Ab initio molecular dynamics simulations of the Li$_4$F$_4$ cluster

A. Heidenreich*, J. Sauer

Max-Planck-Gesellschaft, Arbeitsgruppe Quantenchemie an der Humboldt-Universität zu Berlin, Jägerstrasse 10/11, D-10117 Berlin, Germany

Received: 3 April 1995 / Final version: 15 May 1995

Abstract. Molecular dynamics simulations have been performed directly on the ab initio potential energy surface of Li$_4$F$_4$, which was generated within the Hartree-Fock approximation using a Gaussian basis set (split valence contraction). Trajectories at different temperatures yield the temperature dependence of the infrared spectra and the photoelectron spectra. For the infrared spectra comparison is made with MD results using a shell model ion pair potential function.

PACS: 82.20.Fd; 31.20.Fj; 33.10.-n

1 Introduction

Molecular dynamics techniques which describe the motion of atoms classically are a standard tool for studying dynamic and spectroscopic properties for systems ranging from molecules over clusters to condensed phases. Unlike quantum techniques such as wavepacket dynamics, they are not limited to a few degrees of freedom. The forces acting on the atoms are usually calculated from analytical potential functions. These potentials always contain a compromise between the flexibility and the number of parameters. In most cases it proves difficult to find potential functions which provide an accurate description of all regions of interest of the potential energy surface on which the nuclei move, in particular when making or breaking chemical bonds. In addition, finding the parameters of the potential functions is a tedious task. They are fit either to experimental data or to quantum chemical ab initio results for the potential energy surface. Such problems can be avoided when in each step of the simulation the forces on the nuclei are directly calculated from the quantum chemical ab initio solution of the electronic problem. This approach has been named ab initio MD, AIMD. The feasibility of AIMD simulation depends on the efficiency of the force calculations. Force calculations are rapid when plane waves can be used for expanding the electronic wave function because the Hellmann-Feynman theorem can be applied. This is the case in the pioneering approach of Car and Parrinello [1] which uses pseudopotentials for the core electrons and includes electron correlation through density functional theory. With localized basis functions such as Gaussians, which are almost exclusively used for molecules and clusters, the calculations of forces are more demanding since non-Hellmann-Feynman contributions to the forces occur which require a calculation of derivatives of the numerous two-electron integrals. Therefore, AIMD simulations with Gaussian bases functions emerged only in the nineties [2–7]. With two exceptions [4, 6], the Hartree-Fock (HF) approximation is used since force calculations for post-HF methods which take electron correlation into account are even more demanding.

In this paper, we report AIMD simulations of the Li$_4$F$_4$ cluster and compare them with simulations which use the classical shell model potential for calculating the forces. Previous ab initio studies [8–11] have shown that the structure of alkali halide clusters and the relative energies of different isomers are well described within the HF approximation. Another motivation for selecting this system was that MD simulations using classical potential functions have already been performed for such alkali halide tetrameric clusters [12–15]. We derive the infrared spectra from the simulation and study their temperature dependence. In addition, temperature-dependent line shapes of the photoelectron spectra (PES) are derived using the semiclassical spectral density method of Fried and Mukamel [16], which was developed to simulate the absorption line shape of an electronic two-level system and was applied to van der Waals heteroclusters [17–20]. It belongs to the advantages of AIMD simulations that the HF calculations performed at each configuration

* Present address: School of Chemistry, Tel Aviv University, 69978 Tel Aviv, Israel
provide the information on the transition energies for the PES, namely the ionization energies within the approximation of Koopmans theorem.

2 Methodology and computational details

2.1 Constant energy MD simulations

Constant energy MD simulations were performed for several vibrational excess energies, which are defined as the differences of the total energies and the potential energy of the cube equilibrium structure. The vibrational excess energy ranges from 2500 cm$^{-1}$ to 31000 cm$^{-1}$ corresponding to temperatures between 200 and 1950 K ($T = 2\langle E_{\text{kin}}\rangle/(3N - 6)k_B$; $\langle E_{\text{kin}}\rangle$: trajectory average of the kinetic energy, N: number of atoms, $k_B$: Boltzmann constant). A third-order Gear predictor-corrector algorithm [21] was used to integrate the classical equations of motion. The linear and the angular momentum of the centre of mass was set to zero at the beginning of each trajectory. The time step was chosen between 0.4 fs at low and 0.1 fs at high vibrational excess energies. If not stated otherwise, each trajectory had a temporal length of 8.5 ps. The conservation of the vibrational excess energy was 2–46 cm$^{-1}$ or 0.05–1.8%.

In ab initio MD simulations at each time step a full SCF calculation was carried out as in previous work using Gaussian basis functions [2, 3, 7]. This is different from the approach of Car and Parrinello who simulate the dynamics of the nuclei and at the same time propagate the coefficients of the wavefunction using fictitious masses [1]. Since the number of Gaussian basis functions is typically much smaller than the number of plane waves the iterative diagonalization is more efficient. For the split valence Gaussian basis set selected (SV($\xi_p = 0.7$), vide infra) one MD step involving a converged SCF calculation (energy convergence criterion $10^{-8}$ hartree; 1 hartree = 2625.47 kJ/mol) typically requires 30 seconds real time on an IBM RS/6000-370 workstation; the total time per trajectory is 1–4 weeks, depending on the length of the MD integration step between 0.4 and 0.1 fs. For the force calculations the TURBOMOLE code [22, 23] was used in all AIMD simulations.

2.2 Ab initio potential energy surface

For lithium fluoride clusters two basis sets were optimized by Ochsenfeld and Ahlrichs [10], the “ALiF” basis (256 basis functions for Li$_4$F$_4$) and (2) the “SVPLiF” basis (108 basis functions for Li$_4$F$_4$). At present, it is not practical to simulate trajectories of a temporal length of several ps using the ALiF or the SVPLiF basis sets. Therefore we checked whether a simple split valence (SV) basis set could mimic the potential energy surface obtained by more accurate ab initio approaches. We adopted the standard dynamics of the nuclei and at the same time propagate the coefficients of the wavefunction using fictitious masses the iterative diagonalization is more efficient. For the split valence Gaussian basis set selected (SV($\xi_p = 0.7$), vide infra) one MD step involving a converged SCF calculation (energy convergence criterion $10^{-8}$ hartree; 1 har-