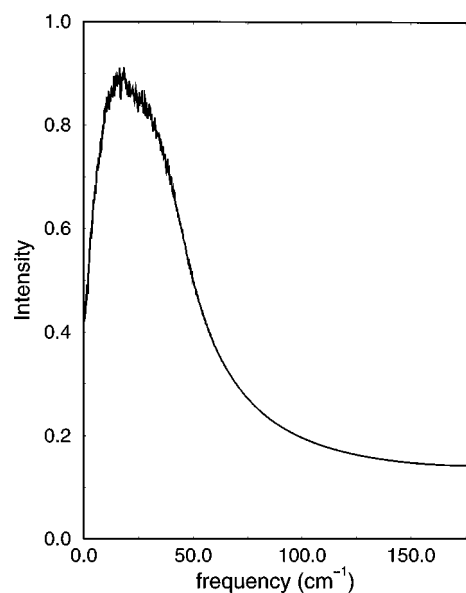


FIG. 8. Tetrachloromethane power spectrum (Fourier transform of the velocity autocorrelation function at 300 K).

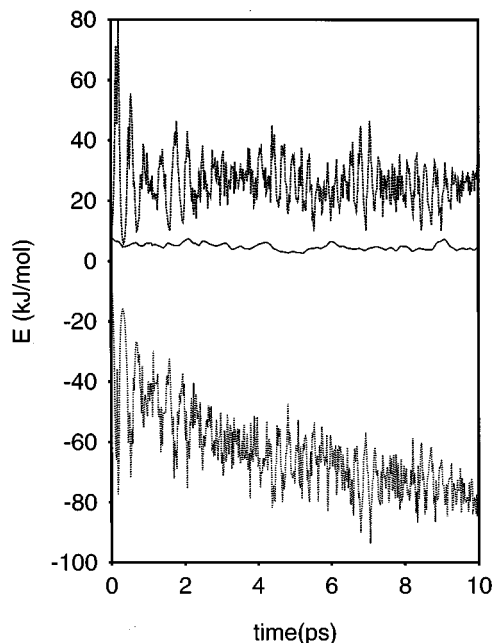


FIG. 9. Mean energies of rotational (upper, dashed curve), translational (middle, continuous curve) and vibrational (lower, dotted curve) modes in the first 10 ps after recombination in tetrachloromethane.

$$E_{\text{tot}} = \frac{1}{2} m (\mathbf{v}_1^2 + \mathbf{v}_2^2) + V(R), \quad (1)$$

$$E_{\text{trans}} = \frac{1}{4} m (\mathbf{v}_1 + \mathbf{v}_2)^2, \quad (2)$$

$$E_{\text{vib}} = \frac{1}{4} m \left[ \left( \mathbf{v}_1 \cdot \frac{\mathbf{R}}{R} \right) - \left( \mathbf{v}_2 \cdot \frac{\mathbf{R}}{R} \right) \right]^2 + V(R), \quad (3)$$

$$E_{\text{rot}} = E_{\text{tot}} - E_{\text{trans}} - E_{\text{vib}}, \quad (4)$$

where  $m$  is the mass of an iodine atom,  $\mathbf{v}_i$  is the velocity vector of the  $i$ -th atom,  $\mathbf{R}$  is the iodine-iodine distance, and  $V(R)$  is the Morse potential energy of the molecule.

In Figs. 9 and 10, the mean energies of the oscillator internal modes are reported in the first 10 ps after the recombination event for tetrachloromethane and silicalite, respectively, while Figs. 11 and 12 show in more detail the trend obtained in the first picosecond.

The main difference between the two environments concerns the higher energy fluctuations in the liquid phase: the flexible network of oxygen atoms is able to absorb and redistribute the impact of the colliding diatomic molecule with greater ease, compared with the compact distribution of heavy spherical atoms of the liquid. The different energy transfer mechanism is also involved in this effect: if a flexible model for tetrachloromethane was used, leading to other possible energy-exchange channels with the molecule, the collisions would be probably “softer” (and the energy fluctuations smaller), as in the zeolite case.

The observed anticorrelation between the rotational and vibrational modes has to be expected on the basis of the above definitions of the energies: every change in the direction of the velocity shifts energy between the two modes.

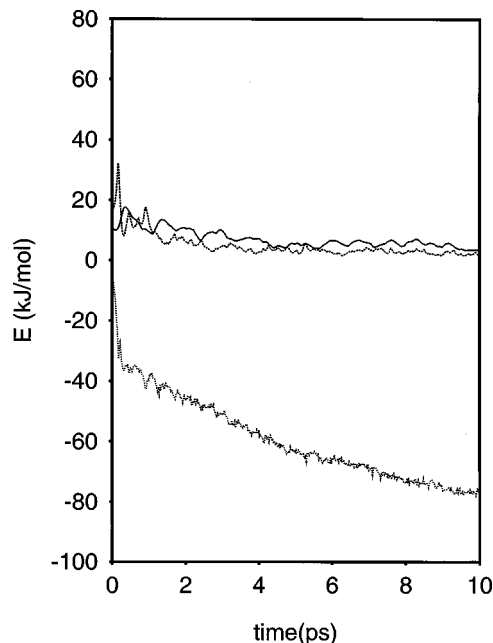


FIG. 10. The same as in Fig. 9 in silicalite.

The internal energy exchange between translational and rotational modes is more marked in the zeolite case, and this fact is already evident in the first picosecond after the recombination (Fig. 12). After that, the vibrational energy seems to decrease almost independently with respect to the rotational and translational motions (Fig. 10). In the liquid solvent, a stronger link between the vibrational and rotational motions is always present, while the translational energy is less involved in the overall relaxation. Obviously, the different energy transfer mechanism between the oscillator and the two environments should again be invoked to explain these inter-

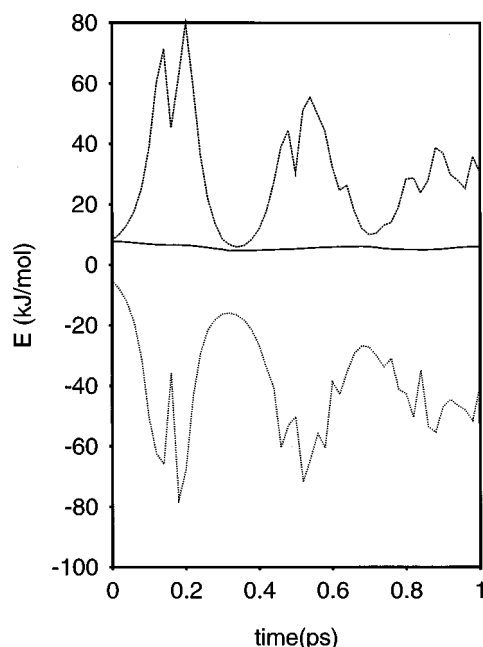


FIG. 11. Mean energies of rotational (upper, dashed curve), translational (middle, continuous curve) and vibrational (lower, dotted curve) modes in the first 1 ps after recombination in tetrachloromethane.

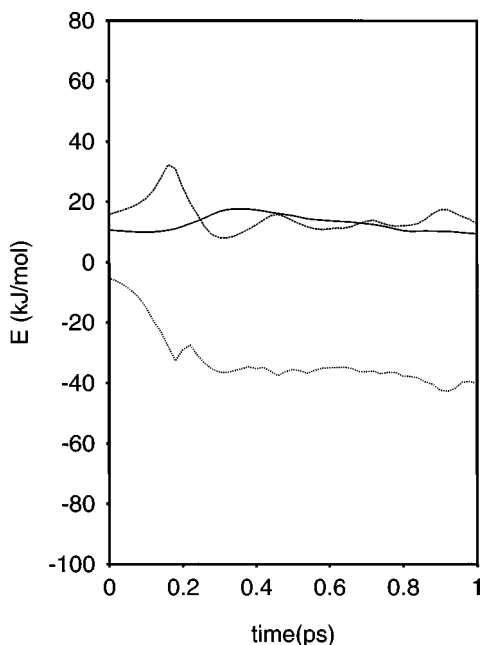


FIG. 12. The same as in Fig. 11 in silicalite.

nal relaxation paths: while the excess vibrational energy can be *directly* transferred to the zeolitic environment through the near-resonant V-V coupling (i.e., without passing through rotational or translational modes), in the liquid case the vibrational energy probably needs to be converted in rotational energy before being transferred to the solvent translational modes.

The correlation between the topology and the recombination path is now clear. Due to worse energy dissipation immediately after the dissociation, in silicalite the radicals collide with a relative kinetic energy higher than in the liquid. Then the greater initial energy of the formed diatomic molecule is dissipated in a longer time, notwithstanding the better efficiency of the single collisions between silicate and oscillator. In other words, silicalite could be the better “solvent” in which the recombinative events can take place. Unfortunately, the lack of a suitable cage (also able to prevent a consistent departure of the dissociating atoms) causes the worse initial (after-dissociation) energy dissipation and a smaller number of reactions. The disadvantage of a lower number of recombinations could probably be overcome with the use of zeolites showing more confining micropore systems. Indeed, the silicalite structure is rather “open,” i.e., the channel’s diameter is always large enough to let the iodine diffuse easily, and no narrow passages are present. Preliminary results on a ZK4-type zeolite (whose pore structure is made of a cubic array of nearly spherical cages interconnected by narrow windows of about 4.2 Å diameter) show a sharp increase in the recombination percentage, and very similar recombination times, compared to the “open” silicalite case. However, the longer lifetimes of radicals in silicalite might not be a disadvantage, if reactions with different species are sought, as they allow the radicals to reach other reactants before recombining. In Ref. 49 it was shown that the primary recombination rate is largely independent of the molecular details of the environment, while the recombina-

tion yield should be solvent dependent. This result agrees with the present calculations, showing similar recombination times, but different yields in the different environments. Work is in progress to better develop our understanding of these aspects.

## CONCLUDING REMARKS

The main contribution of this work is an attempt to understand the influence of the geometrical restrictions due to the silicalite framework on recombination reactions in comparison with a liquid Lennard-Jones solvent. We should comment how reliable our results are, by considering the assumptions made in order to perform the calculations. In the study of the catalytic action of zeolites, at least five different contributions should be taken into account. The most frequently mentioned in the current literature are the selectivity of the reactants, the selectivity of products and the very chemical effect of acid-base and/or transition metal catalysis. However, there are at least two other properties of zeolites which can influence the reactivity of the sorbed species: the heat bath effect of the framework, which can dissipate the excess energy of a chemical process or furnish thermal energy to reactants or products, and the influence of the (often locally strong) electric fields present in the micropores on the electronic energy states of the sorbates. In this paper we focused our study on the heat bath effect, providing a detailed view of the coupled adsorbed molecule-zeolite framework dynamics. In a previous paper<sup>48</sup> we discussed how the framework favors the relaxation of diatomic molecules oscillating at frequencies near to its characteristic vibrational frequencies, and in such cases we found a shorter relaxation time and an increase of the energy exchanged *per collision* with respect to diatomic molecules oscillating at frequencies out of the vibrational spectrum of the zeolite. Our harmonic model of the framework gave a good qualitative description of coupling phenomena connected to the energy exchanges with the sorbed species, and we observed that silicalite can stabilize vibrationally excited species, extracting from it the energy excess, on a picosecond time scale. Therefore we consider it reasonable to use classical MD as a guideline for the study of energy transfer phenomena like the ones which are described in this paper. At the same time, we are extremely conscious that improvements need to be made to the potentials to better represent adsorbate-zeolite interactions. However, in our opinion, to get insight into the physical phenomena which we are considering, it is sufficient to have a qualitative estimation of the adsorbate-adsorbent interaction. Therefore, in the present model only forces of the van der Waals type control the motion of a iodine atom or molecule in the zeolite. Moreover, classical MD models cannot include the quantum nature of the vibrational energy levels and of multiple potential energy hypersurfaces which are present even in a diatomic molecule and are involved in the recombination processes. In summary, quantitative results could be obtained only from lengthy and sophisticated methods, including quantum mechanical effects and the “*ab initio*” evaluation of potential energy hypersurfaces, which for complex reactive mechanisms could be computationally prohibitive. However, we think that the basic assumptions to



which we have drawn attention do not substantially affect our conclusions on the effect of the silicalite topology on simple radicalic reactions.

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