J|A|C|S

A R T I C L E S

Breaking Bonds by Mechanical Stress: When Do Electrons Decide for the Other Side?

Daniel Aktah[†] and Irmgard Frank*

Contribution from the Institut für Physikalische Chemie, LMU München, Butenandtstrasse 5-13, Haus E, 81337 München, Germany

Abstract: Using first-principles molecular dynamics, we have simulated reactions that can be induced by mechanical stress in a polymer. We have stretched a small piece of poly(ethylene glycol) (PEG) in water at finite temperature. Both the molecule and the solvent were described quantum mechanically on an equal level. The formation of ions was observed, which corresponds to a heterolytic bond cleavage. We were able to monitor the motion of the electrons during the reactions. Our simulations show that the electron transfer and the breaking of the bond occur almost simultaneously and that both processes are initiated by the approach of a solvent molecule toward the destabilized bond.

I. Introduction

It is well-known that in many cases the outcome of the breaking of a chemical bond depends critically on the environment. While in the gas phase the formation of radicals in a homolytic reaction is favorable, in solution the formation of ions via a heterolytic mechanism dominates. The transfer of the electrons that form the relevant bond is of primary importance for the understanding of these processes.[1] When trying to model electron transfer by first-principles simulations, one encounters the problem that most of these reactions occur on a time scale that is much too long for performing an unconstrained simulation (i.e., for a simulation in which the reaction coordinate is not pre-assigned). Yet there is an important class of reactions that is accessible to an investigation by first principles, namely reactions that are induced by mechanical stress. Such reactions occur when matter is exposed to extreme conditions.[2,3]

Our present simulation of a system under mechanical stress was motivated by recent AFM experiments.[4,5,6] Single molecules (poly(ethylene glycol) (PEG), polysaccharides, proteins) were stretched between a surface and the tip of an AFM microscope (Figure 1), see refs 7 and 8 for reviews. The resulting forces were monitored until the force vanished, indicating rupture of the strands. Classical molecular dynamics (MD) simulations

Figure 1. Experimental setup. A polymer is expanded with an AFM tip.

were successfully used to explain many of the observed phenomena.[9–11] Furthermore, quantum chemical MP2 calculations have been used to describe the change of conformations in a small piece of PEG under tensil load.[12]

The classical MD approaches are optimally suited for the description of transformations that occur on larger scales. Also, it is possible to model the breaking of hydrogen bonds adequately on this basis. Even reactions that involve ions have been described on the basis of a force field.[13–16] Yet, quantum chemical methods are more powerful in describing the general chemical reactivity of complex systems than present-day force fields. This is especially true if the reaction mechanism is not known in advance but is to be determined from the calculation.

In the previous attempts to describe the bond rupture in AFM experiments quantum chemically using density-functional theory, the bond breaking was described by a homolytic mechanism

---

* To whom correspondence should be addressed.

† Present address: Max-Planck-Institut für Festkörperforschung, Heisenbergstr. 1, 70569 Stuttgart, Germany.

(1) Marcus, R. A. *Angew. Chem.* **1993**, *105*, 1161.
(2) Saitta, A. M.; Soper, P. D.; Wasserman, E.; Klein, M. L. *Nature (London)* **1999**, *399*, 46.
(3) Saitta, A. M.; Klein, M. L. *J. Chem. Phys.* **1999**, *111*, 9434.
(4) Rief, M.; Oesterhelt, F.; Berthold, H.; Gaub, H. E. *Science* **1997**, *275*, 1295.
(5) Rief, M.; Gautel, M.; Oesterhelt, F.; Fernandez, J. M.; Gaub, H. E. *Science* **1997**, *276*, 1109.
(6) Oesterhelt, F.; Rief, M.; Gaub, H. E. *New J. Phys.* **1999**, *1*, 6.1–6.11.
(7) Janshoff, A.; Neitzert, M.; Oberdörfer, Y.; Fuchs, H. *Angew. Chem., Int. Ed.* **2000**, *39*, 3212.
(8) Clausen-Schaumann, H.; Seitz, M.; Krautbauer, R.; Gaub, H. E. *Curr. Opin. Chem. Biol.* **2000**, *4*, 524.
(9) Grubmüller, H.; Heymann, B.; Tavan, P. *Science* **1996**, *271*, 997.
(10) Izrailev, S.; Stepaniants, S.; Balsera, M.; Oono, Y.; Schulten, K. *Biophys. J.* **1997**, *72*, 1568.
(11) Heymann, B.; Grubmüller, H. *Chem. Phys. Lett.* **1999**, *307*, 425.
(12) Kreuzer, H. J.; Wang, R. L. C.; Grunze, M. *New J. Phys.* **1999**, *1*, 21.1–21.16.
(13) Gertner, B. J.; Hynes, J. T. *Science* **1996**, *271*, 1563.
(14) Gertner, B. J.; Hynes, J. T. *Faraday Discuss.* **1998**, *110*, 301.
(15) Geissler, P.; Dellago, C.; Chandler, D. *Phys. Chem. Chem. Phys.* **1999**, *1*, 1317.
(16) Geissler, P.; Dellago, C.; Chandler, D. *J. Phys. Chem. B* **1999**, *103*, 3706.

resulting in two radicals.[17-19] A radicaloid bond breakage was also found in first-principles MD simulations of polyethylene unter tensil load.[2,3] However, AFM experiments have been performed in aqueous solution.[17] It seemed likely that in a protic solvent ionic reaction mechanisms could be of importance. The aim of the present study was thus to determine the fundamental reaction mechanisms that are relevant for mechanically induced bond breaking of polar polymers in aqueous solution and to describe the migration of the electrons during the reactions.

II. Theory

We have employed density-functional theory in the Kohn—Sham formalism[20-22] in combination with Car—Parrinello molecular dynamics (CPMD).[23] This method is very well suited for the investigation of chemical reactions on an atomic scale.[24] In particular, it allows the investigation of complex or previously unknown reaction pathways (see, e.g., refs 25 and 26). Furthermore, due to the use of plane—wave basis sets the inclusion of solvent molecules is possible with only a moderate increase in CPU time. Extensive investigations of pure water have been done by Parrinello and co-workers in recent years (see, e.g., refs 27−30). Also ions in water have been investigated (see, e.g., refs 31−35). On the basis of these developments, today the fully quantum chemical simulation of reactions in aqueous solution and also in other surroundings has become feasible. However, up to now just a few studies have been published (see, e.g., refs 36−38). For a rather complete and actual overview on first-principles MD simulations, see ref 39.

Of course the methodology has clear limitations: since the determination of a first-principles wave function is rather expensive, only simulations in the picosecond regime are feasible with present-day computers. Hence, with our approach, we can find the fastest and most dominant reactions in a system only.

We have performed simulations of the stretching of a piece of PEG in solution (Figure 2) at initial kinetic energies of 250 and 320 K. For the calculations we employed the CPMD code.[40]
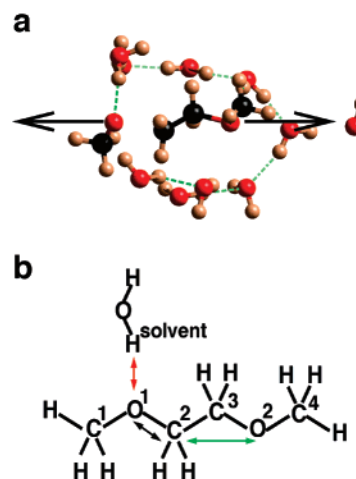
Figure 2. (a) Model of a small piece of PEG in water. Arrows indicate the stretching direction. (b) Schematic representation of the model with numbering of the atoms. Arrows mark the distances that are plotted in Figure 5.

Table 1. Comparison of Dissociation Energies Obtained with Different Theoretical Methods to the Experimental Data

method	ΔE_{diss}(C–O) (kcal/mol)	ΔE_{diss}(C–C) (kcal/mol)
	Radicaloid Bond Breaking	
AM1	65.3	53.9
BLYP/6-31G**	83.9	79.1
B3LYP/6-31G**	84.9	82.4
exptl[54]	85	83
	Ionic Bond Breaking	
AM1	238.1	248.8
BLYP/6-31G**	196.9	258.2
B3LYP/6-31G**	202.0	264.9

We used periodic boundary conditions with a periodically repeated rectangular unit cell (10.6 × 7.4 × 7.4 Å) that contained a piece of poly(ethylene glycol) (PEG) surrounded by 10 water molecules (Figure 2). We employed the Becke—Lee—Yang—Parr (BLYP) density functional[41,42] in its spin-unrestricted form.[43] The BLYP functional is a well-established density functional and is broadly used for the modeling of systems containing hydrogen bonds. Since it is free of Hartree—Fock exchange, it can be used with very large plane—wave basis sets (in contrast to the more accurate B3LYP functional[44]). To assess the quality of the BLYP functional for the system under investigation we have compared the bond-breaking energies to the B3LYP values using Gaussian 98.[45] From Table 1, it is evident that the BLYP energy for homolytic dissociation in the gas phase is close to both the B3LYP and the experimental value

(17) Grandbois, M.; Beyer, M.; Rief, M.; Clausen-Schaumann, H.; Gaub, H. E. *Science* **1999**, *283*, 1727.
(18) Beyer, M. K. *J. Chem. Phys.* **2000**, *112*, 7307.
(19) Garnier, L.; Gauthier-Manuel, B.; van der Vegte, E. W.; Snijders, J.; Hadziioannou, G. *J. Chem. Phys.* **2000**, *113*, 2497.
(20) Hohenberg, P.; Kohn, W. *Phys. Rev. B* **1964**, *136*, 864.
(21) Kohn, W.; Sham, L. J. *Phys. Rev. A* **1965**, *140*, 1133.
(22) Parr, R. G.; Yang, W. *Density-Functional Theory of Atoms and Molecules*; Oxford University Press: Oxford, England, 1989.
(23) Car, R.; Parrinello, M. *Phys. Rev. Lett.* **1985**, *55*, 2471.
(24) Parrinello, M. *Solid State Commun.* **1997**, *102*, 107.
(25) Frank, I.; Parrinello, M.; Klamt, A. *J. Phys. Chem.* **1998**, *102*, 3614.
(26) Frank, I.; Marx, D.; Parrinello, M. *J. Phys. Chem.* **1999**, *103*, 7341.
(27) Laasonen, K.; Sprik, M.; Parrinello, M.; Car, R. *J. Chem. Phys.* **1993**, *99*, 9080.
(28) Sprik, M.; Hutter, J.; Parrinello, M. *J. Chem. Phys.* **1996**, *105*, 1142.
(29) Silvestrelli, P. L.; Parrinello, M. *J. Chem. Phys.* **1999**, *111*, 3572.
(30) Silvestrelli, P. L.; Parrinello, M. *Phys. Rev. Lett.* **1999**, *82*, 3308.
(31) Tuckerman, M. E.; Laasonen, K.; Sprik, M.; Parrinello, M. *J. Phys. Chem.* **1995**, *99*, 5749.
(32) Tuckerman, M. E.; Laasonen, K.; Sprik, M.; Parrinello, M. *J. Chem. Phys.* **1995**, *103*, 150.
(33) Marx, D.; Parrinello, M. *Science* **1999**, *284*, 59.
(34) Marx, D.; Tuckerman, M. E.; Hutter, J.; Parrinello, M. *Nature (London)* **1999**, *397*, 601. Hynes, J. T. *Nature (London)* **1999**, *397*, 565.
(35) Trout, B. L.; Parrinello, M. *J. Phys. Chem.* **1999**, *103*, 7340.
(36) Meijer, E. J.; Sprik, M. *J. Phys. Chem. A* **1998**, *102*, 2893.
(37) Meijer, E. J.; Sprik, M. *J. Am. Chem. Soc.* **1998**, *120*, 6345.
(38) Curioni, A.; Sprik, M.; Andreoni, W.; Schiffer, H.; Hutter, J.; Parrinello, M. *J. Am. Chem. Soc.* **1997**, *119*, 7218.
(39) Marx, D.; Hutter, J. Ab Initio Molecular Dynamics: Theory and Implementation. In *Modern Methods and Algorithms of Quantum Chemistry*; Grotendorst, J., Ed.; NIC Series 1; Forschungszentrum Jülich: Jülich, Germany, 2000; pp 301–449.

(40) Hutter, J.; et al. CPMD. Max-Planck-Institut für Festkörperforschung and IBM Research, 1990−96.
(41) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.
(42) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
(43) Jones, R. O.; Gunnarsson, O. *Rev. Mod. Phys.* **1989**, *61*, 689.
(44) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
(45) Gaussian 98, Revision A.6, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C. Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A.; Gaussian, Inc., Pittsburgh, PA, 1998.
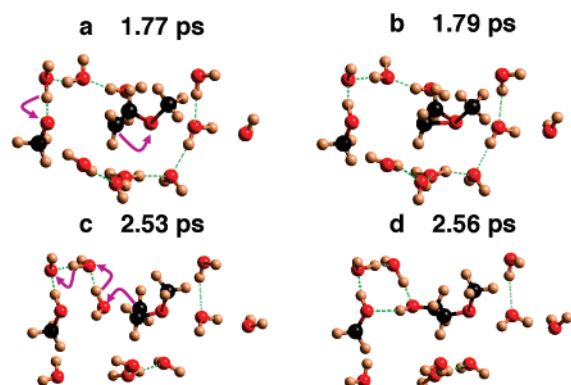
Figure 3. Snapshots of the MD run at 250 K.[55] (a) Beginning of the reaction in the stretched chain. (b) First proton transfer and ring formation. (c) Ring opening and reaction with a second water molecule. (d) Products.

(deviations to B3LYP: 1.0 and 3.3 kcal/mol for the C−O bond dissociation and the C−C bond dissociation, respectively). In view of the fact that the dissociation energy is a rather sensitive quantity, the values are in rather good agreement. This is underlined by the comparison to the performance of the well-established semiempirical method AM1[46] which exhibits much larger deviations (19.6 and 28.5 kcal/mol compared to B3LYP). For the ionic reaction the agreement between BLYP and B3LYP is worse (differences: 5.1 and 6.7 kcal/mol, respectively), but considering the high absolute values, this deviation is still in an acceptable range.

The inner electrons were described by the norm-conserving pseudopotentials of Troullier and Martins.[47] For the Car−Parrinello molecular dynamics a time step of 0.12 fs (5 au) was used. After equilibration of the system the distance between the two oxygen atoms O_1 and O_2 was extended continuously by 0.0001 au per time step. Alternative ways for describing the expansion of a molecular chain have been devised before.[9,48,49] Our approach describes a system that is expanded with constant velocity. Because of the expansion of the molecule, the potential energy rises and the system is nonconservative, which is also true for the experimental system.

III. Results and Discussion

A. The Reaction Pathways. Ionic reaction mechanism were observed in both simulations, as is to be expected for protic solvents. In the simulation at 250 K, the C_2-O_1 bond could be expanded up to a length of 3.2 Å, before a reaction occurred (Figure 3 a). At this point, a water molecule attacks the chain and a proton is transferred to the oxygen atom O_1. Simultaneously, a three-membered ring is formed by the atoms C_2, C_3 and O_2 (Figure 3b) and the two fragments of the chain start to relax. The resulting situation is unstable (hydroxyl anion and positively charged strained ring in close vicinity) and a consecutive reaction is observed after 0.7 ps. The ring is now attacked by another water molecule. In our simulation, this attack does not occur at the bond that was formed immediately before; instead, the other side of the ring is attacked. The ring opens and forms a bond with the oxygen atom of the water molecule (Figure 3c). The resulting positively charged compound is
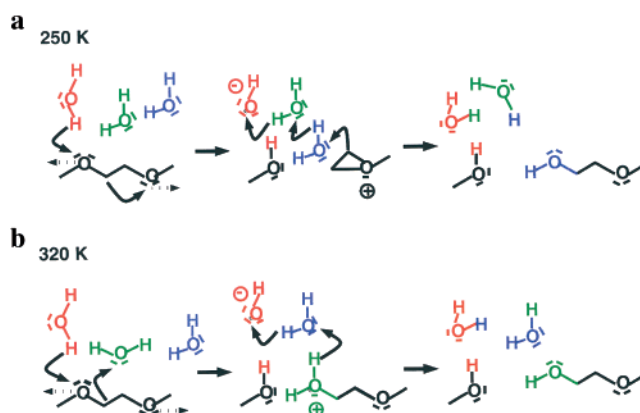
(46) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.
(47) Troullier, N.; Martins, J. L. *Phys. Rev. B* **1991**, *43*, 1993.
(48) Evans, E.; Ritchie, K. *Biophys. J.* **1997**, *72*, 1541.
(49) Merkel, R.; Nassoy, P.; Leung, A.; Ritchie, K.; Evans, E. *Nature (London)* **1999**, *397*, 50.

Figure 4. Schematic plots of the reaction mechanisms at (a) 250 and (b) 320 K. Dotted arrows indicate the stretching direction. Solid arrows mark bond formations.

neutralized by the transfer of a proton to a neighboring water molecule. By further rapid proton exchanges, i.e., by a Grotthus mechanism, a proton is transferred to the hydroxyl anion, thereby neutralizing it (Figure 3d).

In summary, two alcohols surrounded by neutral water molecules result from this series of reactions as would have been expected. Our simulation shows that the insertion of a water molecule in the polymeric chain occurs by a rather complex reaction pathway. Experimentally the ring formation might be verified by detecting the interchange of the two carbon atoms that occurs if the ring opens at the other side.

In such a complex system as a polymer in water there are of course many possible reaction pathways. The ring formation is not the only way for the system to stabilize as is evident from the result of the second simulation at 320 K: Again the oxygen atom of the elongated C_2-O_1 bond is attacked by a water molecule, when the C_2-O_1 bond length reaches a value of about 4.2 Å. Simultaneously, the other part of the molecule reacts immediately with a water molecule without previous ring formation. Likewise the neutralization of the resulting ions occurs by coupled proton transfers, i.e., via a Grotthus mechanism (Figure 4).

It is striking that in each case both parts of the chain react simultaneously (i.e., within about 10 fs) although the distance between them is already quite large (more than 3 Å). The second mechanism is only possible if two water molecules are suitably located for an immediate reaction with the two parts of the molecule.

While with first-principles simulations we can model complex chemical processes involving many degrees of freedom, the approach is very limited in several respects: first, the accessible time scale is very short. At lower pulling velocities alternations in the Grotthus mechanism might be observed. If the water molecules are given more time to rearrange and to enter the space between the two atoms of the breaking bond, eventually also a reaction involving just a single water molecule might be observable. Second, the size of the unit cell is rather small. Since the CPU time depends nonlinearly on the size of the unit cell, our possibilities to model significantly larger systems are rather restricted. However, as has been shown before,[50] the modeling of ionic reactions is already possible with a very small number of water molecules. Third, our statistics is necessarily poor, and

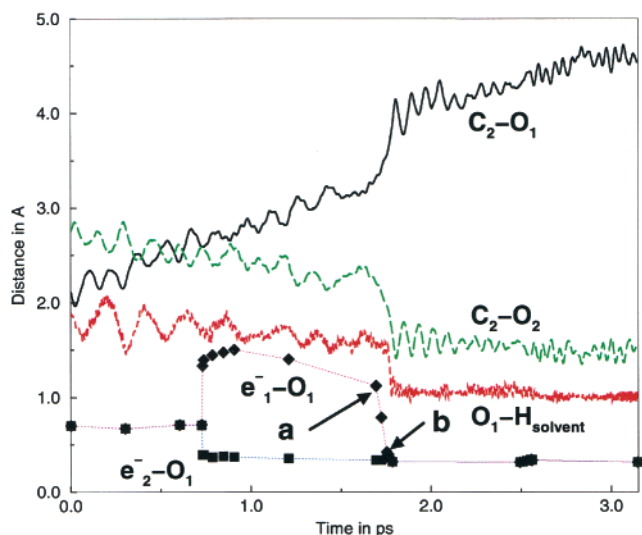(50) Bianco, R.; Hynes, J. T. *J. Phys. Chem. A* **1998**, *102*, 309.

Figure 5. Correlation between ionic and electronic motion. The figure shows the change of the C_2-O_1, C_2-O_2, and $O_1-H_{solvent}$ distances during the MD simulation at 250 K (cf. Figure 2b). For selected points, the average distance of the two electrons forming the C_2-O_1 bond with respect to atom O_1 is plotted ($e^-_1-O_1$ and $e^-_2-O_1$, respectively). These latter values have been calculated using the center of charge of the corresponding localized orbitals. For the two points (a) before and (b) after the electron transfer the localized orbitals of the breaking bond are depicted inf Figure 6.

we cannot claim that we found all reactions that are of relevance in such a system. In particular, the number of water molecules involved in the Grotthus mechanism is likely to vary.[51]

The maximum forces arising during the simulations amount to roughly 3 nN which is significantly lower than the values we obtained for simulations in the gas phase ($\approx$4 nN). The values are still higher than the ones obtained experimentally for the stretching of polysaccharides ($\approx$2−2.5 nN).[17] The remaining deviation to the values reported in ref 17 can be easily explained by the lower pulling velocity in experiment and by a probably weaker attachment to the surface. However, on the basis of our results, we believe that the interpretation of the bond breaking has to be modified: in a protic solvent it is not necessarily the weakest bond that breaks but the one that is attacked most easily by the solvent molecules.

B. The Motion of the Electrons. Having observed these reactions, one might ask when and why the system decides for a heterolytic bond cleavage. The motion of the electrons can be followed most easily if the delocalized molecular orbitals are converted into localized orbitals. In the case of a plane−wave basis set, this corresponds to a unitary transformation of the delocalized orbitals to maximally localized Wannier functions.[52,53] We have done this transformation for selected points of the molecular dynamics runs. The results for the run at 250 K are shown in Figure 5. Here the distances between the centers of charge of the two orbitals that form the C_2-O_1 bond and the oxygen atom O_1 are depicted. The two orbitals are initially paired. When the C_2-O_1 distance reaches a value of 2.8 Å, the orbital centers separate. This indicates that, due to the strong elongation, the system adopts biradicaloid character. In this situation it is very unstable and the attack of a water molecule
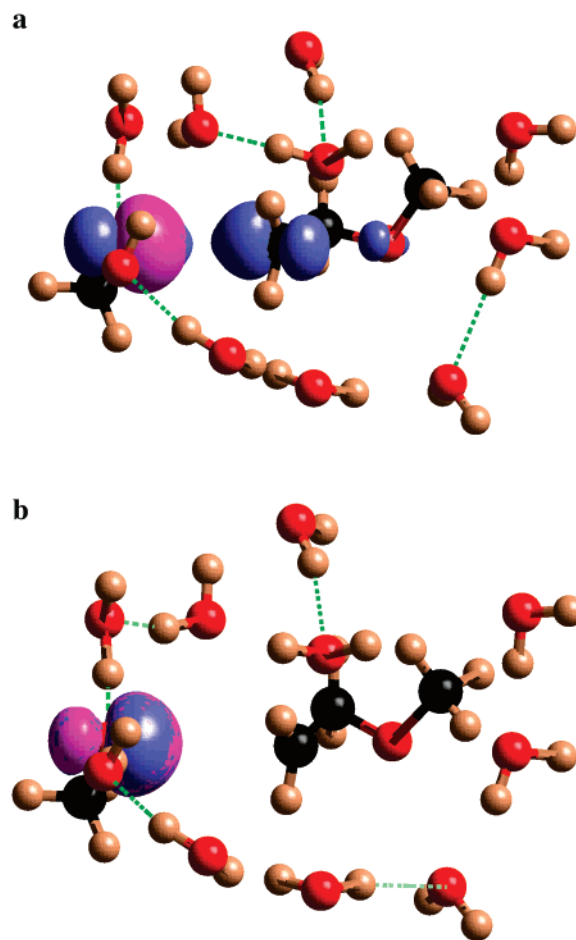
(51) Geissler, P. L.; Dellago, C.; Chandler, D.; Hutter, J.; Parrinello, M. *Science* **2001**, *291*, 2121.
(52) Silvestrelli, P. L.; Marzari, N.; Vanderbilt, D.; Parrinello, M. *Solid State Commun.* **1998**, *107*, 7.
(53) Berghold, G.; Mundy, C.; Romero, A.; Hutter, J.; Parrinello, M. *Phys. Rev. B* **2000**, *61*, 10040.

Figure 6. Orbitals of the breaking bond before and after the electron transfer (see also Figure 5). The two orbitals are plotted in blue and magenta, respectively, with like colors for positive and negative lobes. Before the electron transfer takes place the two orbitals are clearly separated; after the electron-transfer both orbitals occupy the same space.

becomes possible. As can be seen from Figure 5, the $O_1-H_{solvent}$ distance and the C_2-O_2 distance decrease slowly in this first part of the simulation. At some point, the orbitals that form the elongated C_2-O_1 bond start to feel the attraction by the positive partial charge accumulated near atom O_1 and the orbital that had started migrating toward the carbon atom jumps back to the oxygen atom. It is now paired again with the other orbital that previously formed the bond (Figure 6). Almost simultaneously, the $O_1-H_{solvent}$ and C_2-O_2 distances decrease rapidly, meaning that the proton is fully transferred to the oxygen atom and the ring formation is completed. At the same time, the C_2-O_1 distance increases significantly, indicating that now the bond is broken. An analogous behavior was found in the simulation at 320 K; in this case the electron transfer is initiated by the approach of one water molecule at each end of the breaking bond, respectively.

It is not feasible to determine all possible reaction pathways by first-principles simulations. However, from a few simulations, we can derive the chemically relevant concepts. There are two important points in our simulations: the separation of the two electrons and their recombination in connection with bond breakage. The separation of the two electrons clearly depends on the C_2-O_1 distance. Spin densities indicating electron separation appeared in each of our simulations when this distance reached a value of $\approx$2.8 Å. Note that this number

Table 2. Comparison of the Equilibrium C−O Distances and the C−O Distances at Biradical Formation Obtained with Different Theoretical Methods

method	equilibrium C−O distance (Å)	C−O distance at biradical formation (Å)
BLYP/6-31G**	1.44	≈2.8
B3LYP/6-31G**	1.41	≈2.4
BHLYP/6-31G**	1.40	≈2.2

should not be taken literally: in this region both the Born−Oppenheimer approximation as well as the single-determinant approximation are vague. Additional uncertainty is introduced by the fact that we have to use an approximate density functional (BLYP). Other density functionals with more admixture of Hartree−Fock exchange yield an earlier biradical formation as can be seen from Table 2. This indicates that the orbitals in the BLYP wave function tend to be too delocalized.

The second important event, i.e., the formation of ions connected with the breaking of the bond, occurred at variable C_2-O_1 distances. That means it is determined by the arrangement of the surrounding water molecules and not only by the change of the C_2-O_1 distance. Without the surrounding water molecules that can initialize a ionic reaction, the extension of the C_2-O_1 distance goes on until the well-known radicaloid bond breaking is observed. The extension at which ion formation occurs can be expected to depend on the pulling velocity: At the much lower pulling velocities applied in the experiment, the water molecules have more time to rearrange in order to initiate the electron transfer.

IV. Conclusions

With first-principles simulations using periodic boundary conditions, we have described a condensed-phase reaction in which solvent molecules are actively involved. Our molecular dynamics study shows that the heterolytic breaking of a stretched bond in solution is initiated by the attack of a solvent molecule. Because of the approach of a solvent proton carrying a positive partial charge, the localization of both electrons at one side of the stretched bond becomes favorable. Immediately after this electron transfer, the transfer of the solvent proton is completed. Simultaneously, a stabilizing reaction in the other part of the broken chain is observed. The ions that are formed in this initial process are consequently neutralized on a time scale of a few hundred femtoseconds by coupled proton transfers.

We were able to show that mechanical stress can cause not only a simple homolytic bond breakage but also considerably more complicated reactions. The simulation of stress-induced reactions offers the possibility to systematically investigate the reactivity of organic compounds in solution by first-principles techniques. This opens a way to a more thorough understanding of complex reactions involving solvent molecules.

(54) Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry*; 4th ed.; Longman Higher Education: Harlow, England, 1993.
(55) Pictures of the MD simulations were generated with Cerius2, graphics program, MSI Inc. A movie of the electron transfer is available from our web page: http://www.chemie.uni-muenchen.de/pc/frank.