

# A quantum mechanics-molecular mechanics study of dissociative electron transfer: The methylchloride radical anion in aqueous solution

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The dissociative electron transfer reaction  $\text{CH}_3\text{Cl} + e^- \rightarrow \text{CH}_3^\bullet + \text{Cl}^-$  in aqueous solution is studied by using a QM/MM method. In this work the quantum subsystem (a methylchloride molecule plus an electron) is described using density functional theory while the solvent (300 water molecules) is described using the TIP3P classical potential. By means of molecular dynamics simulations and the thermodynamic integration technique we obtained the potential of mean force (PMF) for the carbon–chlorine bond dissociation of the neutral and radical anion species. Combining these two free energy curves we found a quadratic dependence of the activation free energy on the reaction free energy in agreement with Marcus' relationship, originally developed for electron transfer processes not involving bond breaking. We also investigated dynamical aspects by means of 60 dissociative trajectories started with the addition of an extra electron to different configurations of a methylchloride molecule in solution. The PMF shows the existence of a very flat region, in which the system is trapped during some finite time if the quantum subsystem quickly losses its excess kinetic energy transferring it to the solvent molecules. One of the most important factors determining the effectiveness of this energy transfer seems to be the existence of close contacts (hydrogen bonds) between the solute and the solvent. © 2002 American Institute of Physics.

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## I. INTRODUCTION

The term dissociative electron transfer is used for describing the process of electron attachment to a molecule with a potentially cleavable bond. Electron attachment to these molecules leads to the formation of temporary radical anions which decay with lifetimes usually varying between  $10^{-13}$  and  $10^{-15}$  s.<sup>1,2</sup> One of the most typical examples of this kind of reactions is the electrochemical dissociation of alkyl and aryl halides  $\text{RX}$  (where  $\text{X}=\text{F}, \text{Cl}, \text{Br}, \text{I}$ ), which is a powerful technique for the production of alkyl and aryl radicals.<sup>3</sup> These reactions can be classified into two categories: consecutive or concerted dissociative reactions,<sup>4</sup> depending on the particular reaction mechanism followed (1 or 2):



The reaction mechanism is in fact determined by the lifetime of possible intermediates, in this case of the radical anion  $\text{RX}^{\bullet-}$ .

Alkyl and aryl halides constitute the most investigated group of organic molecules suffering dissociative electron reduction. Their rate constants have been determined by pulse radiolysis or electrochemical methods.<sup>5–9</sup> A pronounced effect of the solvent has been observed, the cleavage rates being generally higher in dipolar aprotic solvents

than in water.<sup>8</sup> Thus, for 4-nitrobenzylchloride, the rate constant increases in a factor of  $10^2$  when changing the solvent from water to dimethylformamide.<sup>4</sup> There is also some evidence of solvent-induced change from consecutive to concerted reaction mechanisms.<sup>9</sup> The radical anions of organic halides can also be generated by  $\gamma$  irradiation in low-temperature matrices of inert solvents and studied by means of EPR spectroscopy.<sup>10–12</sup> The most unstable halide radical anions are characterized as being of  $\sigma^*$  type, i.e., the attached electron resides in a  $\sigma$  antibonding C–X orbital. Nitroaryl-containing radical anions, which are more persistent have the attached electron in a mixed  $\pi^* - \sigma^*$  orbital. For simple alkyl halides, the radical anion is described as a charge transfer complex between the alkyl radical ( $\text{R}^\bullet$ ) and the halide anion ( $\text{X}^-$ ).

Several theoretical papers have been devoted to the study of electron attachment to some alkyl halides, namely, methylfluoride,<sup>13–15</sup> methylchloride,<sup>13,15–18</sup> methylbromide,<sup>18</sup> methyliodide,<sup>18</sup> and some perhalogenated methylhalides.<sup>18,19</sup> In these studies, the dissociation curves for the neutral and radical anionic species have been constructed at different computational levels, including Hartree–Fock,<sup>16</sup> Møller–Plesset perturbation theory,<sup>17–19</sup> configuration interaction,<sup>15</sup> CASSCF,<sup>13</sup> and coupled cluster.<sup>14</sup> The question of the selection of an appropriate basis set has been of particular interest. The inclusion of diffuse functions in the description of anions and their dissociation has been discussed by several authors.<sup>13–15,20–23</sup> Pérez *et al.*<sup>15</sup> argued that an adiabatic or diabatic description of the alkylhalide dissociation is obtained depending on the nature of the diffuse functions added

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to the basis set. It has been usually assumed that the dissociation of both the neutral and anionic species takes place along a  $C_{3v}$  path.<sup>14–16</sup> In the case of methylchloride, a shallow energy minimum is found along the  $C_{3v}$  dissociation curve of the radical anion, at carbon-chlorine distances of about 4.0 Å, corresponding to a weak complex between chloride anion and methyl radical. However, Tada *et al.*<sup>17</sup> showed that the absolute minimum for the methylchloride radical anion is a  $C_{2v}$  structure, the crossing of both  $C_{3v}$  and  $C_{2v}$  dissociation curves of the radical anion taking place at a carbon–chlorine distance of about 3.2 Å.

The activation energy for the dissociative electron transfer in the gas phase is highly dependent on the computational level, ranging from 19 to 31 kcal/mol for methylchloride.<sup>4</sup> Solvent effects have been considered in some studies, usually by means of continuum models.<sup>13,17,18</sup> In solution, the radical anion species is largely stabilized relatively to the neutral molecule, the dissociation process being clearly favored. In particular, the existence of a minimum energy structure on the potential energy surface of the anion radical in solution has been not clearly established. It is worth to mention a Monte Carlo simulation of the electrochemical dissociation of methylfluoride and methylchloride along the  $C_{3v}$  curves, showing the limits of the Marcus,<sup>24</sup> relationship to describe these kind of electron transfer reactions involving bond breaking.<sup>15</sup> The theory developed by Marcus and others<sup>24</sup> established, for reactions not involving the breaking or formation of bonds, a quadratic driving force-activation free energy relationship. Savéant<sup>25</sup> extended the validity of this relationship for dissociative electron transfer reactions on the basis of a Morse curve description of the solute internal potential energies and a dielectric treatment of the solvent. However, the results of the Monte Carlo simulation cited above suggested that the extension of the Marcus' relationship to this kind of reactions should be valid only under some specific circumstances, obtaining a large error when applied to methylchloride.<sup>15</sup>

In summary, the knowledge obtained from quantum chemical calculations about dissociative electron transfer is still somewhat uncertain. The nature of the dissociation path has been not completely established and the existence of a minimum energy complex on this path is still controversial, especially regarding the process in solution. Moreover, dynamical aspects of the dissociation process, and the coupling with the solvent dynamics, has been not tackled in previous works. Here we present a molecular dynamics (MD) study of the dissociative electron transfer of methyl chloride in water solution, in which a hybrid quantum mechanics/molecular mechanics (QM/MM) potential is employed. The QM/MM methodology, which has received a considerable attention during the last years,<sup>26–32</sup> seems quite well adapted for analyzing these kind of systems, where bonds are broken or formed in a limited part of the system. This part (the methylchloride molecule in our case) constitutes the QM subsystem as far as a quantum mechanical treatment is needed in order to get a correct description of the electron reorganization. The rest of the system (water, or more generally, solvent molecules) is the MM subsystem and can be adequately represented by means of a molecular mechanics potential.

QM/MM schemes were originally developed for semiempirical Hamiltonians,<sup>26,27</sup> mainly because of the computational resources required for a simulation. However, a semiempirical description of the quantum part is not always an appropriate selection to describe many chemical processes, and dissociative electron transfer is clearly one good example. Fortunately, *ab initio*<sup>30</sup> and density functional<sup>31,32</sup> treatments of the quantum subsystems has been also implemented in QM/MM schemes, broadening the scope of this methodology to a vast variety of chemical processes.

## II. METHODOLOGY

In our study the total system is composed by a methylchloride molecule (plus an electron when studying the radical anion) surrounded by a box of 300 water molecules. The quantum subsystem is the methylchloride molecule and is described using density functional theory (DFT).<sup>33</sup> The water molecules constitute the molecular mechanics subsystem. Simulations are carried out using our DFT/MM program which has been described elsewhere.<sup>34,35</sup> The electron density of the quantum subsystem is obtained solving the corresponding Kohn–Sham equations<sup>36</sup> using a double-zeta plus polarization basis set, Cl [4s3p1d], C [3s2p1d], H [2s] [these basis sets are named Cl-(6321/521/1), C-(621/41/1), H-(41) in the DEMON program, indicating the number of gaussian functions used]. The auxiliary basis sets for the electron density and exchange-correlation fit were Cl (5,4;5,4), C (4,3;4,3), and H(4;4). See DEMON program documentation for details.<sup>37</sup> In all our calculations a Becke–Perdew nonlocal functional was employed for the exchange-correlation term.<sup>38,39</sup> The Lennard-Jones parameters employed for the quantum atoms in the calculation of the dispersion-repulsion interaction between the quantum and classical subsystems were taken from Ref. 40. The molecular mechanics subsystem was described by means of the TIP3P potential.<sup>41</sup> Forces are obtained from the analytical derivatives of the energy with respect to the positions of quantum nuclei and classical sites. Using these forces one is able to integrate the corresponding equations of motion to obtain the new atom positions and velocities. In this way, a trajectory of the full system can be followed. Simulations have been carried out at the NVE ensemble in a cubic box of 20.84 Å. The equations of motion of the molecular mechanical molecules are solved using a quaternion based leapfrog algorithm due to Fincham<sup>42</sup> and for the quantum subsystem a velocity Verlet algorithm.<sup>43</sup> Equilibration of the different simulations (see below) was carried out at 25 °C by scaling the velocities of the quantum atoms and classical water molecules. Periodic boundary conditions and a cutoff distance of 10.0 Å have been applied. Quantum hydrogen atoms have the mass of deuterium, while the rest have the usual values.

## III. RESULTS

### A. Dissociation energy curves

We have first explored the dissociation curves of the neutral methylchloride and the radical anion in the gas phase in order to compare with experimental data and previous theoretical studies. The dissociation curve of the neutral mol-

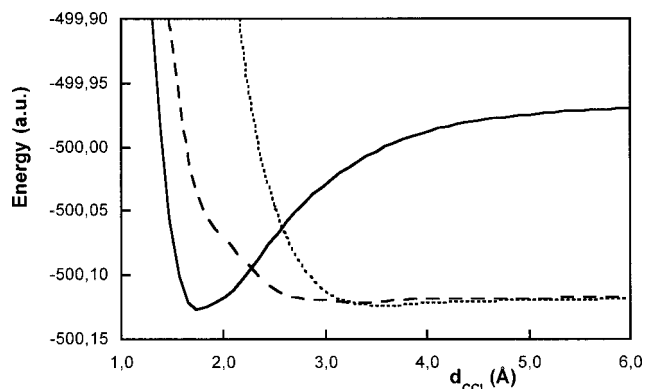


FIG. 1. Gas phase energy curves for the dissociation of methylchloride molecule (continuous line) and the radical anion, assuming  $C_{3v}$  symmetry (long-dashed line) or  $C_{2v}$  symmetry (short-dashed line).

ecule has been obtained using  $C_{3v}$  symmetry, while for the radical anion we explored both the  $C_{3v}$  and  $C_{2v}$  dissociation paths. The three energy curves are given in Fig. 1, and in Table I some characteristics of the neutral molecule are collected and compared with experimental values. The neutral molecule presents an energy minimum with a C–Cl distance of 1.802 Å, close to the experimental value of 1.78 Å. This species dissociates to neutral methyl radical and chlorine atom with a dissociation energy of 87.1 kcal/mol to be compared with the experimental value of 83.4 kcal/mol. With respect to the radical anion dissociation curves, the  $C_{3v}$  path is the minimum energy one for C–Cl distances shorter than 3.24 Å. For larger distances, the  $C_{2v}$  curve is placed below the  $C_{3v}$  one. Both curves present a shallow energy minimum. The  $C_{3v}$  stationary point appears at a carbon–chlorine distance of 3.203 Å and dissociates to methyl radical and chloride anion with a dissociation energy of 3.57 kcal/mol [2.54 kcal/mol if we add the counterpoise correction for the basis set superposition error (BSSE)]. The  $C_{2v}$  minimum energy structure appears at a C–Cl distance of 3.618 Å with a dissociation energy of 5.09 kcal/mol (4.05 kcal/mol when corrected for the BSSE). A similar energy minimum was previously reported by Tada *et al.*<sup>17</sup> at a carbon–chlorine distance of 3.75 Å using the UMP2/6-31+G\* level of theory. These authors also found that the  $C_{3v}$  stationary point of the radical anion had a doubly degenerated imaginary frequency at that computational level. We also confirmed the relative position

TABLE I. Calculated and experimental characteristics of neutral methylchloride molecule in the gas phase.  $d_{\text{CCl}}$  is the carbon–chlorine distance (in Å),  $D_e$  the bond dissociation energy (in kcal/mol), VEA the vertical electron affinity (in kcal/mol), EA(Cl) the electron affinity of chlorine atom (in kcal/mol), and  $\mu$  the dipole moment (in Debyes).

|                  | Experiment        | Calculated |
|------------------|-------------------|------------|
| $d_{\text{CCl}}$ | 1.78 <sup>a</sup> | 1.802      |
| $D_e$            | 83.5 <sup>b</sup> | 87.1       |
| VEA              | 79.5 <sup>c</sup> | 65.4       |
| EA(Cl)           | 83.2 <sup>d</sup> | 80.7       |
| $\mu$            | 1.94 <sup>e</sup> | 2.18       |

<sup>a</sup>Reference 44.

<sup>d</sup>Reference 47.

<sup>b</sup>Reference 45.

<sup>e</sup>Reference 48.

<sup>c</sup>Reference 46.

of the  $C_{2v}$  and  $C_{3v}$  minima using a higher theoretical level, UMP2/6-311++G(3d2f,2p). At this level we found the  $C_{2v}$  and  $C_{3v}$  radical anion minima at carbon–chlorine distances of 3.641 and 3.398 Å, respectively. The dissociation energies are 4.24 and 1.23 kcal/mol, respectively (3.68 and 0.80 kcal/mol if we correct for the BSSE). This means that; at this computational level, the  $C_{2v}$  structure is 3.01 kcal mol<sup>-1</sup> more stable than the  $C_{3v}$  one (2.88 kcal/mol when correcting for the BSSE) in good agreement with our DFT computational model. Other calculated values appearing in Table I, such as the electron affinity of the chlorine atom and the vertical electron affinity of methylchloride compares well with experimental values and also with previously reported theoretical estimations,<sup>13,17,18</sup> confirming the goodness of the selected computational level for describing our quantum system.

It is worth mentioning an additional question about the electron transfer to methylchloride in the gas phase. The dissociation curves presented above have been drawn assuming an initial zero energy level for the electron to be attached. This means that for carbon–chlorine distances shorter than the crossing point between neutral and anionic curves (2.26 Å), the radical anion is unstable as compared to the neutral molecule plus a free electron (i.e., it has a negative electron affinity). These curves, which could be referred as diabatic,<sup>15</sup> are a consequence of the lack of diffuse functions in the basis set. In our case, the added electron occupies a  $\sigma^*$  C–Cl antibonding molecular orbital for carbon–chlorine distances shorter than 2.26 Å. If diffuse functions are added to the basis set, for distances shorter than the crossing point, the added electron would occupy the most diffuse orbital available, and the system could be described as a neutral molecule plus a free electron. In this way the anionic and neutral dissociation curves would become identical.<sup>14,15</sup> After the corresponding crossing point, the electron would occupy the  $\sigma^*$  C–Cl antibonding molecular orbital and the results would be close to those obtained without diffuse functions. The dissociation curve obtained in this way is usually referred as the adiabatic curve.<sup>15</sup> As pointed out above, the problem associated with the inclusion of diffuse functions in the basis sets for the description of anionic systems has been discussed by several authors.<sup>13–15,20–23</sup> Of course, this is only an ad hoc procedure to obtain a diabatic representation. However, this is not really relevant for the main purpose of our work, the dissociation process in solution, which takes place along the radical anion curve, placed below the neutral one. Then, both descriptions, using or not diffuse functions, should be qualitatively identical. There is one more reason for avoiding the use of these basis functions in our QM/MM treatment; the addition of diffuse functions on the QM subsystem could lead to unphysical charge transfer to the MM centers. In any case, we have estimated that the addition of diffuse functions would stabilize the anion complex by about 0.5–1.0 kcal/mol, an error which is partially cancelled out by the BSSE.

In solution, we have computed the potential of mean force (PMF) as a function of the carbon–chlorine distance for both the neutral molecule and the radical anion. In this

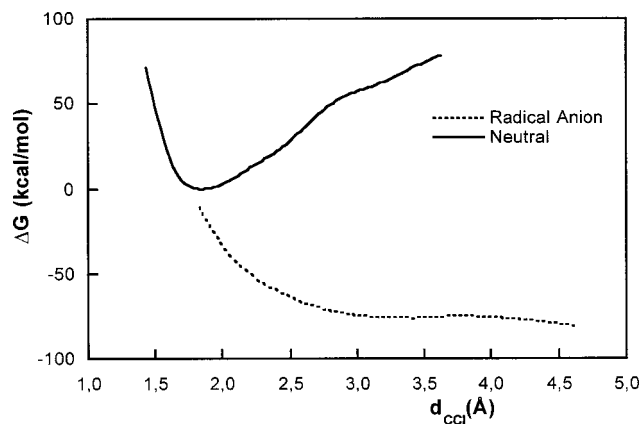


FIG. 2. Potential of mean force for the dissociation of methyl chloride (continuous line) and its radical anion (dashed line) in aqueous solution.

work, the PMF is obtained by means of combined QM/MM molecular dynamics simulations using a thermodynamic integration technique. At each step of this method the carbon–chlorine distance is fixed and the time averaged force along the C–Cl axis is calculated. This average force is subsequently integrated to give the PMF. The curve corresponding to the neutral methylchloride was obtained with increments of  $\pm 0.2$  Å, starting at the equilibrium carbon–chlorine distance, 1.827 Å, obtained as the 60 ps averaged distance from a nonrestricted MD simulation (see below for details). The curve of the radical anion was also started at the same distance with increments of 0.1/0.2 Å. Attempts to simulate the methylchloride radical anion in solution with shorter C–Cl distances (i.e., for negative increments) resulted in spontaneous breaking of a C–H bond. Each point in the PMF was equilibrated during 40 ps and the averaging procedure was carried out also during 40 ps, using in both cases a time step of 1 fs. In this conditions, each point of the PMF took about 240 h of CPU in a Silicon Graphics R12000 processor at 300 MHz. A total of 11 points were used for the neutral species and 16 for the anionic one.

The two PMF are shown in Fig. 2. In order to place one PMF curve relatively to the other we assumed an initial zero energy for the electron to be added and then we calculated the free energy for the transformation of the neutral methylchloride to the radical anion in aqueous solution at a fixed carbon–chlorine distance (1.827 Å in this case). This free energy was estimated as the sum of two contributions,

$$\Delta G \approx \Delta G_{\text{sol}} + \Delta E_{\text{ele}}, \quad (3)$$

where the first term is the differential solvation free energy between the two species and the second one is the differential electronic and nuclear energy.<sup>49</sup> The obtained free energy for the neutral→anion transformation was of  $-8.6$  kcal/mol.<sup>52</sup> The radical anion PMF is clearly dissociative and no minimum energy structure appears for bonded carbon–chlorine distances. This free energy curve displays a very flat region ranging from 3.4 to 4.0 Å, with a very shallow minimum placed at a carbon–chlorine distance of approximately 3.6 Å. From this structure the dissociation free energy barrier is only of about 0.8 kcal/mol. Thus, because of the uncertainties and errors associated to the methodology (for example

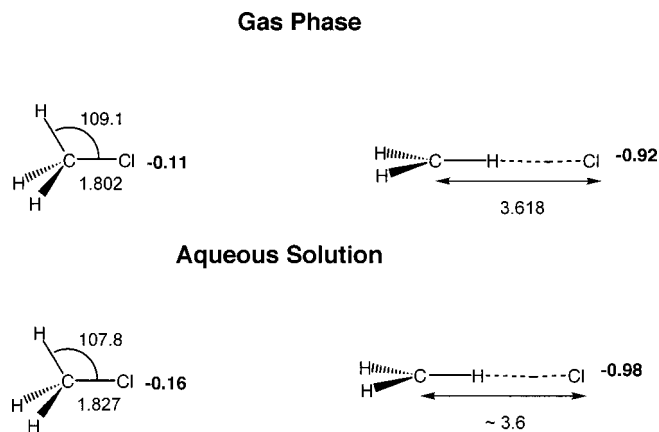


FIG. 3. Gas phase and aqueous solution minimum energy structures for the neutral methylchloride molecule ( $C_{3v}$ ) and its radical anion ( $C_{2v}$ ). Mulliken charge on the chlorine atom appears in bold characters.

cutoff effects, low number of points,...), this structure should not be considered as a true minimum but as a representative structure of a rather flat region of the free energy surface.

The minimum energy structures found for the neutral methylchloride molecule and its radical anion in the gas phase and in aqueous solution are shown in Fig. 3. Solvation lengthens the carbon–chlorine distance in neutral methylchloride and increases the negative charge on this last atom, both effects leading to an increase of the molecular dipole moment (2.18 D in the gas phase and 2.68 D in aqueous solution) and thus of the solute–solvent interaction energy. The structure of the methylchloride radical anion absolute energy minimum in the gas phase has  $C_{2v}$  symmetry. In solution, a molecular dynamics simulation of the radical anion with the carbon–chlorine distance fixed at 3.6 Å showed that the symmetry was not clearly defined for this structure. The angle formed between the methyl hydrogens' plane vector and the CCl vector (which takes the values of  $180^\circ/0^\circ$  and  $90^\circ$  for pure  $C_{3v}$  and  $C_{2v}$  structures, respectively) presents an average value close to the value corresponding to a  $C_{2v}$  structure but its time evolution shows oscillations of very large amplitude, approximately  $\pm 40^\circ$ , indicating a not-well defined relative orientation of the methyl radical with respect to the carbon–chlorine axis. The Mulliken charge of the chlorine atom in the radical anion is  $-0.92$  a.u. in gas phase and  $-0.98$  a.u. in solution, these values being in good agreement with the degree of charge transfer observed for these complexes in argon matrix.<sup>4,10–12</sup> Figure 4 shows the water hydrogens–chlorine atom radial distribution functions (RDF). In the case of the neutral molecule, the solute–solvent interaction is not enough to give a well-defined solvation shell around the chlorine atom. According to the negative charge localized on the chlorine atom, the H–Cl RDF for the radical anion shows two well-defined solvation shells around this atom. The coordination number obtained by integration of the RDF first peak is of 6.6, close to the value obtained from a simulation of a chloride anion in aqueous solution (7.4).<sup>53</sup> For comparison purposes, Fig. 4 also shows the H–Cl RDF for the radical anion when the carbon–chlorine distance is constrained to the value corresponding to the neutral molecule. In this case, we also observe two well-

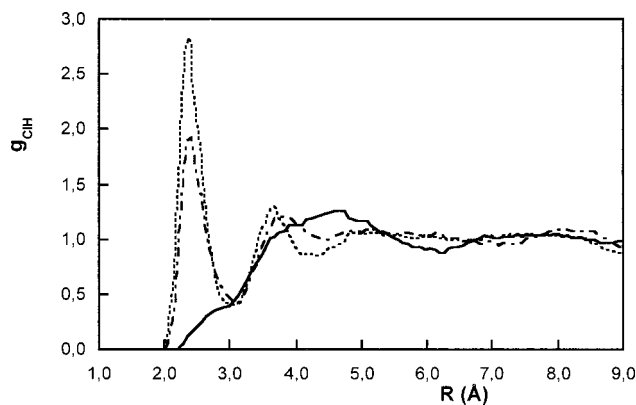


FIG. 4. Radial distribution function of solvent hydrogen atoms around quantum mechanical chlorine atom for the neutral methylchlorine molecule (continuous line), for the radical anion with the carbon–chlorine distance restricted to the average value of the neutral molecule (long-dashed line), and for the relaxed radical anion (short-dashed line).

defined solvation shells, being the coordination number of the chlorine atom of 5.4. So, anion solvation appears as one of the driving forces contributing to dissociation after the electron transfer and thus coupling between solute and solvent dynamics can be one of the important factors in determining the mechanism.

### B. Electron transfer activation free energies

From the dissociation free energy curves obtained for the neutral molecule and the anion radical (Fig. 2) we can also obtain information about the activation free energies for the electron transfer. Once the two PMF curves are placed relatively each other, their final relative position actually changes depending on the initial energy of the added electron. Thus, assuming different values for the electron energy, the neutral dissociation curve can be displaced relatively to the anionic dissociation curve. In this way we can get couples of values for the activation free energy (calculated as the free energy difference between the crossing point of the diabatic curves and the reactants) and the reaction free energy (obtained as the free energy difference between products and reactants). A representation of the activation free energy versus the reaction free energy is shown in Fig. 5. These values can be fitted to a Marcus' type equation with two fitting parameters  $a$  and  $b$ ,

$$\Delta G^\ddagger = a \left( 1 + \frac{(\Delta G^0 + b)}{4a} \right)^2, \quad (4)$$

where  $a$  is the activation free energy at zero driving force and  $b$  corrects the reaction free energy from the fact that our PMF were too short and from other methodological errors. A least square fit gives  $a = 15.5$  kcal/mol,  $b = 12.1$  kcal/mol. The obtained correlation coefficient (0.9996) reflects the excellent fit between the Marcus' predictions and our calculated values. Savéant extended the applicability of Marcus' relationship to dissociative electron transfer reactions on the basis of a Morse description of the potential energy, obtaining a satisfactory agreement between experimental data and theory.<sup>25</sup> However, after Monte Carlo simulations, Pérez *et al.* limited the validity of the relationship to those cases in

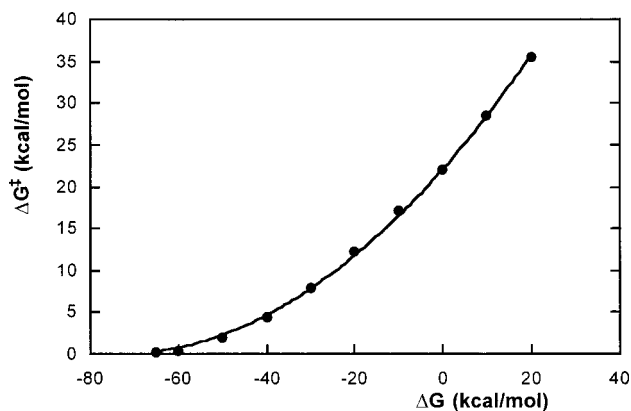


FIG. 5. Activation free energies vs reaction free energies. The line represents the fitting of the data to a quadratic relationship (see text).

which the gas phase diabatic potentials of the neutral molecule and radical anion can be described by a Morse curve and its repulsive part and for those systems in which the chemical bond to be broken is not very strong. For the particular case of methylchloride, these authors obtained large error when using Marcus' relationship to predict the activation free energy.<sup>15</sup> Our results seem to indicate that the Marcus' relationship also holds for this system, at least for reaction free energies ranging from  $-60$  to  $+20$  kcal/mol. For more positive reaction free energies the errors obtained using Eq. (3) are larger (4% and 14% for reaction free energies of 40 and 50 kcal/mol, respectively). It is worth to mention that activation energies obtained from the gas phase potential energy curves also fulfill a Marcus' relationship (with  $a = 15.2$  kcal/mol,  $b = 0$ , and  $R = 0.9990$ ) in spite of the fact that the dissociation curve of the radical anion is not correctly represented by the repulsive part of the Morse function fitted to the neutral curve, as required in the Savéant's original work.<sup>25</sup> Thus, it seems that quadratic relationships between activation and reaction energies for dissociative electron transfer processes could be of more general applicability than anticipated.

### C. Dissociation dynamics in solution

After extensive equilibration of a system composed by a quantum neutral methylchloride molecule and 300 classical water molecules, we ran a 60 ps long molecular dynamics simulation of the system with a step size of 1 fs. During this simulation the geometry of the quantum molecule was free to relax and we saved one full solute-solvent configuration each 1 ps of simulation. In this way we generated a total of 60 configurations from which we started independent trajectories adding a new electron to the quantum subsystem. In this way we simulated nonactivated electron attachment processes, this is, those electron transfers in which the initial electron energy level is above  $-8.6$  kcal/mol. In each one of these trajectories a total of 500 fs were produced with a step size of only 0.1 fs because of the large changes taking place in the system. No temperature scaling was attempted in order to conserve the total energy of the system.

Analysis of the trajectories showed fast changes in the quantum subsystem structure. Classification of the trajectory-

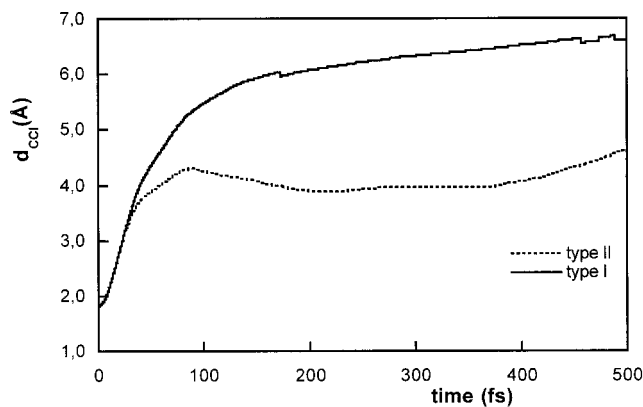


FIG. 6. Averaged value of the carbon–chlorine distance vs time for both types of trajectories (see text).

ries was based on the evolution of the carbon–chlorine distance and bond order. Type I corresponds to those trajectories in which the carbon–chlorine distance continuously grows up to complete dissociation, while type II corresponds to those trajectories in which a temporary methyl radical–chloride anion complex is observed. Of the total of 60 trajectories we classified 11 as belonging to type II and 49 to type I. In order to analyze the results obtained, we averaged for all the trajectories belonging to the same type. Figure 6 shows the average evolution of the internal geometry of the methylchloride radical anion for both types of trajectories. After 30 fs the average representation of both types of trajectories clearly diverges, and for type II the average carbon–chlorine distances remains essentially constant in the range 3.8–4.0 Å during at least 400 fs. It is worth to mention here that we continued the 11 trajectories belonging to type II for 500 additional femtoseconds and observed full dissociation in 6 of them, while for the other 5 trajectories the complex survived during the whole 1 ps-long simulation.

Figure 7 shows the change in the potential energy of the quantum subsystem ( $E_{QM}$ ), the interaction energy ( $E_{QM/MM}$ ), and the kinetic energy of the quantum subsystem ( $T_{QM}$ ) for both types of trajectories. The dissociation of the methylchloride radical anion is driven by intramolecular as well as intermolecular forces. During the dissociation process the potential energy of the quantum subsystem drops by about 50 kcal/mol. The largest part of the variation of this potential energy component takes place during the first 20 fs of the trajectory. At this time, the potential energy of the quantum subsystem (not the full potential energy) presents a minimum as a consequence of the electronic polarization due to the solvent electric field, and afterwards reaches a plateau, where the average energy of type II trajectories is lower than for type I, reflecting the existence of a chloride anion–methyl radical complex. After the first 20 fs the dissociation process is driven by the solute–solvent interaction energy, which drops by about 120 kcal/mol. This value is due to two different processes: the solvent relaxation after the sudden addition of a negative charge and the dissociation process in which the charge of the methylchloride radical anion is now localized on the chloride anion. It is interesting to note, that the initial ( $t=0$ ) interaction energies are  $-3.8$  and  $-7.4$

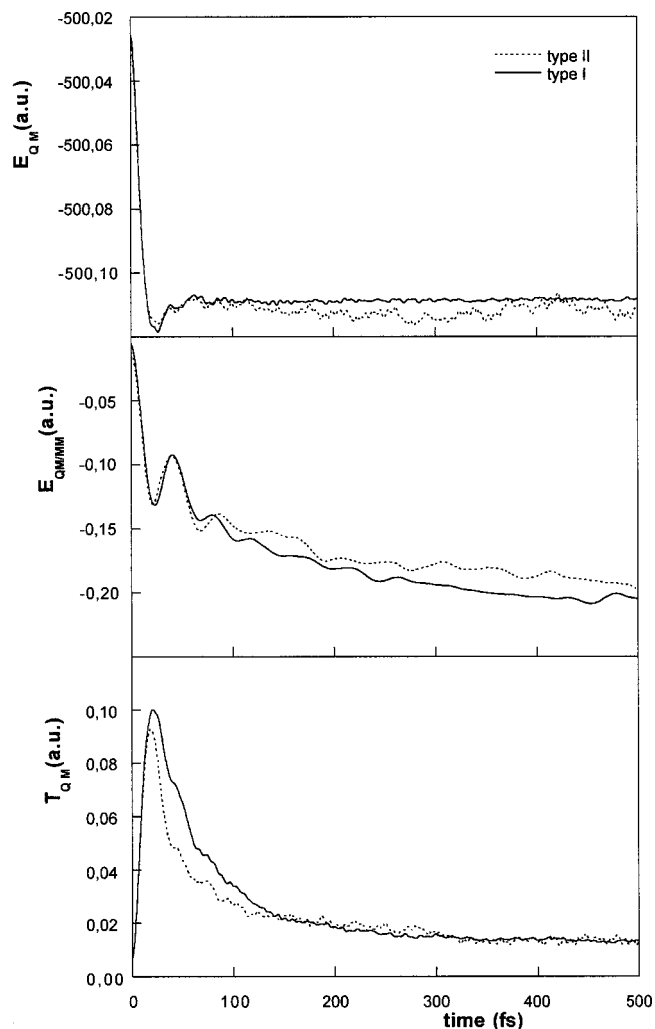


FIG. 7. Averaged value of the potential energy of the quantum mechanical subsystem ( $E_{QM}$ ), the solute–solvent interaction energy ( $E_{QM/MM}$ ), and the kinetic energy of the quantum subsystem ( $T_{QM}$ ) vector vs time for both types of trajectories.

kcal/mol for types I and II, respectively, this is, 3.6 kcal/mol more negative for type II, indicating a better solute–solvent interaction in the initial configuration for these trajectories. In both cases, the QM/MM interaction energy curve presents a shoulder reflecting the differences in the characteristic relaxation times of these two processes which take place simultaneously. This shoulder is placed at ca.  $t=40$  fs, which is, approximately, the time needed to break the carbon–chlorine bond and thus to localize the charge on the leaving chlorine atom (40 fs after the electron transfer, the carbon–chlorine distance is about 3.8 Å for both types of trajectories, see Fig. 5, and then the averaged Mulliken charge on the chlorine changes from  $-0.53$  a.u. to ca.  $-1$  a.u.) Once the C–Cl bond has been broken and the excess charge has been localized on the chloride anion, the solute–solvent interaction energy increases, in absolute value, because of the solvent relaxation around the negative charge. During the whole process, the potential energy of the system is converted into kinetic energy. The kinetic energy of the quantum subsystem increases very quickly, reaching a maximum at about 20 fs. This increase of the kinetic energy is essentially due to the

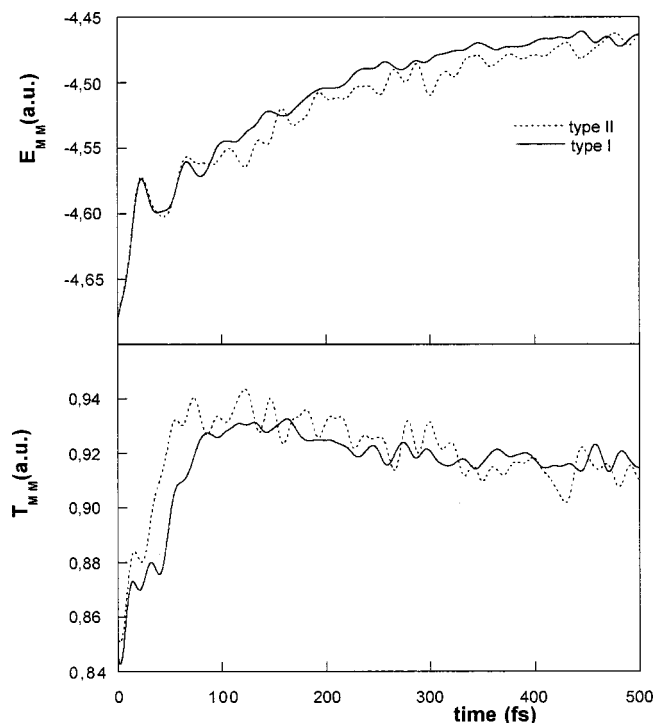


FIG. 8. Averaged value of the potential energy of the molecular mechanics subsystem ( $E_{MM}$ ) and its kinetic energy ( $T_{MM}$ ) vector vs time for both types of trajectories.

relative speed between the two dissociation fragments, but we have also verified that other molecular motions (such as the methyl umbrella vibration) are also highly activated. After reaching the maximum, the kinetic energy is dissipated following an exponential decay. Comparing type I and II curves, it can be seen that this dissipation process is much more effective for type II trajectories. This means that for type II trajectories, the methylchloride radical anion reaches the flat region of the free energy surface located at carbon–chlorine distances between 3.4 and 4.0 Å (40 fs after the addition of the electron) with less kinetic energy and then the system can be trapped in this configuration. As we will discuss below, this fact is related to the best solute–solvent interaction found for the initial configurations of type II trajectories.

Figure 8 shows the change in the average potential and kinetic energy of the solvent for types I and II ( $E_{MM}$  and  $T_{MM}$ , respectively). From the potential energy point of view both sets of trajectories are very similar. The solvent potential energy increases in about 130 kcal/mol as a consequence of the charge plus dissociation process. When passing from a slightly polar solute, such as methylchloride, to a charged species, the solvent structure is broken because solvent molecules are now more strongly oriented by the solute electric field. The average value for type II trajectories is slightly lower than for type I, indicating a somewhat less broken solvent structure in the first case. Important differences are found in the variation of the solvent kinetic energy between type I and II trajectories. In both cases the kinetic energy of the solvent increases during the first 100 fs after the electron addition to methylchloride. The evolution of the solvent kinetic energy can be related to the variation of the solute

kinetic energy. In Fig. 7 we saw that for type II trajectories the solute was able to dissipate its excess kinetic energy more efficiently than for type I trajectories. We now see that the kinetic energy is transferred from the quantum solute to the solvent molecules, but this transfer is much faster and effective for type II than for type I.

The picture that emerges from our results is that methylchloride radical anion dissociation can take place with or without formation of a temporary complex between methyl radical and chloride anion. The PMF shows the existence of a very flat region in which the system could be trapped during some time if the system quickly loses its excess kinetic energy transferring it to the solvent molecules. There are several factors that can affect the efficiency of this transfer process. One of the most important can be the formation of hydrogen bonds between solute and solvent molecules. After dissociation ( $t=500$  fs) the number of water molecules hydrogen bonded<sup>53</sup> to the leaving chloride anion is 7.0 for type I trajectories, close to the coordination number of free chloride anion which is 7.4 in a similar computational scheme.<sup>53</sup> For type II the number is 6.5, smaller than for type I, due to the presence of the methyl radical in the neighborhood of the chlorine anion. Interesting differences are found at  $t=0$ : for type I trajectories the average number of water molecules initially hydrogen bonded to chlorine atom is 1.5 while for type II, this average number is 2.0. This change in the number of hydrogen bonds established between the solute and solvent molecules in the initial configurations is also reflected in the more negative interaction energy we found for type II trajectories. The existence of more or stronger hydrogen bonds can determine the effectiveness of the kinetic energy transfer from solute to solvent molecules. If the electron is added to the solute in a configuration in which there are more close contacts (hydrogen bonds) between the chlorine and the solvent molecules, then the excess potential energy of the dissociative solute is transformed into kinetic energy that can be quickly transferred to the solvent molecules and then a weak complex corresponding to a very flat region of the free energy surface is formed between the chloride anion and the methyl radical. This conclusion seems to agree with the experimental observation that in some cases a change from a protic solvent (water) to an aprotic one (dimethylformamide) seems to induce a transition from a consecutive to a concerted dissociation mechanism.<sup>9</sup> This effect of the hydrogen bonds could also be related to the fact that dissociation rates are generally higher in dipolar aprotic solvents than in water.<sup>4,8</sup>

#### IV. CONCLUSIONS

In this paper we have studied an example of dissociative electron transfer of alkylhalides in solution. By means of QM/MM simulations we have studied the chemical processes taking place after the addition of an electron to a methylchloride molecule in aqueous solution. In first place we obtained the free energy curves for the dissociation of the neutral methylchloride molecule and its corresponding radical anion in water. Molecular dynamics simulations and thermodynamic integration techniques were employed to get the potential of mean force as a function of the carbon–chlorine

distance. The PMF of the radical anion displays a very flat region in the range of 3.4–4.0 Å, corresponding to a weak complex between a methyl radical and a chloride anion with the average geometry corresponding to a  $C_{2v}$  symmetry. The dissociation free energy curves of the neutral and radical anion molecules show the existence of a quadratic dependence of the activation free energy on the reaction free energy.

We also analyzed dynamical aspects of the dissociative electron transfer reaction. For a set of 60 trajectories, started from configurations corresponding to an equilibrium simulation of methylchloride in aqueous solution, we observed two different behaviors (I and II). For trajectories of type I, the system directly evolved to separated products, methyl radical and chloride anion. For type II trajectories, a temporary weak complex between methyl radical and chloride anion, with a carbon–chlorine distance of about 3.8 Å, is observed during some finite time. From the analysis of intramolecular and intermolecular factors, the picture that emerges from our results is that methylchloride radical anion dissociation can take place with or without formation of a temporary complex between methyl radical and chloride anion. As said before, the PMF shows the existence of a very flat region in which the system can be trapped during some time if the quantum molecule quickly transfers its kinetic energy to the solvent molecules. One of the most important factors determining the effectiveness of this energy transfer is the existence of hydrogen bonds between the solute and the solvent. Type II trajectories, i.e., those trajectories in which a temporary complex is found, show an average number of solvent water molecules initially hydrogen bonded to the chlorine atom larger than for type I trajectories. This fact seems to agree with some experimental findings about solvent effects on dissociative electron transfer processes.

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