Eur. Phys. J. D **35**, 479–481 (2005)
DOI: 10.1140/epjd/e2005-00180-y

THE EUROPEAN PHYSICAL JOURNAL D

Molecular dynamics study of the reaction $C_3 + H_3^+$

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Received 27 July 2004 / Received in final form 28 April 2005

Abstract. Both a quantum molecular dynamic method and high level ab initio calculations (MP2, CCSD(T)) have been used to investigate the mechanism of the $C_3 + H_3^+$ reaction, which is part of the ion chemistry in interstellar clouds. Furthermore statistic initial orientations in collision simulations have been set up in order to determinate reaction cross-sections and rate coefficients of all occurring reaction channels. Our analysis shows that the revealed mechanism is strongly determined by dynamic effects.

PACS. 31.15.Qg Molecular dynamics and other numerical methods – 36.40.Jn Reactivity of clusters

1 Introduction

Small carbon and hydrocarbon molecules resp. ions are known to be part of the composition of interstellar clouds [1]. These species are supposed to be important precursors of complex interstellar matter such as polyaromatic hydrocarbons (PAHs) [2]. Therefore, it is an essential task to understand the elementary steps which control the dynamic evolution of complex interstellar matter. These activities include systematic empirical laboratory investigations as well as basic research where fundamental questions are answered either by experiment or basic theory [3,4].

With increasing dimensionality, i.e. increasing number of atoms in the systems, computations considering quantum dynamics and electronic transitions (non-adiabatic processes) become numerically demanding. For studying the reaction dynamics of such systems approximate simulation methods such as density functional based approaches are a good compromise between precision and numerical performance. Yet, they allow a realistic treatment of the electronic states.

Simulations based on DFTB molecular dynamics which theoretical details are reviewed in [5] or [6]. For validation of the method and further application to complex reaction systems, we focused first mainly on the reaction system C_3 and H_3^+. These results will be summarized in this paper. Again, ion molecule reaction with H_3^+ seems to be one of the simplest occurring reaction type in interstellar clouds [7].

2 Computational details

The electronic wave functions (Kohn-Sham orbitals) $\psi_i(\mathbf{r})$ are written as linear combinations of atomic orbitals, centered at the nuclei j (LCAO ansatz). The valence wave functions are considered in the LCAO ansatz. Each wave function is represented by a set of Slater type functions. The effective one particle potential V_{eff} in the Kohn-Sham Hamiltonian $\hat{h} = \hat{t} + V_{\text{eff}}(\mathbf{r})$ is approximated as a sum of potentials of neutral atoms. Consistent with this approximation one has to neglect several contributions to the Hamiltonian matrix elements $h_{\mu\nu}$. Furthermore, we use an empirical ansatz for the repulsive force between the atoms at small distances (for details see [5]).

The Verlet algorithm was applied for the integration of Newton equations of motion. A step size of 2.41×10^{-16} s was used to guarantee the conservation of energy. All trajectories were initiated at an interaction-free distance, i.e. with a center of mass distance of 8×10^{-10} to 15×10^{-10} m but in detail depending on the system. In order to avoid collision orientation correlations, collisions are simulated considering a statistical distribution of relative orientations of the colliding particles. The initial velocities are chosen according to the collision energy and to keep the center of mass stationary. In the present simulations we did not consider rotational or vibrational excitations in the initial state of the colliding system. Every trajectory was allowed to propagate over a time period of at least 2.5×10^{-12} s. In order to achieve convergence in the reaction probabilities, up to 3 000 trajectories have been calculated for every collision energy. The reaction cross-section was calculated by integrating the reaction probability $P(b)$ over the impact parameter b. Thermal reaction rate coefficients k(T) are derived from the proper average $\langle\sigma(\epsilon)\epsilon\rangle$.

Reference single point calculations concerning reaction energies were made using Gaussian98 [8]. Besides single point calculations of significant stationary points and molecular dynamics, DFTB has been coupled with the nudged elastic band (NEB) method (see e.g. [9]) in order to compute minimum energy paths. Initial guess of the

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Table 1. Calculated reaction energies (in eV) for C_3 + H_3^+.

	MP2/ cc-pVTZ	CCSD(T)/ cc-pVTZ	DFTB
→ C_3H^+ + H_2			
C-CH-C^+	–0.5034	–1.0540	–1.2350
C-C-CH^+	–3.4580	–3.4536	–2.9134
→ $C_3H_2^+$ + H			
HC-C-CH^+	–3.3803	–3.0900	–1.5408
H_2C-C-C^+	–1.7075	–1.4541	–1.1811
→ $C_3H_3^+$			
C-C-CH_3^+	–1.2372	–1.6394	-
C-CH-CH_2^+	–4.0520	–4.5823	–6.0946
HC-C-CH_2^+	–8.0094	–7.8927	–7.5751
c-$C_3H_3^+$	–9.4041	-9.1216	–7.8493

Table 2. Calculated reaction cross-sections for C_3 + H_3^+ as a function of collision energy.

ε / eV	σ_r / 10^{-20} m^2	
	C_3H^+	residual channels
0.0025	70.05	0.085
0.005	64.98	0.146
0.01	61.32	0.070
0.025	54.67	0.176
0.05	49.27	0.068
0.075	46.20	0.090
0.10	44.43	0.030
0.15	38.63	0.027
0.25	34.40	0.083
0.35	29.36	0.050
0.50	26.70	0.191
0.75	24.05	0.463

Table 3. Calculated thermal rate constants for C_3 + H_3^+.

T / K	$k(T)$ / $10^{-10}\,\mathrm{cm^3\,s^{-1}}$	
	C_3H^+	residual channels
100	5.124	0.011
200	6.674	0.015
300	7.680	0.015
400	8.450	0.015
500	9.076	0.015

reaction path can be obtained from analyzing the molecular dynamic simulations.

3 Results

The calculated reaction energies for the different product channels, listed in Table 1, exhibit that according to MP2 and CCSD(T) calculations the association reaction C_3 + H_3^+ → $C_3H_3^+$ has a reaction energy of about 8.0 eV The protonation reaction C_3 + H_3^+ → C_3H^+ + H_2 and the competing reaction C_3 + H_3^+ → $C_3H_2^+$ + H have a reaction energy of about 3.4 eV.

The most stable isomer of the $C_3H_3^+$ potential energy surface is the cyclopropargyl cation *c*-$C_3H_3^+$ lying 9.4 eV below the energy of the reactants (according to MP2). However, it is known [10] that there is a high activation barrier to form the cyclic isomer from $C_3H_3^+$. The HC-C-CH_2^+ propagyl cation is the most stable straight-chain isomer. The energy of propenylidene cation (HC-C-CH^+) + hydrogen (H) is located 3.4 eV below the energy of the reactants. The reaction energy for the protonation, leading to linear C_3H^+ is 3.4 eV, the other isomer C-CH-C^+ is 2.9 eV less stable. The results of the DFTB calculation are in good agreement with the ab initio calculations for the closed shell channels (see Tab. 1).

Results of the molecular dynamic simulations in dependency of collision parameter and collision energy are shown in Table 2. In agreement with the experimental findings, our results exhibit that the protonation is the dominant reaction channel. There are two possible mechanisms: direct protonation C_3 + H_3^+ → C_3H^+ + H_2 or passage through a vibrationally exited intermediate C_3 + H_3^+ → $C_3H_3^+$ → C_3H^+ + H_2. However, the second mechanism is found rarely. Other reaction channels may occur as well such as $C_3H_3^+$ but also $C_3H_2^+$ + H or C_2H_2 + CH^+. The latter two product constellations are the result of $C_3H_3^+$ dissociation after a certain simulation time, their rate increases slightly with the increasing collision energy. Fluctuations in the calculated reaction cross-sections are probably due to the still low resolution of the used statistics.

Thermal reaction rate coefficients $k(T)$, derived from the proper average $\langle\sigma(\epsilon)\epsilon\rangle$, are listed in Table 3. The rate coefficient of the protonation channel at 300 K ($7.7 \times 10^{-10}\,\mathrm{cm^3}$) is below the Langevin value $20 \times 10^{-10}\,\mathrm{cm^3}$ [11]. This is caused by the approximation of the long-range forces within the used method.

Detailed analysis of single trajectories concerning for example the distribution of kinetic energy per atom over simulation time could reveal aspects of the reaction mechanism. Therefore, the distribution of the kinetic energy of a typical reactive trajectory is shown in Figure 1, whereas Figure 2 is an enlarged presentation. Considering more trajectories it can be deduced that between 5 and 10% of the reaction energy is released as translation energy, mainly of the H_2 molecule formed in the reaction.

The energetically lowest reaction path of each reaction channel has been obtained by NEB computations. Figure 3 shows the optimized reaction path of the protonation reaction which has obviously no reaction barrier. The other reaction mechanism leading to the association product $C_3H_3^+$ has no reaction barrier as well. Of course, processes such as proton-shifting or cyclization of $C_3H_3^+$ are defined by a reaction barrier.

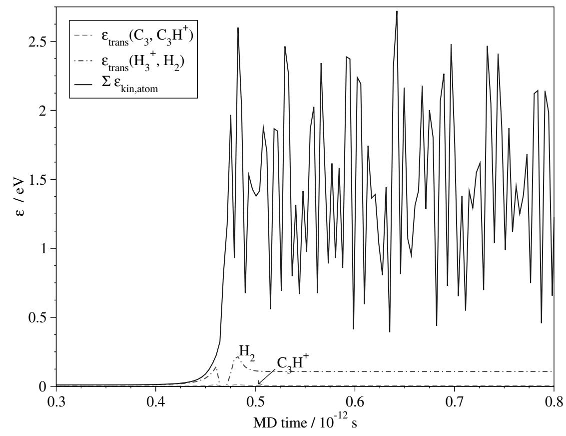

Fig. 1. Time evolution of the total kinetic energy ($\Sigma\,\varepsilon_{\mathrm{kin,\,atom}}$) and the translation energy of the molecular mass centers ($\varepsilon_{\mathrm{trans}}(\mathrm{X})$) taken from a typical reactive trajectory.

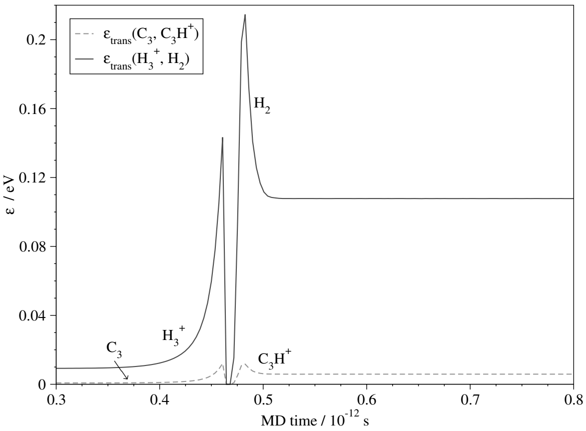

Fig. 2. Translation energy of a typical reactive trajectory. Enlarged presentation of Figure 1. For description see Figure 1.

4 Conclusions

Comparison between reference ab initio and DFTB calculation of closed shell reaction channels showed a good agreement. Furthermore we have succeeded calculations of the reaction paths by implementation of the DFTB into the NEB method. Investigated mechanism of the protonation and association reaction are characterized by no reaction barrier which is in agreement with the general properties of ion molecule reactions. Dynamic simulations showed that the reaction is strongly dominated by dynamic effects. Determined rate coefficients of the protonation reaction are close to the Langevin value. Therefore, molecular dynamics simulation on the basis of an approximated DFT method can be used to investigate mechanism of further astrochemical reactions, playing an important role in the evolution of complex matter such as formation leading to aromatic and polyaromatic hydrocarbons. Additionally, we currently perform non-adiabatic molecular dynamic simulations of the reaction system described in this paper based on a further development of the DFTB code [12]. Results will be discussed in a forthcoming publication.

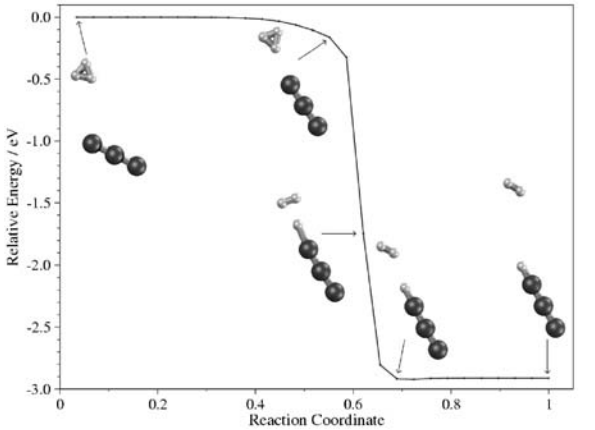

Fig. 3. Minimum energy path of reaction channel $C_3 + H_3^+$ to $C_3H^+ + H_2$.

This work was supported by the DFG Forschergruppe Laboratory Astrophysics. The authors wish to thank D. Gerlich, I. Savic and I. Cermák (TU Chemnitz) for discussions.

References

1. D. Smith, Chem. Rev. **92**, 1473 (1992)
2. D. Böhme, Chem. Rev. **92**, 1487 (1992)
3. *Laboratory Astrophysics and Space Research*, edited by P. Ehrenfreund, C. Krafft, H. Kochan, V. Pirronello, (Kluwer, Dordrecht, 1999)
4. D. Gerlich, S. Horning, Chem. Rev. **92**, 1509 (1992)
5. G. Seifert, D. Porezag, T. Frauenheim, Int. J. Quant. Chem. **58**, 185 (1996)
6. J. Schulte, G. Seifert, Chem. Phys. Lett. **221**, 230 (1994)
7. B. McCall, K. Hinkle, T. Geballe, T. Oka, Faraday Discuss. **109**, 267 (1998)
8. M. J. Frisch et al., *Gaussian 98, Revision A.7*, Gaussian, Inc., Pittsburgh USA, 1998
9. G. Henkelman, B. Uberuaga, H. Jónsson, J. Chem. Phys. **113**, 9901 (2000)
10. S.A. Maluendes, A.D. McLean, K. Yamashitaand, E. Herbst, J. Chem. Phys. **99**, 282 (1993)
11. T.J. Millar, Y.H.L. Teuff, A.J. Markwick, A&AS **146**, 157 (2000)
12. T. Frauenheim et al., J. Phys.: Condens. Matter **14**, 3015 (2002)