ENERGY-DEPENDENT FRAGMENTATION DYNAMICS OF ELECTRON-IMPACT IONIZED MOLECULAR CATIONS

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ABSTRACT

Fragmentation of molecular cations formed by electron-impact ionization is governed primarily by the redistribution of internal energy deposited during the collision event. A detailed understanding of how this energy drives the transition from bound vibrational motion to irreversible bond cleavage is essential for interpreting energy-resolved fragmentation measurements. In this work, we analyze the dependence of dissociation behavior on internal energy using a controlled diatomic benchmark system. Electron-impact ionization is represented through controlled initialization of internal energy on the molecular cation potential energy surface, followed by classical propagation of the nuclear motion. The study focuses on identifying effective dissociation thresholds, characterizing near-threshold dynamical regimes, and examining the scaling of fragmentation times with increasing internal energy. Ensemble simulations are employed to determine dissociation probability as a function of deposited energy and to analyze the redistribution between kinetic and potential energy during bond stretching. The results provide a physically transparent description of energy-driven molecular breakup and offer a reference for interpreting energy-dependent fragmentation phenomena investigated within the ATMOLCOL project.

Keywords: energy redistribution, dissociation threshold, electron-impact ionization, molecular dynamics, fragmentation dynamics.

INTRODUCTION

Fragmentation of molecular ions produced by electron-impact ionization is primarily governed by the redistribution of internal energy deposited during the collision event. Once ionization occurs, the excess energy introduced into the molecular system is redistributed among the internal degrees of freedom and may eventually drive the system from bound vibrational motion toward irreversible bond cleavage. Understanding how this energy redistribution translates

into observable fragmentation behaviour is essential for interpreting energy-resolved measurements in electron–molecule collision experiments. Studies of low-energy electron interactions with molecules have demonstrated that such processes play an important role in a wide range of environments, including plasmas, atmospheric chemistry, and radiation-induced molecular processes [1,2].

In many experiments the final fragments produced after the collision can be detected with high accuracy, while the intermediate nuclear dynamics that lead from ionization to dissociation remain inaccessible to direct observation. Consequently, theoretical and computational approaches are required in order to connect the measured fragment distributions with the underlying molecular motion. In particular, the characterization of energy thresholds separating bound and dissociative regimes is crucial for understanding the onset of fragmentation and the dependence of dissociation rates on the internal energy of the system

Near the dissociation threshold, molecular systems often exhibit complex dynamical behaviour. Instead of immediate bond rupture, the nuclear motion may remain temporarily confined within the potential well, undergoing extended vibrational motion before escaping toward dissociation. Such near-threshold dynamics lead to broad distributions of dissociation times and introduce strong sensitivity to the amount of internal energy deposited during the ionization event. Similar behaviour has been discussed in studies of molecular dissociation dynamics where the competition between vibrational trapping and bond rupture produces distinct dynamical regimes near the dissociation limit [3].

Because of the intrinsic complexity of polyatomic molecular systems, simplified benchmark models are often used to gain insight into the fundamental mechanisms governing energy-driven fragmentation. Diatomic molecular ions provide particularly useful reference systems in this context. Despite their structural simplicity, they retain the essential ingredients required to describe bond stretching, anharmonic vibrational motion, and dissociation processes. The Morse potential has long been used as an effective model potential to describe the anharmonic behaviour of diatomic bonds and their dissociation properties [4,5].

In the present work we investigate how internal energy influences the dissociation dynamics of an ionized diatomic molecule using classical molecular dynamics simulations on an effective potential energy surface. Electron-impact ionization is represented through controlled initialization of internal energy in the molecular cation, while the subsequent nuclear motion is propagated using a classical trajectory approach. By systematically varying the deposited energy, we identify different dynamical regimes of motion, determine effective dissociation thresholds, and examine the dependence of dissociation times on internal energy. Ensemble simulations are further employed to explore the statistical distribution of dissociation events in the near-threshold region.

The results provide a transparent physical picture of the transition from bound vibrational motion to dissociation as a function of internal energy. Such an approach offers a useful reference framework for interpreting energy-dependent fragmentation phenomena in electron–molecule collision experiments and contributes to the broader effort of understanding radiation-induced molecular dynamics within the ATMOLCOL project.

While previous work focused primarily on the development and validation of the dynamical model, the present study concentrates on the role of internal energy in determining the fragmentation dynamics.

ENERGY DEPOSITION AND FRAGMENTATION DYNAMICS

When a molecule undergoes electron-impact ionization, a part of the kinetic energy of the incident electron is transferred to the molecular system and appears as internal excitation of the resulting molecular ion. The deposited energy can be redistributed among the vibrational degrees of freedom of the molecule and may eventually lead to bond stretching and dissociation. The amount of internal energy available after ionization therefore plays a central role in determining the subsequent nuclear dynamics of the system and the probability of fragmentation.

In collision experiments the energy transferred during the primary ionization event can vary over a relatively wide range, leading to different dynamical regimes of motion. For low internal energies the molecular ion remains confined within the potential well and performs bound vibrational motion. In this regime the system oscillates around the equilibrium bond length and no dissociation occurs on the simulated time scale. As the internal energy increases, the system approaches the dissociation limit of the molecular potential. In this near-threshold region the dynamics become particularly sensitive to the exact amount of deposited energy.

Close to the dissociation threshold the nuclear motion may remain temporarily trapped in the potential well before eventually escaping toward dissociation. This behaviour leads to long dissociation times and a strong trajectory-to-trajectory variability in the fragmentation dynamics. Such near-threshold behaviour has been discussed in theoretical studies of diatomic dissociation where the competition between vibrational motion and escape toward dissociation produces distinct dynamical regimes [6]. As a consequence, the transition from bound motion to fragmentation does not occur abruptly at a single energy value but rather through a gradual increase in dissociation probability.

Because of the complexity of real molecular systems, simplified model descriptions are often employed in order to isolate the fundamental physical mechanisms governing the dynamics. In particular, diatomic molecular ions provide a convenient reference system for studying the transition from bound vibrational motion to dissociation. Despite their structural simplicity, they capture the essential physics associated with bond stretching, anharmonic motion and the existence of a dissociation limit. The Morse potential offers a realistic representation of such behaviour and has therefore been widely used to model vibrational dynamics and dissociation processes in diatomic molecules [7, 8].

Within this framework, the present study focuses on the role of internal energy as the primary control parameter governing the fragmentation dynamics. By systematically varying the initial energy of the molecular ion, it becomes possible to identify the emergence of different dynamical regimes and to analyze the dependence of dissociation times and probabilities on the deposited energy.

DYNAMICAL MODEL AND NUMERICAL APPROACH

In order to investigate the influence of internal energy on fragmentation dynamics, we consider a simplified model system consisting of a diatomic molecular cation. Although real molecular systems involve many internal degrees of freedom, diatomic systems provide a convenient framework for studying the fundamental mechanisms governing bond stretching and dissociation. Their reduced dimensionality allows the nuclear motions to be analyzed in a transparent manner while retaining the essential physical features associated with anharmonic vibrational motion and the existence of a dissociation limit. In the present study the model is applied to the N^{2+} molecular ion, which serves as a representative diatomic benchmark system.

Analytical potential energy functions are widely used to describe the vibrational motion of diatomic molecules. Among them, Morse-type potential remains particularly useful due to their simplicity and ability to reproduce anharmonic vibrational spectra [9-13]. In the present model this interaction between the two nuclei is described using the Morse potential:

$$V(x) = D\left[1 - e^{-a(x-x_0)}\right]^2$$

where D is the dissociation energy, a determines the curvature of the potential well, and x_0 is the equilibrium bond distance. This potential provides a simple analytical representation of anharmonic molecular bonds and reproduces both vibrational motion near equilibrium and the asymptotic behavior associated with bond dissociation [9]. In the present work, the Morse potential is primarily used to explore how different values of internal energy drive the transition between bound vibrational motion and dissociative trajectories.

The nuclear motion is described within a classical framework where the internuclear coordinate evolves according to the forces derived from the potential energy surface. The primary electron impact ionization event is not treated explicitly. Instead, its effect is represented through controlled initialization of the internal energy of the molecular ion. In practice, the deposited energy is introduced by assigning an initial velocity to the internuclear coordinate while the initial bond distance is chosen close to the equilibrium position. By varying the magnitude of the initial velocity, different values of the total internal energy can be generated, allowing the dependence of fragmentation dynamics on the deposited energy to be systematically explored. The trajectories are propagated numerically and monitored in order to determine whether the molecular system remains in the bound vibrational regime or evolves toward dissociation. A trajectory is considered dissociative once the internuclear distance exceeds a predefined threshold value, providing a practical measure of fragmentation time for each simulated trajectory.

RESULTS

We begin by examining the dynamical behavior of the N^{2+} molecular ion for relatively low values of internal energy. In this regime the total energy of the system remains well below the dissociation limit of the potential energy surface, and the nuclear motion is confined within the potential well. The resulting trajectories correspond to bound vibrational motion around the equilibrium bond distance.

A representative example of such dynamics is shown in Figure 1, where the bond coordinate exhibits periodic oscillations characteristic of anharmonic vibrational motion in the Morse potential. The amplitude of the oscillation increases with increasing internal energy, but the system remains confined within the potential well and no dissociation occurs during the simulated time interval.

This behaviour reflects the fact that, for energies below the dissociation threshold, the molecular ion is dynamically stable and the internal energy is stored in vibrational motion of the bond coordinate. In this regime the nuclear dynamics are dominated by oscillatory motion around the equilibrium configuration, and the probability of fragmentation remains negligible.

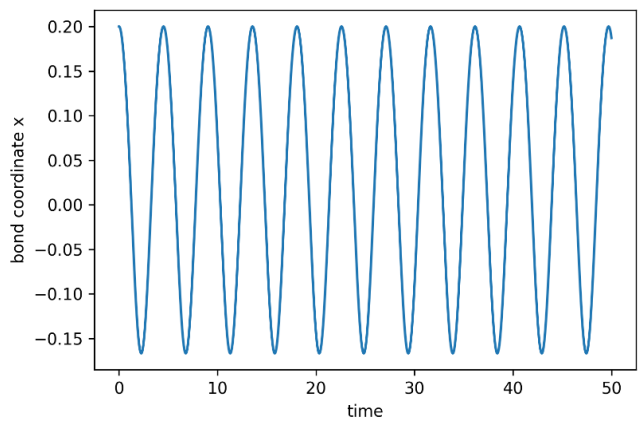


Figure 1. Bound vibrational motion of the diatomic molecular ion in the Morse potential for internal energy below the dissociation threshold. The internuclear distance oscillates around the equilibrium bond length, illustrating stable vibrational dynamics in the bound regime.

As the internal energy of the system approaches the dissociation limit of the potential, the dynamical behaviour changes qualitatively. For sufficiently large initial energies the molecular bond is no longer confined within the potential well and the trajectory eventually escapes toward dissociation. An example of such behaviour is illustrated in Figure 2, which shows the temporal evolution of the bond coordinate for a trajectory that undergoes dissociation. After an initial period

of vibrational motion within the potential well, the bond length increases rapidly and eventually exceeds the dissociation threshold distance defined in the numerical model. This transition marks the onset of fragmentation in the system. Once the internuclear distance becomes sufficiently large, the interaction between the fragments becomes negligible and the molecule can be considered dissociated. The time required to reach this threshold provides a convenient measure of the fragmentation dynamics.

A key objective of the present study is to investigate how the dissociation dynamics depend on the amount of internal energy deposited during the ionization event. To this end, simulations were performed for a range of initial energies and the dissociation time was determined for each trajectory. The resulting dependence of dissociation time on internal energy is shown in Figure 3. A clear trend can be observed: trajectories with higher internal energy tend to dissociate more rapidly, while those with energies close to the dissociation threshold exhibit significantly longer dissociation times. This behaviour can be understood in terms of the available excess energy above the dissociation limit. When the internal energy is only slightly above the threshold, the system may remain temporarily trapped within the potential well before eventually escaping toward dissociation. As the energy increases further, the potential barrier becomes easier to overcome and the dissociation process occurs more rapidly

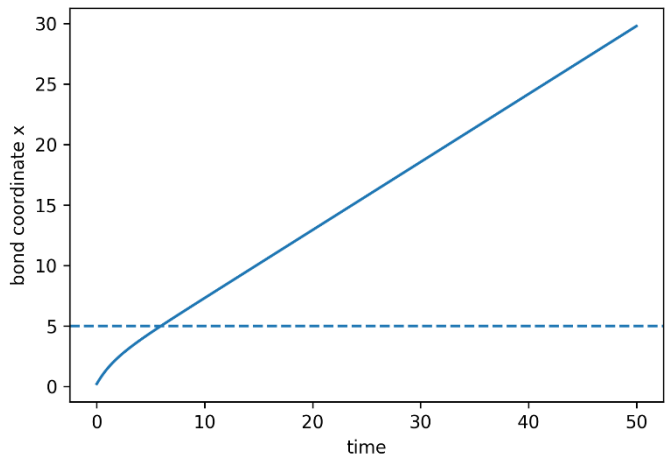


Figure 2. Representative dissociative trajectory for internal energy above the dissociation threshold. Following an initial period of bound vibrational motion, the internuclear distance increases rapidly and crosses the dissociation threshold (dashed horizontal line), indicating fragmentation of the molecular ion.

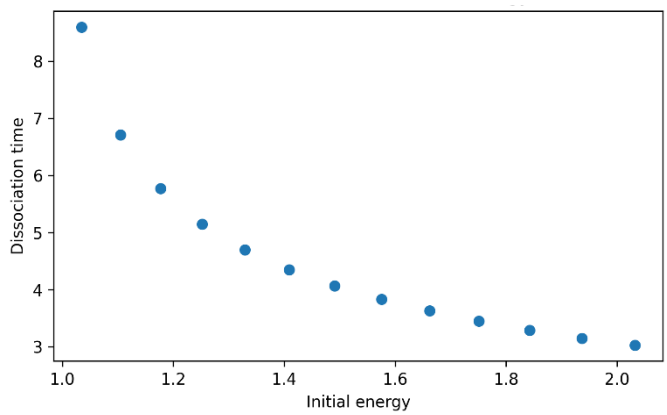


Figure 3. Dependence of the dissociation time on the initial internal energy of the molecular ion. Trajectories with energies close to the dissociation threshold exhibit significantly longer dissociation times, while higher energies lead to faster fragmentation.

In addition to individual dissociation trajectories, ensemble simulations provide information about the probability of fragmentation as a function of internal energy. For each selected energy value multiple trajectories were generated with small variations in the initial conditions, allowing the fraction of dissociative trajectories to be determined. The resulting dissociation probability is presented in Figure 4. For low internal energies the probability of dissociation is close to zero, indicating that the system remains in the bound vibrational regime. As the internal energy increases, the probability of fragmentation rises sharply and eventually approaches unity for sufficiently large energies.This behaviour reflects the existence of an effective dissociation threshold separating bound and dissociative dynamical regimes. Instead of a sharp transition at a single energy value, the onset of fragmentation occurs gradually over a finite energy interval due to the sensitivity of the dynamics to the exact initial conditions.

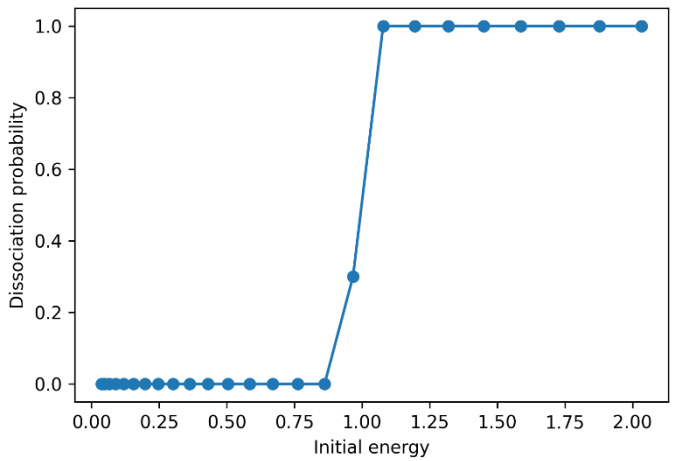


Figure 4. Dissociation probability as a function of internal energy obtained from ensemble simulations. The probability of fragmentation increases gradually as the internal energy approaches and exceeds the dissociation threshold, indicating a transition between bound and dissociative dynamical regimes.

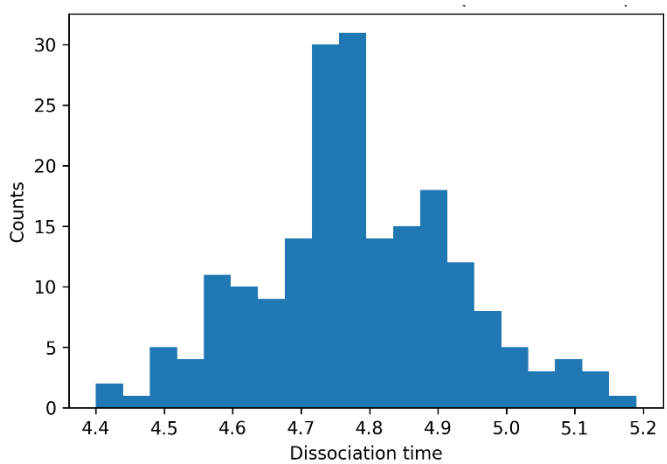


Figure 5. Distribution of dissociation times obtained from ensemble simulations in the near-threshold region. The broad distribution reflects the variability of fragmentation dynamics and the sensitivity of dissociation times to the initial conditions.

Additional insight into the fragmentation dynamics can be obtained by examining the statistical distribution of dissociation times for trajectories with energies close to the threshold region. In this regime the nuclear motion may remain confined within the potential well for extended periods before eventually escaping toward dissociation. The distribution of dissociation times obtained from ensemble simulations is shown in Figure 5. The histogram reveals a broad spread of dissociation times, indicating significant variability between different trajectories. Some trajectories dissociate relatively quickly, while others remain trapped within the potential well for longer times before fragmentation occurs. Such behavior is characteristic of near-threshold dynamical regimes, where the competition between vibrational motion and escape toward dissociation leads to complex trajectory-dependent dynamics. The presence of a wide distribution of dissociation times therefore reflects the sensitive dependence of the fragmentation process on the initial internal energy and the detailed structure of the potential energy surface.

DISCUSSION

The results obtained in the present simulations provide a clear picture of how the internal energy deposited during the ionization process governs the fragmentation dynamics of the molecular ion. The numerical experiments reveal the existence of distinct dynamical regimes that emerge as the internal energy approaches and exceeds the dissociation limit of the molecular potential. For internal energies well below the dissociation threshold the molecular ion remains dynamically stable and the nuclear motion is confined within the potential well. In this regime the system performs bound vibrational motion around the equilibrium bond length and no fragmentation occurs within the simulated time interval. The energy introduced into the system is therefore stored in vibrational excitation rather than being converted into dissociation.

As the internal energy increases toward the dissociation limit, the dynamics become increasingly sensitive to the precise value of the deposited energy. In this near-threshold regime the system may remain temporarily trapped within the potential well before eventually escaping toward dissociation. The numerical simulations show that trajectories with similar initial energies can exhibit significantly different dissociation times, leading to a broad distribution of fragmentation times observed in the ensemble simulations.

Such behaviour reflects the competition between vibrational motion and the gradual escape of the system toward the dissociation region of the potential energy surface. Instead of an immediate rupture of the bond, the system may undergo several oscillations before accumulating sufficient energy along the dissociative coordinate to overcome the effective barrier associated with the potential well. This mechanism naturally leads to the appearance of long dissociation times in the near-threshold region.

The ensemble simulations further demonstrate that the onset of fragmentation occurs over a finite interval of internal energies rather than at a single well-defined threshold value. The dissociation probability increases gradually as the internal energy rises above the dissociation limit. This behaviour reflects the intrinsic sensitivity of nonlinear dynamical systems to initial conditions and highlights the importance of statistical approaches when analysing fragmentation processes near the threshold.

Although the present model represents a simplified description of molecular fragmentation, it captures several essential features of energy-driven dissociation dynamics. In particular, the simulations reproduce the transition from bound vibrational motion to dissociative trajectories and reveal the strong dependence of fragmentation times on internal energy. These results illustrate how relatively simple dynamical models can provide valuable insight into the mechanisms governing fragmentation processes following electron-impact ionization.

Within the broader context of the ATMOLCOL project, such simplified dynamical descriptions can serve as a useful reference framework for interpreting experimental measurements of electron-induced fragmentation. While real molecular systems may involve additional degrees of freedom and more complex potential energy surfaces, the fundamental mechanisms identified here—energy-dependent dissociation thresholds and trajectory-dependent

fragmentation times—are expected to play an important role in a wide range of electron-molecule collision processes.

CONCLUSION

In this work we investigated how the internal energy deposited during electron-impact ionization influences the fragmentation dynamics of a diatomic molecular cation. The dynamical simulations indicate a transition between distinct regimes of motion depending on the available internal energy.

For energies below the dissociation limit, the molecular ion remains in bound vibrational states, while higher energies lead to dissociative trajectories. Near the threshold region the simulations show delayed fragmentation and a broad distribution of dissociation times, reflecting the sensitivity of the dynamics to the initial energy of the system. Although based on a simplified diatomic model, the present approach illustrates how controlled initialization of internal energy can be used to analyze energy dependent fragmentation dynamics. Such descriptions may provide a useful reference for interpreting electron impact induced molecular processes investigated within the ATMOLCOL framework.

Future work will focus on extending the present approach to more complex molecular systems and exploring how additional degrees of freedom influence the fragmentation dynamics and the associated dissociation thresholds.

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DECLARATIONS OF INTEREST STATEMENT

The authors affirm that there are no conflicts of interest to declare in relation to the research presented in this paper.

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