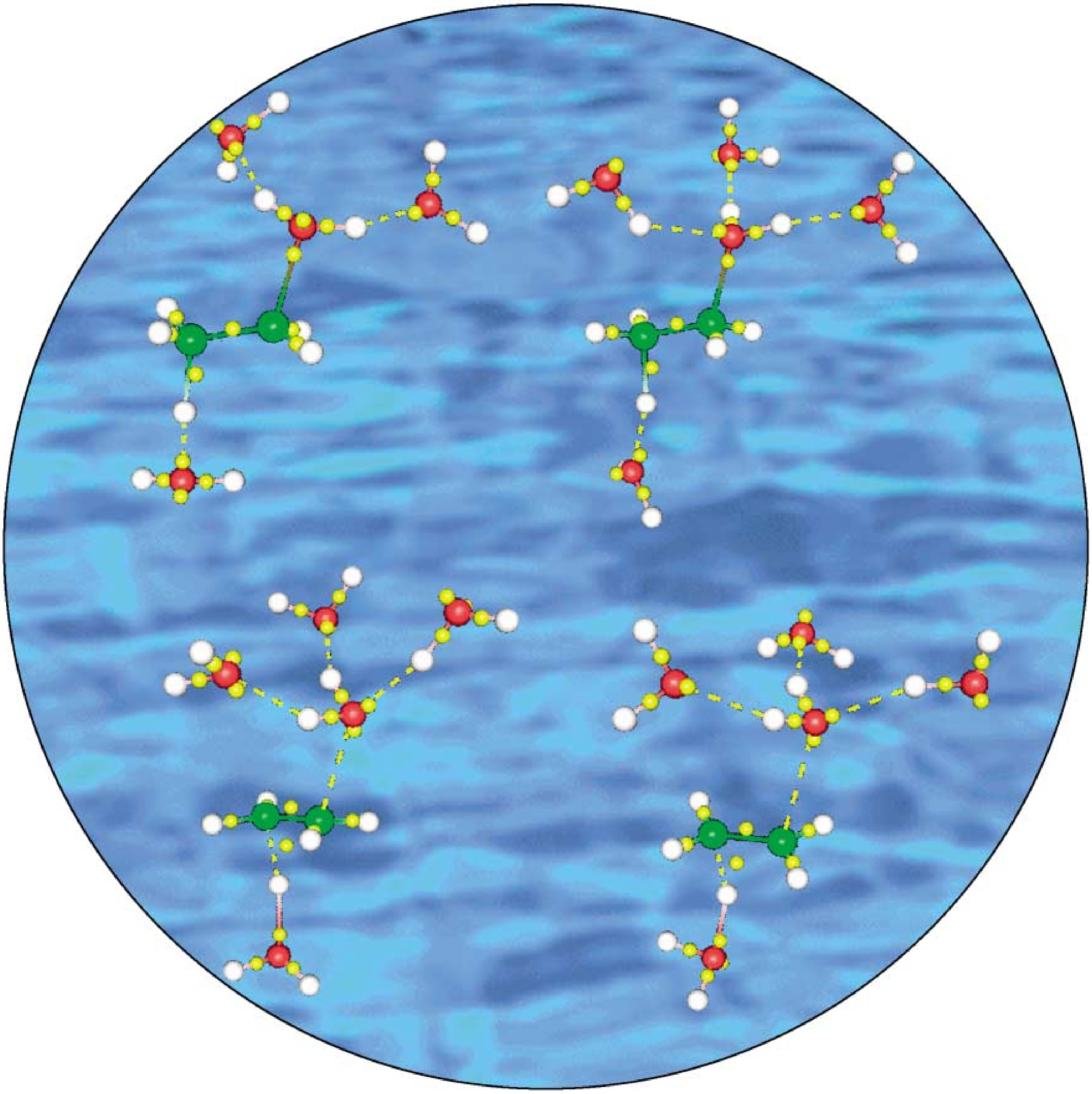
Zuschriften



Die Struktur der Solvathülle spielt eine wichtige Rolle in der wässrigen Chemie. So kann die Einleitung von Reaktionsschritten entscheidend von Details der Koordination von Wassermolekülen an einer reaktiven Spezies abhängen, wie T. S. van Erp und E. J. Meijer auf den folgenden Seiten anhand einer Moleküldynamiksimulation der protonenunterstützten Hydratation von Ethylen zeigen.

DOI: 10.1002/ange.200353103

Proton Transport

Proton-Assisted Ethylene Hydration in Aqueous Solution[**]

*Titus S. van Erp and Evert Jan Meijer**

Recent studies have revealed an accurate atomistic picture of proton transport in bulk water, the prime prototype proton-transport reaction. For example, femtosecond pump–probe spectroscopy[1] of the OH stretch vibration in liquid water has clarified the first stage of water deprotonation. Earlier, the nature of the mechanism and dynamics of proton transfer in bulk water has been addressed in a computational study using ab initio molecular dynamics.[2,3] In the present paper we go beyond proton transport in bulk water and address the fundamental chemical process of acid-catalyzed addition of water to an alkene double bond. This serves as a primary example of chemistry induced by exchange of protons in an aqueous environment. Although the basic principles are well established and part of undergraduate textbooks, the detailed understanding of the mechanism and dynamics is still lacking. For example, it has been a matter of long debate[4–7] whether the acid-catalyzed hydration of alkenes is a sequential process (Ad_E2) where the formation of a protonated alkene (carbocation) precedes the nucleophilic attack by a water molecule, or a concerted process (Ad_E3) where the protonation and nucleophilic attack occur simultaneously.[8]

Here we report on an ab initio molecular dynamics simulation study of proton-assisted hydration of ethylene in aqueous solution. An alternative hydration mechanism, involving an intermediate ethylene radical cation, has been addressed in an earlier study,[9] which used the same computational approach as in this work. Simulations[10–12] were performed of a system consisting of an excess proton in a solution of one ethylene molecule and 32 water molecules. The simulation cell is a periodically replicated cubic box with a size corresponding to the density of a solution of ethylene in water (1:32) under ambient conditions. The temperature is set at $T = 300$ K and imposed with a Nosé–Hoover thermostat. We should note that the size of the periodic cell in our study is relatively small, allowing for incorporation of only a single full ethylene/ethanol solvation shell. However, a recent study[13] has shown that the despite the small system size the solvation of ethylene and ethanol is reasonably well described.

As the rate of hydration is by far outside the timescale, ≈ 10 ps, accessible to ab initio molecular dynamics, the reactive events are enforced by using the method of constraints. Starting from an initial configuration consisting of a hydronium–ethylene complex, a reactive event was enforced by transferring a hydronium proton stepwise to an ethylene carbon. The transfer was controlled by fixing the asymmetric stretch coordinate $q = r_{OH^+} - r_{H^+C}$. Here, r_{OH^+} is the distance between the hydronium oxygen and the hydronium proton, and r_{H^+C} the distance between the hydronium proton and one of the ethylene carbons. The reverse reaction, that is, the dehydration of ethanol, was also simulated.

The snapshots of four stages along the ethylene hydration pathway shown in Figure 1 indicate that the enforced proton transfer results in the formation of a protonated ethanol, which rapidly donates its proton to the solution. Figure 2 shows the calculated force profile together with the associated free-energy profile. The steepness of the force profile near the maximum shows that the transition occurs in a narrow window of the proton-transfer coordinate q. In this region both the simulations along the hydration and the dehydration pathway show a sudden jump and sign-reversal of the

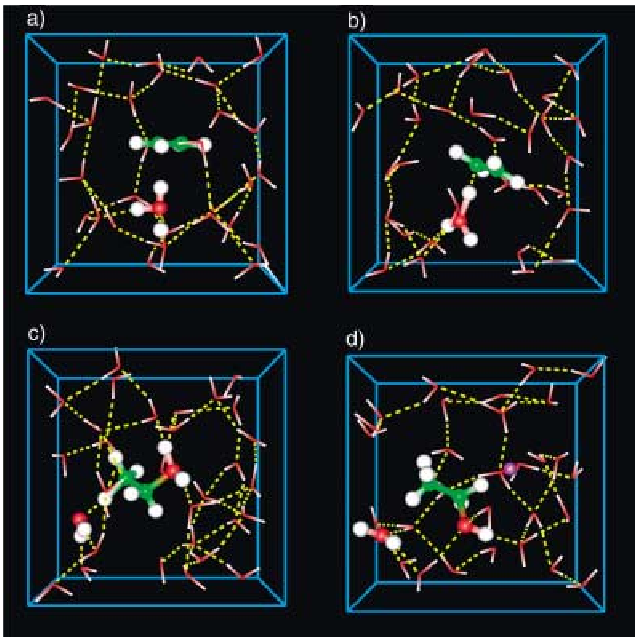


Figure 1. Snapshots of representative configurations of ab initio molecular dynamics simulations of the proton-assisted hydration of ethylene. Molecules involved in the reaction are shown as ball-and-stick models. Other molecules are represented with lines. White, red, and green indicate hydrogen, oxygen, and carbon atoms, respectively. Dashed yellow lines indicate hydrogen bonds. Edges of the periodically replicated cubic simulation cell are in blue. q is the proton-transfer reaction coordinate. a) $q = -1.1$ Å, initial stage showing the hydronium–ethylene complex. b) $q = 0.0$ Å, just before the transition state. The proton transfer within the hydronium–ethylene complex is halfway between the water oxygen and one of the ethylene carbon atoms. Ethylene is not yet hydrated. c) $q = 0.11$ Å, just after the transition state. The proton transfer has been accompanied by formation of a C—O bond between the other ethylene carbon atom and a water molecule, thus converting ethylene into a protonated ethanol. d) $q = 1.1$ Å. Proton transfer has been completed. The proton (purple ball) has been released into solution.

---

[*] Dr. T. S. van Erp, Dr. E. J. Meijer
Department of Chemical Engineering
University of Amsterdam
Nieuwe Achtergracht 166, 1018 WV Amsterdam (The Netherlands)
Fax: (+31) 20-5255604
E-mail: ejmeijer@science.uva.nl

[**] This work has been supported by the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO), the Royal Netherlands Academy of Art and Sciences, and the Stichting Nationale Computerfacileiten (NCF).

DOI: 10.1002/ange.200353103

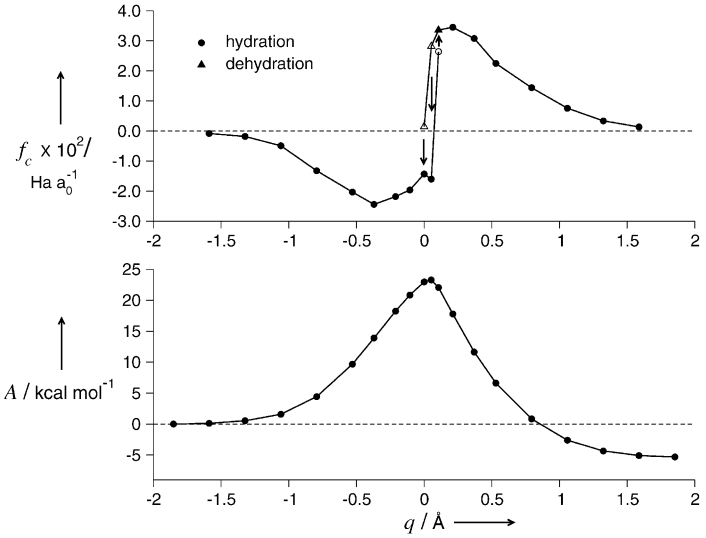


Figure 2. Calculated constraint force and associated free-energy profile along the reaction path of the acid-catalyzed interconversion of ethylene and ethanol. Results were obtained from trajectories of 5–10 ps with a prior equilibration of 1 ps. In the plot of the constraint force, the circles indicate the results obtained for the ethylene-hydration pathway and the triangles are the results for the ethanol-dehydration route. Open symbols indicate trajectories for which the constraint force showed a significant sign-reversing change in the direction of the arrow. The free-energy profile is obtained by integrating the connecting line through the calculated constraint force points.[25] Here, the first point of the hydration route ($q = -1.6$ Å) is taken as reference.

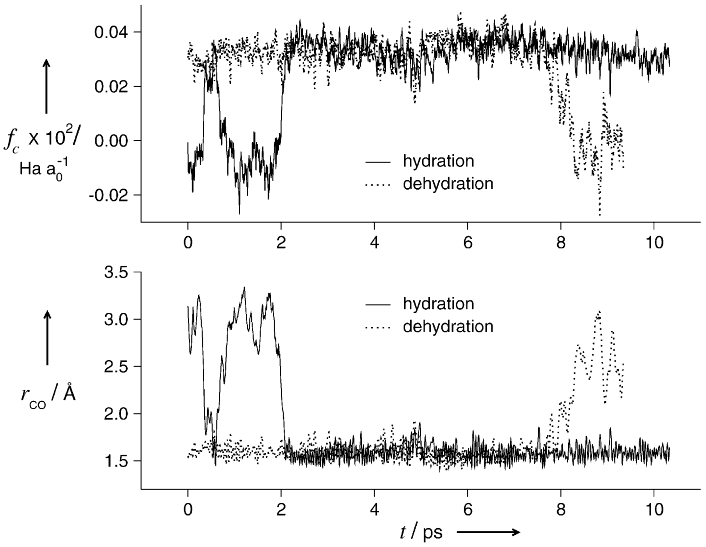


Figure 3. Time evolution of the constraint force (top) and C–O bond length [Å] (bottom) in simulations of hydration (solid line) and dehydration (dashed line) at reaction-coordinate values of $q = 0.11$ and $q = 0.05$, respectively. The sudden significant sign-reversing change of the constraint force is accompanied by C–O bond formation (hydration) and breaking (dehydration).

constraint force. This is accompanied by a formation or cleavage of a C–O bond, as shown in Figure 3. This behavior and the associated mismatch between the force profiles for hydration and dehydration indicates the presence of hysteresis. It shows that the reaction mechanism also involves structural rearrangements that are not accounted for by the imposed proton-transfer reaction coordinate. Analysis of the reactive events shows that the formation of the C–O and C–H$^+$ bonds occurs simultaneously, indicating that the reaction is an Ad$_E$3 addition. Consequently, the reverse reaction, that is, the proton-assisted dehydration of ethanol, is an E2 elimination reaction. The calculated hydration activation energy of 23 kcal mol^{-1} is near the experimental values for the activation barriers of the hydration of isobutene[14] (23 kcal mol^{-1}) and 2-methyl-2-butene[15] (19 kcal mol^{-1}) in acidic solution.

Figures 2 and 3 show that the trajectory at $q = 0.11$ Å along the hydration route and the trajectories at $q = 0.05$ and 0.00 Å along the dehydration route exhibit reactive events with the force on the proton-transfer coordinate changing sign and the C–O bond either forming or breaking. First we consider the trajectory for ethanol dehydration at $q = 0.05$ Å. Just before the C–O bond breaks at ≈ 8 ps, the OH$_2$ group leaving the protonated ethanol is hydrogen-bonded to three water molecules, with the C–O bond length around 1.8 Å. Figure 4b shows the configuration of the protonated ethanol and its hydrogen-bonded water molecules at that moment. In the first 8 ps of this trajectory various configurations appeared that had a similar C–O bond length but did not evolve into a dehydration reaction. A typical example is shown in Figure 4a. The distinction between this nonreactive configuration and the reactive configuration at 8 ps is clear: the reactive configuration shows the ethanol OH$_2$ group threefold hydrogen-

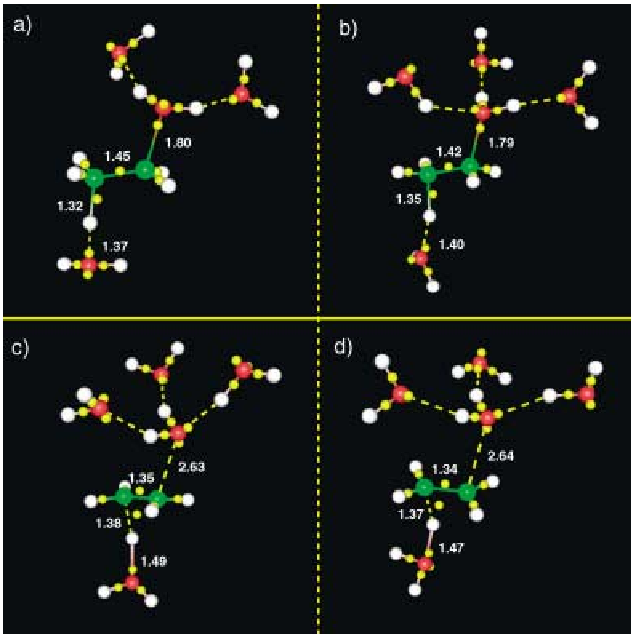


Figure 4. Nonreactive (a) and reactive (b) configurations for the dehydration of protonated ethanol. Nonreactive (c) and reactive (d) configurations for the hydration of ethylene. The color codes are the same as in Figure 1. Yellow balls denote Wannier function centers.[26] Numbers indicate bond lengths [Å]. Solvent molecules not directly involved in the reaction are omitted for clarity.

bonded, whereas in the nonreactive configuration the OH_2 group is twofold hydrogen-bonded. Apparently, a threefold coordination of the ethanol OH_2 group is required for it to be able to leave as a water molecule.

Next we consider the $q = 0.11$ Å trajectory along the hydration route. Just before the reactive event at ≈ 2 ps, the hydrating water molecule is coordinated by three water molecules at a C–O distance of 2.64 Å and a $\mathrm{C-H^+}$ distance of 1.37 Å (Figure 4d). We identified several configurations in the short time before this reactive event with nearly the same C–O and $\mathrm{C-H^+}$ distances that did not evolve directly into a reactive event. Figure 4c shows a typical example of one of these configurations. The distinction between the reactive and nonreactive configuration is the angular arrangement of the coordination of the hydrating water molecule: the reactive configuration has a near-tetrahedral arrangement of the three hydrogen-bonded water molecules and the ethylene carbon, with COO angles in the range of 98–118°. In contrast, the coordination in the nonreactive configuration deviates significantly from the tetrahedral structure, with COO angles in the range of 90–149°. To restore the favorable tetrahedral-like arrangement between the water molecules, the hydrating water molecule should move away from the ethylene and consequently does not form a bond with the carbon. The stable tetrahedral-like coordination allows the molecule to remain in position near the ethylene and form a C–O bond.

The important role of the structure and relaxation of the solvation shell found in our simulation of the proton-assisted hydration of ethylene is reminiscent of the solvent reorganization reported for the hydration of an ethylene radical cation.[9]. Obviously, given the rather different nature of a radical and a protonated ethylene, the detailed geometries of the solvation structures show quantitative differences. In conclusion, our results point out that local solvation structures are crucial in aqueous chemistry involving protons. Consequently, the common computational approach of complementing a quantum-chemical description of the reacting species with a continuum model to incorporate the presence of the solvent will fail to capture these effects. A proper understanding of aqueous chemistry requires computational and experimental studies to probe the reacting species and the molecules of the nearest solvation shells on an atomistic level.

Received: October 16, 2003 [Z53103]

Keywords: ab initio calculations · molecular dynamics · proton transport · reaction mechanisms · solvent effects

---

[1] H. J. Bakker, H.-K. Nienhuys, *Science* **2002**, *297*, 587 – 590.

[2] M. Tuckerman, K. Laasonen, M. Sprik, M. Parrinello, *J. Chem. Phys.* **1995**, *103*, 150.

[3] D. Marx, M. E. Tuckerman, J. Hutter, M. Parrinello, *Nature* **1999**, *397*, 601 – 604.

[4] B. T. Baliga, E. Whalley, *Can. J. Chem.* **1965**, *43*, 2453.

[5] W. K. Chwang, V. J. Nowlan, T. T. Tidwell, *J. Am. Chem. Soc.* **1977**, *99*, 7233 – 7238.

[6] P. E. Dietze, W. P. Jencks, *J. Am. Chem. Soc.* **1987**, *109*, 2057 – 2062.

[7] X. Xu, C. P. de Almeida, and M. J. Antal, *Ind. Eng. Chem. Res.* **1991**, *30*, 1478 – 1485.

[8] The reverse of the Ad_E2 and Ad_E3 water-addition mechanisms are referred to as the E1 and E2 water-elimination mechanisms, respectively.

[9] M. Mohr, D. Marx, M. Parrinello, H. Zipse, *Chem. Eur. J.* **2000**, *6*, 4009 – 4015.

[10] R. Car, M. Parrinello, *Phys. Rev. Lett.* **1985**, *55*, 2471 – 2474.

[11] The electronic structure was calculated using the Kohn–Sham formulation of density functional theory (DFT) and employing the BLYP functional.[16,17] BLYP has proven to give an accurate description of the structure and dynamics of water[18–20] and aqueous proton solvation.[2,3,21]

[12] Calculations were performed with the CPMD package.[22] Semi-local norm-conserving Martins–Trouillier pseudopotentials are used, with core radii for H, C, and O of 0.50, 1.23, and 1.11 a.u., respectively. Electronic states are expanded in plane waves with a wavenumber of up to 70 Ry. The mass associated with the fictitious electronic degree-of-freedom is 900 a.u. The time-step in the numerically integrated equations-of-motion is 0.145 fs.

[13] T. S. van Erp, E. J. Meijer, *J. Chem. Phys.* **2003**, *118*, 8831 – 8840.

[14] H. J. Lucas, W. F. Eberz, *J. Am. Chem. Soc.* **1934**, *56*, 460 – 456.

[15] H. J. Lucas, Y.-P. Liu, *J. Am. Chem. Soc.* **1934**, *56*, 2138 – 2140.

[16] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785 – 789.

[17] A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098 – 3100.

[18] K. Laasonen, M. Sprik, M. Parrinello, R. Car, *J. Chem. Phys.* **1993**, *99*, 9080 – 9089.

[19] M. Sprik, J. Hutter, M. Parrinello, *J. Chem. Phys.* **1996**, *105*, 1142 – 1152.

[20] P. L. Silvestrelli, M. Parrinello, *J. Chem. Phys.* **1999**, *111*, 3572 – 3580.

[21] M. Tuckerman, K. Laasonen, M. Sprik, M. Parrinello, *J. Phys. Chem.* **1995**, *99*, 5749.

[22] CPMD, version 3.0 h, developed by J. Hutter, P. Ballone, M. Bernasconi, P. Focher, E. Fois, S. Goedecker, M. Parrinello, and M. Tuckermann, at MPI für Festkörperforschung and IBM Zurich Research Laboratory (**1990–1997**).

[23] N. Marzari, D. Vanderbilt, *Phys. Rev. B* **1997**, *56*, 12847 – 12865.

[24] P. L. Silvestrelli, N. Marzari, D. Vanderbilt, M. Parrinello, *Solid State Commun.* **1998**, *107*, 7 – 11.

[25] E. A. Carter, G. Ciccotti, J. T. Hynes, R. Kapral, *Chem. Phys. Lett.* **1989**, *156*, 472.

[26] The electronic charge distribution is quantified by maximally localized Wannier functions, whose centers can be assigned a chemical meaning such as being associated with a bonding or lone pair of electrons.[23,24]