Energy Localization and Molecular Dissociation

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We study analytically as well as numerically the role that large-amplitude vibrations play during the process of molecular dissociation. Our model consists of a linear three-atom molecule composed of identical atoms interacting with their nearest neighbors by the Morse potentials. We find a close relation between energy localization and bond breaking and evaluate numerically the corresponding reaction paths.

I. INTRODUCTION

The familiar normal mode model has long been used to describe vibrations of polyatomic molecules. [1] As a zeroth-order description, it works well as long as the anharmonicity of molecular vibrations is negligibly small compared to harmonic vibrations. A general vibrational state of a given molecule can then be expressed as a superposition of normal-mode-vibrations, in terms of which the standard theory can be formulated both in classical and quantum levels. In a certain sense, normal coordinates extends over whole regions of molecules. Simplicity and transparency of situations in vibrational properties of molecules as well as solids cease to hold as soon as we enter into the regime where linearity as well as anharmonicity coexist. This regime must be handled through solving nonlinear equations of motion for the dynamics of atomic displacement in the classical level for which no general standard procedure exists. In the quantum level, anharmonicity is usually taken care of by employing perturbation-theoretic methods which are generally involved, giving different results for different cases.

On the other hand, a local mode (LM) model being counter-intuitive to the normal mode model was put forward in chemistry long time ago to explain the overtone absorption spectra of polyatomic molecules. [2], [3] It presumes the existence of vibrational modes in which the motion (and the energy) are more or less confined to a single bond. It has been argued that the local mode can exist even when they are embedded in a dense manifold of other vibrational modes, sometimes referred to as a "bath". In spite of its long history and accumulation of a wealth of spectroscopic data, the concept of the LM itself in chemistry appears to have remained in empirical or phenomenological stage.

It should be remarked in this connection that a concept somewhat similar to the local mode model in chemistry, viz. that of an intrinsic localized mode (ILM) or a discrete breather (DB), has been employed in solid state and mathematical physics since 1988 [4], [5], [6]. An ILM or DB is a time-periodic, spatially localized mode in "pure" nonlinear lattices for which many theories and numerical experiments have been developed [7]. In spite of extensive works on ILMs or DBs, little attention has been paid on the interrelationship between the ILM in physics and the LM in chemistry except for a few exceptional cases. It is the purpose of this paper to apply the concept of the ILM to molecular vibrations with a spirit entirely different from that in chemistry. We are concerned with formulating a non-perturbative theory of anharmonic molecular vibrations from first principles and performing numerical calculations to solve coupled nonlinear differential equations. Our particular concern in doing this is to explore general principles for large-amplitude molecular vibrations leading eventually to molecular dissociation. To achieve our objective, we confine ourselves to a very simplified model of a 3-atom molecule composed of linearly arranged identical atoms; Little is known about a model of this type in the physics community.

II. EQUATIONS OF MOTION AND BOND ENERGY

We consider vibrations of a linear molecule composed of three identical atoms A, B, C with atomic mass m. Let the displacement of the A, B, and C atoms from their equilibrium position be u_1, u_2 and u_3, respectively. We assume that each atom interacts only with its nearest neighbors. The interatomic potential between the A and B atoms, U_1, and that between the B and C atoms, U_2 is taken to be of the form

$$U_1 \equiv U_1(|u_1 - u_2|), \qquad U_2 \equiv U_2(|u_2 - u_3|) \tag{1}$$

Here an explicit expression for the U_i $(i = 1, 2)$'s is chosen as the Morse potential, i.e.

$$U_i(|u_i - u_{i+1}|) = D_i(1 - \exp[-a_i|u_i - u_{i+1}|])^2, \quad i = 1,2 \tag{2}$$

where D_i and a_i are constants. Equations of motion for the atoms in the molecule are then written in terms of the relative displacements

$$x_1 = u_1 - u_2, \qquad x_2 = u_3 - u_2 \tag{3}$$

as

$$\ddot{x}_1 = -\frac{1}{\mu}\frac{dU_1(x_1)}{dx_1} - \frac{1}{m}\frac{dU_2(x_2)}{dx_2} \quad \text{(oscillator 1)} \tag{4}$$

$$\ddot{x}_2 = -\frac{1}{m}\frac{dU_1(x_1)}{dx_1} - \frac{1}{\mu}\frac{dU_2(x_2)}{dx_2}, \quad \text{(oscillator 2)} \tag{5}$$

where $\mu = m/2$ is the reduced mass. Under the nearest neighbor approximation, we have reduced our three-body problem to a pair of coupled nonlinear differential equations, Eqs. (4) and (5), that are generally non-integrable. We introduce the bond energy for the bond A-B (B-C) referring to x_1 (x_2) by the equation

$$h_i = \frac{\mu}{2}\dot{x}_i^2 + U_i(x_i) \equiv h_i(t) \quad (i = 1,\ 2) \tag{6}$$

Equation for x_i, when multiplied by the factor $\dot{x}_i$ $(i = 1,2)$, yields

$$\frac{dh_1}{dt} = -\frac{\mu}{m}\frac{dU_2(x_2)}{dx_2}\frac{dx_1}{dt} = \frac{\mu}{m}F_2\dot{x}_1 \quad \text{or} \quad h_1 = \frac{\mu}{m}\int F_2 dx_1 \tag{7}$$

$$\frac{dh_2}{dt} = -\frac{\mu}{m}\frac{dU_1(x_1)}{dx_1}\frac{dx_2}{dt} = \frac{\mu}{m}F_1\dot{x}_2 \quad \text{or} \quad h_2 = \frac{\mu}{m}\int F_1 dx_2 \tag{8}$$

where

$$F_i = -\frac{dU_i(x_i)}{dx_i} \quad (i = 1,2) \tag{9}$$

From Eqs.(7) and (8), we obtain

$$\dot{h}_1\dot{h}_2 = \frac{\mu^2}{m^2}\dot{U}_1\dot{U}_2 \tag{10}$$

Several formal results on the dynamical properties of the system can be obtained from Eq.(10). These are given below in succession:

1. *Identical oscillators*

If entirely the same initial condition is given to the oscillator 1 and the oscillator 2 governed by Eqs.(4) and (5), respectively, these two oscillators become identical. Dropping the subscripts for the quantities x_i, h_i, U_i, a_i, D_i $(i = 1,2)$, we then obtain

$$h(t) = \pm\frac{\mu}{m}U(t) \quad \text{or} \quad \ddot{x} = -\left(\frac{1}{\mu} \mp \frac{\mu}{m}\right)\frac{dU(x)}{dx} \tag{11}$$

Thus, the coupled nonlinear oscillator equations reduce to a pair of single Morse oscillator equations in which the coefficient of the Morse potential changes from c to $(1 + \frac{\mu}{m})c$.

2. A pair of uncoupled oscillators under fluctuating field

Equation (10) can be rewritten as

$$\frac{\dot{h}_1}{\frac{\mu}{m}\dot{U}_1} = \frac{\frac{\mu}{m}\dot{U}_2}{\dot{h}_2} \equiv f(t). \tag{12}$$

or

$$\dot{h}_1 - \frac{\mu}{m} f(t)\dot{U}_1 = 0 \quad \dot{h}_2 - \frac{\mu}{m}\frac{1}{f(t)}\dot{U}_2 = 0 \tag{13}$$

Equations (13) show that each of the oscillators 1 and 2 is under fluctuating force. In spite of being of separable form, they are non-integrable and intractable. In this case, we must go back to Eqs.(4) and (5).

3. Energy localization and bond breaking

We note that Eqs. (7) and (8) gives useful information on the relationship between the energy localization and bond breaking. Suppose that breaking of the bond B-C takes place at $t = t_0$. This implies that

$$\vec{F}_2 \quad \rightarrow 0 \qquad \text{as} \quad t \rightarrow \quad t_0 \tag{14}$$

Then, we obtain

$$h_2 \gg \; h_1 \qquad \text{as} \quad t \rightarrow \quad t_0 \tag{15}$$

Equation (15) shows that energy localization takes place is generally associated with bond breaking.

III. POTENTIAL ENERGY LANDSCAPE AND REACTION PATH

Let us introduce the two-dimensional potential function and the potential energy surface

$$U(x_1, x_2) = U_1(x_1) + U_2(x_2) \quad \text{and} \quad f(x_1, x_2) = U(x_1, x_2) - c = 0 \tag{16}$$

where c is a constant. Three-dimensional plot of the potential function $U(x_1, x_2)$ and the equi-potential energy line corresponding to various value of c in $f(x_1, x_2)$, the potential energy contour, referred here to as a potential energy landscape (PEL) are depicted in Fig.1 (three dimensional portrait as well as the projection onto the x_1, x_2 axes) for the specific values $a_1 = a_2 = D_1 = D_2 = 1$. The global properties of the contour is described by the existence of two kinds of curves, closed ones around the point (0,0) and open ones, the former and the latter being separated by a separatrix which is not shown here. It is seen that there exists two trenches starting from the bottom (0,0) of the potential function and running in parallel to the x_1-and x_2-axis, the former and the latter being perpendicular to the extrema (c,0) and (0,c) of the contour curves. Natural question here is: What is the trajectory of the representative point in our dynamical system which is defined as a locus of the two-dimensional phase-space point $(x_1(t), x_2(t))$ as t evolves, where $x_1(t)$ and $x_2(t)$ are solutions to Eqs.(4) and (5) for a given initial condition, respectively. By physical intuition, it is presumed that the trajectory tends to run along these two trenches as the amplitude of molecular vibrations get large. Such a trajectory may be considered as going eventually over to the reaction path associated with the chemical dissociation due to bond breaking; these paths are visible in Figure 1.

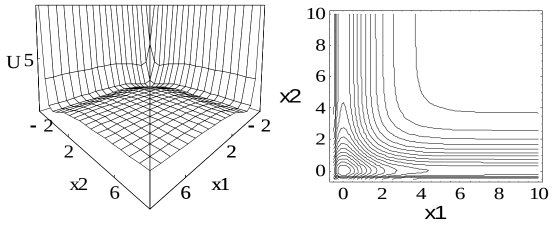


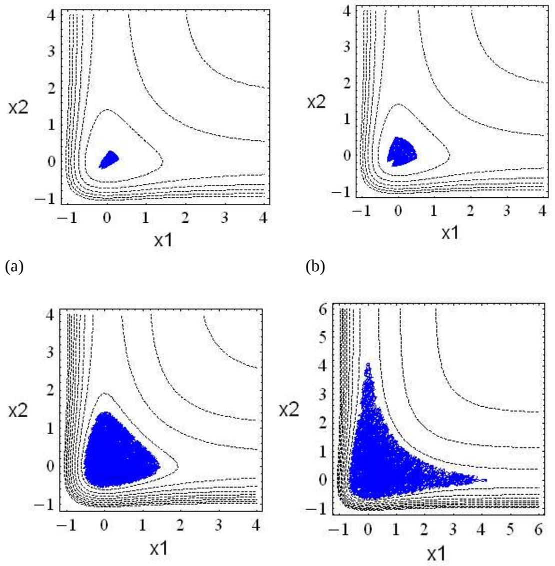
FIG. 1. Potential energy landscape for the linear three mass molecule. On the left the three dimensional structure is depicted while on the right we show the corresponding projection onto the two relative position coordinates x_1 and x_2 designated in the figures as $x1$ and $x2$ respectively. The dissociation trenches consist of the two paths parallel to the coordinate axes. The parameters used are $a_1 = a_2 = D_1 = D_2 = 1$.

IV. NUMERICAL CALCULATIONS

Keeping the above qualitative arguments in mind, we solved Eqs.(4) and (5) numerically by setting $a_1 = a_2 = D_1 = D_2 = 1$ under the initial condition

$$x_1(t=0) = x_2(t_0) = 0 \quad \text{and} \quad \dot{x}_1(t=0) = 0.5, \quad \dot{x}_2(t=0) = v, \tag{17}$$

taking v as a parameter. Our particular concern here is: (1) What are the general properties of the trajectory of the representative points $(x_1(t), x_2(t)$ and how they change as v increases. (2) How does the bond energy change as v increases and (3) whch orbits can be identified as reaction paths associated with bond breaking. Results of numerical calculations are shown in conjunction with the potential energy landscape $U(x_1, x_2)$ in Figures 2 and 3 for several specific cases. We classify the results into three typical groups designated respectively as type-I, II and III motions respectively. In Figure 2 we show the potential landscape projections for type-I motion with $v = 0.4$ (a), $v = 0.8$ (b), $v = 1.5$ (c) as well as type-II motion with $v = 1.9$ (d), while in Fig 3 we have type-III motion with $v = 1.935$ (a) and (III-2) $v = 1.95$ (b). It is seen that from case I (a) to (c) that the area covered by the trajectory around the origin at $(0, 0)$ changes from a cross section of a cone lying along the (1,1)-direction to a domain which covers almost the whole region enclosed by a potential-energy contour. In the separating type-II case, the domain covered by the orbit tends to extends almost equally in the direction of the rays of the potential function. In type-III motion shown in Fig. 3, the trajectory elongates indefinitely along the x_2 direction, showing that breaking of bond 2 takes place. This line is identified as a reaction path. We conclude that the molecular orbits can be classified broadly into three cases, viz. (I), (II) and (III). It is only in the case (I) that the conventional normal mode concept holds, where energy are equally partitioned in the bond 1 and the bond 2 as exemplified by Fig. 4 for case (I).



(a) (b)

(c) (d)

FIG. 2. Molecular trajectories in the potential energy landscape of the linear three atom molecule for various initial relative velocities in bond 2. We show here two types of trajectories, viz. type I with (a) $v = 0.4$, (b) $v = 0.8$, (c) $v = 1.5$ as well as type II with (d) $v = 1.9$. Conventional normal mode theory applies only to type I trajectories corresponding to fast exchanges between the two oscillators. The type-II trajectory delimits the separation between the stable linearized energy exchange between the oscillators and the unbounded motion.

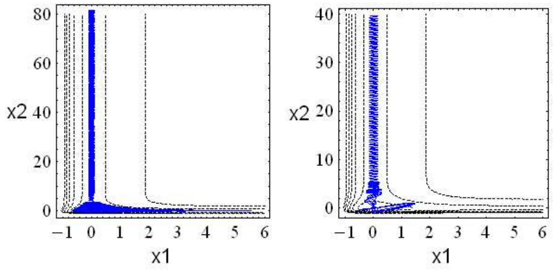


FIG. 3. Molecular trajectories in the potential energy landscape for unbounded motion leading to bond breaking and dissociation. Type-III motion with $v = 1.935$ (left panel) and $v = 1.95$ (right panel).

We are now concerned with seeking general principles, if any, in the bond breaking process. Prior to this, let us first investigate more closely the vibrational properties from the point of view of the energy exchange. In Figure 4 we show the energy quantities $h_1(t)$ and $h_2(t)$ as a function of time for the various cases discussed previously. In Fig. 4 we have type-I (top and bottom figures on lhs) and type-II (top and bottom figures on rhs) motion; the first pair clearly shows a rapid energy exchange between the bonds, as expected by the analysis done previously. For type-II motion we display the quantities $h_1(t), h_2(t)$ for $1250 \geq t \geq 1300$ and observe, in contrast to the type-I regime energy localization in each bond that is subsequently transfered to the other one. The process of energy exchange proceeds now in ”packets” and not in the continuous manner of the type-I linearized motion. This process of exchange of localized energy between the bonds continues indefinitely and, as a result, we may consider this case as the pre-bond breaking regime. A critical value v_c of v above which bond breaking takes place is given by $v_c \approx 1.92$. For v slightly larger than v_c, a very small change in the value of v induces alternation of the breaking at bond 1 and bond 2. In this sense, type-II motion may be related to a quasi-chaotic regime. As v increases further, the system goes over to type-III motion displayed in Figure 5. From the numerical calculation of $h_1(t)$ and $h_2(t)$ we observe that bond 2 breaks definitely even though almost complete transfer of energy from bond 2 to bond 1 may take place. These bouncing exchanges become less pronounced as v and thus the initial energy increases. Physically, breaking of a bond in chemical dissociation is equivalent to transition from bounded motion to unbounded one. In the latter case equipartition of the system energy between kinetic energy and the potential energy breaks down and almost all system energy is transformed into potential energy localized in the breaking bond. This accumulation of potential energy in bond 2 at the expense of kinetic energies and potential energy in bond 1 leads to molecular dissociation.

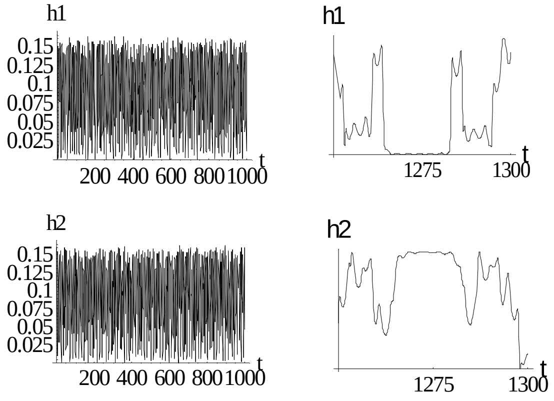


FIG. 4. Total energies $h_1(t)$ and $h_2(t)$ accumulated in each bond as a function of time. The left two plots correspond to type-I motion ($v = 0.8$) while the right two figures correspond to type-II, intermittent motion ($v = 1.9$). The continuous energy exchange seen in the linearized regime is sharply contrasted by the intermittent predissociation exchange in type-II motion.

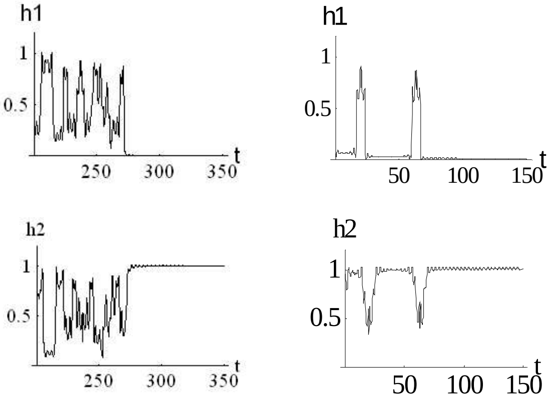


FIG. 5. Total energies $h_1(t)$ and $h_2(t)$ accumulated in each bond as a function of time for type-III motion. The left panels correspond to $v = 1.935$ while the right panels to $v = 1.5$. Dissociation occurs after initial energy localization and exchange of the localized energy between the two bonds. As initial energy increases, bond breaking occurs faster and with less or eventually no exchange of the localized energy.

V. CONCLUDING REMARKS

In this work we studied analytically and numerically classical vibrational states of a linear three-atom molecule composed of three identical atoms in mutual interaction via Morse potentials. Our emphasis was to understand the onset of molecular dissociation and isolate general mechanisms that lead to it. Due to the large parameter space of the problem, we focused on a specific set of initial conditions where one of the two bonds is initially at rest while the second acquires a variable initial kinetic energy. We found three vibrational regimes of which the lowest energy one does not lead to dissociation; in this regime the masses vibrate around the stable bond lengths with linear or quasilinear oscillations and with energy exchanged in a continuous fashion between the bonds. The second regime is more interesting and leads to intermittent bond oscillations that proceed through initial bond energy accumulation while the resulting transfer is not continuously varying as in the type-I motion. This dynamical vibrational state of the molecule can be seen as a chaotic pre-dissociation regime. Further increase of bond energy takes us to the third regime where there is a transition from bounded to unbounded motion associated with the breakdown of the Louiville theorem. Dissociation occurs then through system energy concentration to potential energy of a given bond at the expense of kinetic energy. Numerics show large bond openings accompanied by some type of resonant transfer of this accumulated energy between the bonds that is somehow reminiscent of targeted energy transfer [8]. This resonant energy accumulation and exchange may take place for a substantially long time before leading to molecular dissociation. This process is clearly dependent on the initial bond energy; as the initial kinetic energy becomes larger, localized energy oscillations become less frequent leading to an almost instantaneous bond breaking at very large initial energies.

Even though the system we studied is small, we found that the dynamics is quite rich and that molecular dissociation may proceed via energy accumulation and localization in a given bond and subsequent resonant energy exchange between the bonds. Although it would be interesting to find specific precursors to dissociation, as discussed in the melting of solids [9,10], such precursors were hard to quantify in the present study. Furthermore, it would be interesting to connect the specific process for dissociation through energy accumulation and transfer found here with applications of dynamical systems approaches to dissociation [11]. These issues as well as corresponding processes in larger molecules will be left for a subsequent study.

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