Excitation and Relaxation in Atom-Cluster Collisions

U. Saalmann

Max-Planck-Institut für Physik komplexer Systeme, Nöthnitzer Straße 38, 01187 Dresden, Germany

R. Schmidt

Institut für Theoretische Physik, Technische Universität Dresden, 01062 Dresden, Germany

Electronic and vibrational degrees of freedom in atom-cluster collisions are treated simultaneously and self-consistently by combining time-dependent density functional theory with classical molecular dynamics. The gradual change of the excitation mechanisms (electronic and vibrational) as well as the related relaxation phenomena (phase transitions and fragmentation) are studied in a common framework as a function of the impact energy (eV $\rightarrow$ MeV). Cluster "transparency" characterized by practically undisturbed atom-cluster penetration is predicted to be an important reaction mechanism within a particular window of impact energies. [S0031-9007(98)05778-0]

Collisions with atomic clusters represent a relatively new branch of collision physics as compared to the well established fields of ion-atom collisions [1] and ion-solid interaction [2]. The study of cluster collisions is of particular interest and importance because it offers the possibility to tackle bridge-building questions (like the continuous transition from individual excitations in the elementary ion-atom collision to the macroscopic stopping power in solids) as well as fundamental problems (like phase transitions in finite systems). It is also an extremely challenging and complicated field, as the comprehensive understanding of these collisions still requires the development of basically new techniques for both large-scale (multiparametric) experiment and many-body (quantum-mechanical) theory. In this respect, the present situation resembles very much that of nuclear physics at the beginning of the 1980s [3].

Experimentally, great progress has been made, meanwhile, in the investigation of *adiabatic* cluster collisions where the reaction mechanism is determined by vibrational excitations only. Typical examples are the study of the vibrational energy transfer [4], the fusion between clusters [5], the formation of endohedral complexes [6], and the collision induced dissociation (CID) [7]. There is also a lasting interest to study *nonadiabatic* cluster collisions where electronic transitions occur. Experiments in this field concern the measurements of the charge transfer [8–10], ionization and electronic excitation [11], as well as the *selective* observation of vibrational and electronic excitations [12].

Theoretically, adiabatic cluster collisions can be well described by quantum molecular dynamics (QMD) or molecular dynamics (MD) [13–17]. Also, isomeric [18] and solid-liquid phase transitions [19,20] in clusters as well as the fission process of clusters [21] have been studied with MD or QMD where, basically, electronic excitations are not considered. On the other hand, electronic

transitions in nonadiabatic cluster collisions have been treated with classical [22,23], semiclassical [24], or one-electron quantum mechanical [25,26] approaches where the atomic structure, and thus the vibrational degrees of freedom, are not taken into account. Recently, a general theory has been developed [27] which is able to describe simultaneously adiabatic and nonadiabatic collisions and, in particular, also the still completely unknown transition regime where both electronic and vibrational excitations occur. This so-called nonadiabatic quantum molecular dynamics (NA-QMD) [27] can also be used to study, for the first time, phase transitions in and fragmentation of clusters induced by electron-vibration coupling.

In this work, different excitation mechanisms (electronic and vibrational) as well as related relaxation phenomena (phase transitions and fragmentation) in cluster collisions are studied in the microscopic framework of NA-QMD. This theory treats electronic and vibrational degrees of freedom simultaneously and self-consistently in atomic many-body systems by combining time-dependent density functional theory [28] with classical MD. The key point, in order to derive computationally tractable equations of motion, is the split of the total electronic density into the adiabatic and a remaining part, treating afterwards the exchange-correlation terms with the adiabatic density only [27]. This approximation has been applied and successfully tested against experimental data, so far, for the interpretation of fragment correlations in CID [29] and the calculation of absolute cross sections for charge transfer [30] in cluster reactions. Here the universal NA-QMD approach is used to investigate the gradual change of the excitation and relaxation mechanisms as a function of the impact energy in a wide range for two basically different collision systems, $Na_9^+ + Na$ (with attractive adiabatic forces between projectile and target) and $Na_9^+ + He$ (with dominating repulsive forces and a "magic" initial electronic configuration).

In Fig. 1, the total kinetic energy loss (TKEL) of the collision, $\Delta E = E_{cm} - E_{cm}(t \to +\infty)$, with E_{cm} the impact energy and $E_{cm}(t \to +\infty)$ the final kinetic energy of the relative motion between cluster-projectile and atomic target in the center-of-mass system is shown calculated for a fixed collision geometry (with impact parameter $b = 0$) but in a wide range of impact energies $E_{cm} = 0.2$ eV–1 MeV. For "real" scattering events (see below), ΔE describes the change of the internal energy of the system generally connected with excitations in the cases studied here. In order to decide between electronic and vibrational contributions to ΔE the NA-QMD results are compared to those obtained from adiabatic QMD [27] calculations performed with the same collision geometry. At impact energies below $E_{cm} \lesssim 200$ eV, QMD and NA-QMD results are clearly seen to be identical and, thus, only vibrational excitations occur (adiabatic regime). Above $E_{cm} \gtrsim 5$ keV electronic transitions dominate (nonadiabatic regime). In the intermediate range of E_{cm} both mechanisms compete (transition regime). Maximal TKEL—namely, $\Delta E = E_{cm}$—is practically realized at all impact energies below $E_{cm} \lesssim 10$ eV and is connected with the formation of relatively long-living but in general unstable intermediate compounds Na_{10}^+ [31]. The real scattering events with incomplete energy loss appear above $E_{cm} \gtrsim 10$ eV.

In Fig. 2, the time dependence of $\Delta E(t) = E_{cm} - E_{cm}(t)$, with $E_{cm}(t)$ the actual kinetic energy of the relative motion, and the displacement of the cluster atoms $d(t)$ are shown for characteristic impact energies. The quantity $\Delta E(t)$ gives insight into the collision and
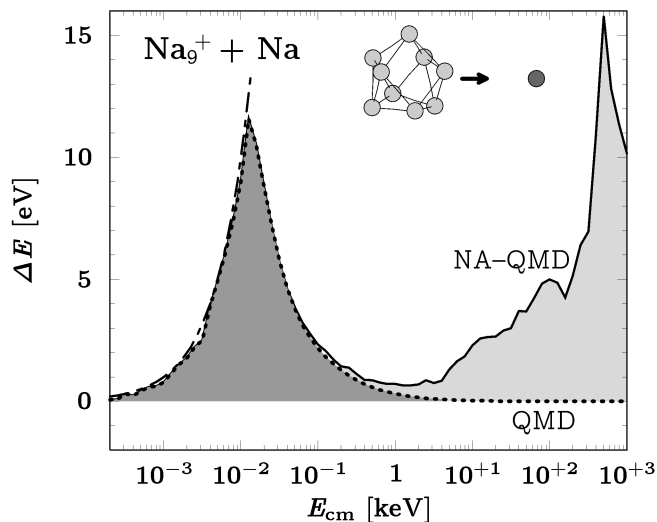
excitation dynamics (forces, interaction time, TKEL). The displacement, defined as $d(t) := \{\sum_{A=1}^{N}[\mathbf{R}_A(t) - \mathbf{R}_A(0)]^2\}^{1/2}/NR$ with $\mathbf{R}_A(0)$ the equilibrium positions of the N atoms in the ground state configuration and R the cluster radius, characterizes quantitatively the relaxation, i.e., if d is well below one a "solid" configuration is described, if d lies in the vicinity of one a "liquid" state is realized, and if d goes to infinity fragmentation occurs. Excitation and relaxation mechanisms and, in particular, the related time scales are basically different in all cases. In the pure adiabatic regime ($E_{cm} = 200$ eV), the vibrational excitation of the cluster ($\Delta E \approx 1.4$ eV) is immediately connected with a fragmentation process which, in contrast to statistical evaporation, starts to proceed already during the interaction time of $\sim$40 fs

FIG. 1. Total kinetic energy loss of relative motion ΔE in central $Na_9^+ + Na$ collisions for a fixed collision geometry (see inset) as a function of the center-of-mass impact energy E_{cm} calculated with NA-QMD (solid line) and QMD (dotted line). Vibrational and electronic contributions to ΔE are distinguished by gray and light-gray shaded areas, respectively. The dot-dashed line corresponds to $\Delta E = E_{cm}$.
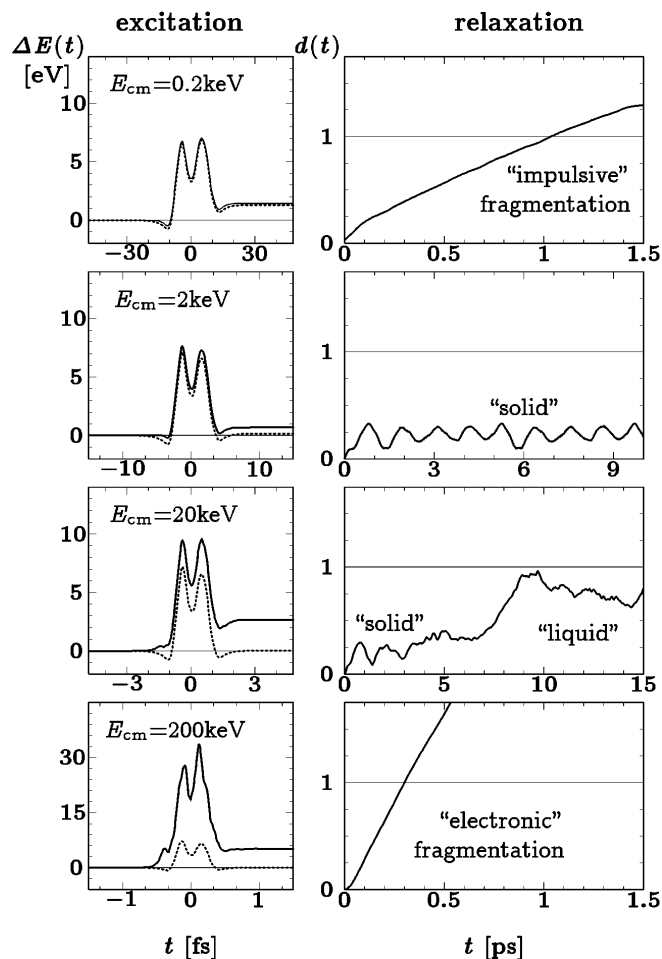

FIG. 2. Difference of the impact energy and the actual kinetic energy of relative motion $\Delta E(t)$ (left column) and displacement of the cluster atoms $d(t)$ (right column) as a function of time t for four impact energies $E_{cm} = 0.2, 2, 20,$ and 200 keV and the same collision geometry as used in Fig. 1, calculated with NA-QMD (dark solid lines). In the left column, the corresponding adiabatic QMD calculations (dotted lines) are also shown for comparison. Note the different time scales for the excitation processes (femtoseconds) and the relaxation phenomena (picoseconds).

(see left part of Fig. 2) as a consequence of sufficient momentum transfer between projectile and target atoms. Such nonstatistical fragmentation has been experimentally verified only very recently [12] (called "impulsive" fragmentation mechanism). On the contrary, in the high-energetic nonadiabatic region $E_{cm} = 200$ keV electronic excitation (~ 1 fs) and fragmentation (~ 300 fs) processes are separated by 2 orders of magnitude. Obviously, electron-vibration coupling needs time to become effective and to induce dissociation ("electronic" fragmentation). At an impact energy of $E_{cm} = 2$ keV the cluster remains stable after the collision with a total excitation energy of $\Delta E \approx 0.7$ eV originally stored predominantly in electronic excitation (cf. adiabatic and nonadiabatic contributions to ΔE in the left part of Fig. 2). Electron-vibration coupling leads, however, to the excitation of collective surface vibrations indicated by the regular oscillating behavior of $d(t)$ well developed after about 1 ps. At $E_{cm} = 20$ keV the first step of the relaxation phase is very similar to that observed at $E_{cm} = 2$ keV. But in this case electron-vibration coupling induces clearly a phase transition from solid to liquid in a second relaxation step coming about 10 ps after the collision. Owing to the large TKEL ($\Delta E \approx 2.7$ eV) one should expect statistical evaporation as the final decay channel.

The excitation and relaxation mechanisms, summarized in Figs. 1 and 2, appear in a well-defined order as a function of the impact energy due to the deliberately fixed collision geometry. For a given impact energy and, in particular, for comparison with experiment the impact parameter dependence of measurable quantities averaged over different orientations of the cluster with respect to the beam axis is of interest. For the TKEL this dependence is shown in Fig. 3 for an impact energy in the nonadiabatic regim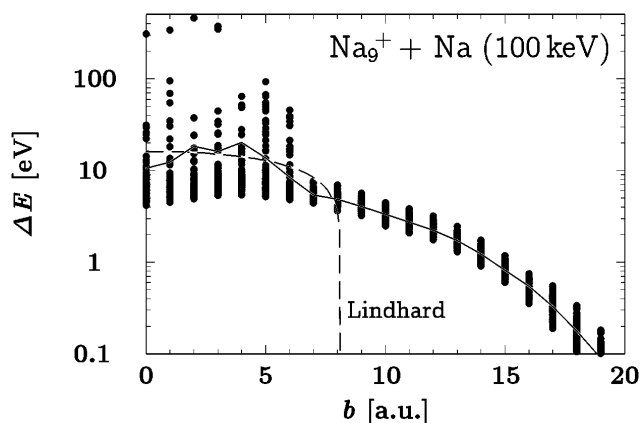e. The results are compared to the well-known Lindhard model [32] of the electronic stopping power in solids. This phenomenological model describes surprisingly well the mean value of ΔE for impact parameters smaller than the cluster radius, $b \lesssim 8$ a.u. There are, however, two characteristic and measurable peculiarities of $\Delta E(b)$ in the microscopic calculations. First, for small impact parameters $b \lesssim 6$ a.u., there are a few events with a very large TKEL. They result from binary atom collisions between the Na target and a cluster atom, leading to very fast fragment monomers. In a macroscopic language, these direct "knock-out" collisions correspond to the nuclear stopping power [2]. Second, for impact parameters larger than the cluster radius, $b \gtrsim 8$ a.u., the calculated (in that case purely electronic) TKEL are not small as compared to the dissociation energy of the cluster. Consequently, electronic fragmentation (cf. Fig. 2) may essentially contribute to the total fragmentation cross section which can be expected to be several times larger than the geometrical one.

The most interesting and unexpected phenomenon of the studies performed so far is the occurrence of cluster "transparency" in the closed shell system $Na_9^+ +$ He. This mechanism is characterized by a practically

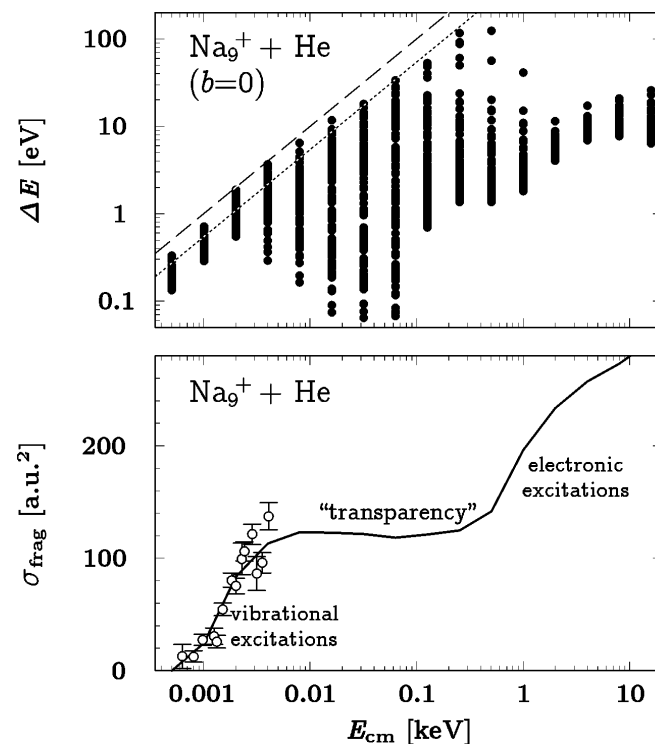FIG. 3. Total kinetic energy loss ΔE in $Na_9^+ +$ Na collisions ($E_{cm} = 100$ keV) for randomly chosen cluster orientations as a function of the impact parameter b calculated with NA-QMD (dots) as well as the resulting mean value (solid line). The prediction of the Lindhard model [32] is also shown (dashed line).

FIG. 4. Upper panel: Total kinetic energy loss ΔE in $Na_9^+ +$ He collisions as a function of the center-of-mass impact energy E_{cm} calculated with NA-QMD using randomly chosen orientations (dots). The lines correspond to a complete energy loss $\Delta E = E_{cm}$ (dashed) and the maximal energy loss for a binary collision of the He atom with *one* cluster atom (dotted) [31,33]. Lower panel: Total fragmentation cross sections as a function of E_{cm} calculated with NA-QMD (solid line). Available experimental data (circles) are from [33].

undisturbed atom-cluster penetration in a certain, small range of E_{cm} within the transition regime. In Fig. 4, the TKEL as a function of E_{cm} calculated for random orientations with impact parameter $b = 0$ is shown. It can be clearly seen that in the window between $E_{cm} \sim 10$ eV and ~ 100 eV the variance of ΔE becomes markedly large and there are a lot of events with an extremely small energy loss. It seems to be that for specific collision geometries in this range of E_{cm} the relative velocity between projectile and target becomes too large to excite vibrational degrees of freedom and is, on the other hand, still too small to induce electronic transitions. As a consequence, the cluster appears to be transparent even in central collisions. A final interpretation of this effect, however, requires further investigations (see below).

One possibility to study the change in the excitation mechanisms and in particular the occurrence of transparency, is to consider the total fragmentation cross section as a function of E_{cm} (lower part of Fig. 4). The theoretical cross section σ_{frag} has been calculated by taking into account an initial temperature of the clusters according to recent experiments [33]. An excellent agreement between theory and experiment is found in the adiabatic regime where experimental data are available at present, i.e., $E_{cm} \lesssim 4$ eV. It is just the transparency effect which leads to a pronounced plateau in σ_{frag} between 10 and 100 eV before electronic excitations induce a further increase of $\sigma_{frag}(E_{cm})$.

In summary, we have shown how different excitation mechanisms compete and various relaxation phenomena occur in atom-cluster collisions. First relations and basic differences to macroscopic systems have been discussed. Cluster transparency has been predicted to be an important reaction mechanism in $Na_9^+ + He$. A systematic investigation of different collision systems (in particular the size dependence of transparency [34], its eventual relation to the channeling effects in solids [35], the temperature dependence, etc.) will be the scope of future studies.

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