HEAVY MASS BARRIER TO INTRAMOLECULAR ENERGY TRANSFER ☆

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The dynamics of a collection of seven Morse or harmonic oscillators are investigated to model a molecule in which two halves are separated by a heavy atom. The results are related to a recent experiment on intramolecular dynamics and suggest an extension of the anharmonic local mode concept to groups.

1. Introduction

Recently, in an interesting experiment with atomic fluorine and tetrallyl tin, Rogers et al. [1] studied a chemical activation leading to dissociation into CH_2=CHF with retention of the Sn–C bonds. The authors reported that the lifetime of the vibrationally-excited intermediate was consistent with an RRKM molecule involving only one of the carbon chains rather than all four. The time scale of the experiment was ≈1 ns. Thus, the heavy tin atom appeared to block the transmission of vibrational energy from the chemically activated allyl to the other allyls. In the present note preliminary calculations on this effect are described and some of the underlying theory discussed.

The effect of a heavy mass (carbon for example) on isolating the motion of hydrogens in triatomic (e.g. H_2O), tetrahedral (e.g. CH_4) and other molecules is well known, both from experiment and theory [2–4]. The effect occurs particularly when the excitation is to a state where the instantaneous distribution of energy between the equivalent bonds is very uneven. From such experiments the "local mode" concept for CH and OH vibrations has become well established. In this letter this concept is extended to "local group modes", wherein the motion of a collection of atoms is localized on a group of bonds rather than just one.

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2. Calculations

We have made for this preliminary report classical trajectory calculations for a linear chain C–C–C–Sn–C–C–C, where the carbon bonds and carbon–tin bonds are Morse oscillators, and where there are bond–bond momentum cross terms. In the center of mass system of internal coordinates r_i the hamiltonian used was

$$H = \frac{1}{2}\sum_{i,j=1}^{6} G_{ij}p_ip_j + \sum_{i=1}^{6} V_i(r_i)\,, \qquad (1)$$

where $V_i(r_i)$ is the Morse potential, $D_i\{1-\exp[a(r_i - r_i^e)]\}^2$, r_i^e being the equilibrium value of r_i. For convenience all D_i were taken as equal. The parameters used were D_i = 0.134 au (84.1 kcal mole^{-1}), a = 0.815 au^{-1} (1.54 Å^{-1}), r_e = 2.91 au (1.54 Å).

The Wilson G matrix elements G_{ij} were obtained in a straightforward way [5]. With an energy in the first bond initially of $\frac{1}{3}D_i$ and with a zero-point energy in the remaining bonds, the results in fig. 1 were obtained for the energy of the left- and right-hand portions of the molecule. The energy of the left portion includes the i,j = 1 to 3 terms in eq. (1), while the right portion includes the i,j = 4 to 6. (The G_{34} momentum cross term, which is small for figs. 1 and 2, is not assigned to either left or right.) The calculation was made for 400 vibrational periods, one period being that of the Morse oscillator at zero energy and with a reduced mass of the isolated first bond.

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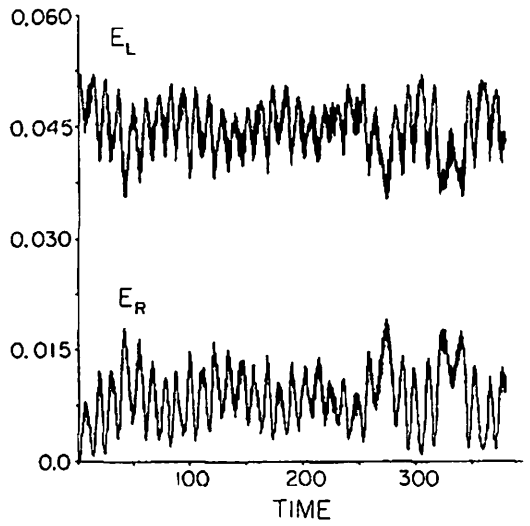

Fig. 1. Energy E_L and E_R in left- and right-hand portion of the molecule versus time, respectively. Initial energy in the first bond E_1 is $\frac{1}{3} D_i$ with zero-point energy in all other bonds. The energy units are au.

When a much smaller amount of energy was initially placed in the left-hand side the results in fig. 2 were obtained. To test a possible explanation of this marked difference between figs. 1 and 2, a calculation was made where the Morse oscillators in eq. (1) were replaced by harmonic oscillators whose force constants equalled those of Morse oscillators at zero energy. The results are given in fig. 3. The effect of mass is seen in fig. 4, where the conditions are the same as in fig. 1, except that the mass of the tin is reduced by one half.

The transfer is also dependent on the C–Sn–C bond angle. The bond is tetrahedral rather than linear,

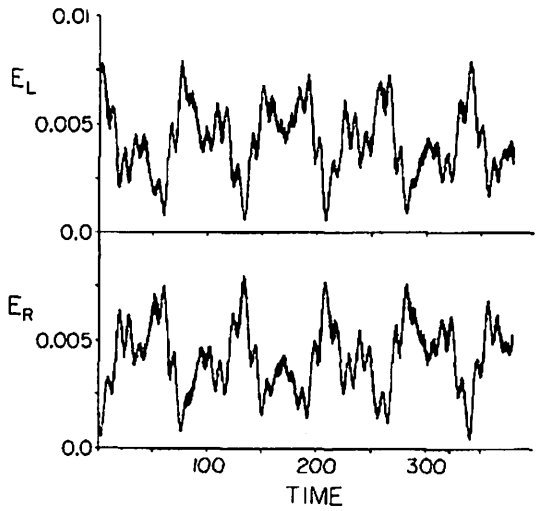

Fig. 2. Same as fig. 1 but with $E_1 = 0.05\, D_i$ (bond quantum ≈ 2).

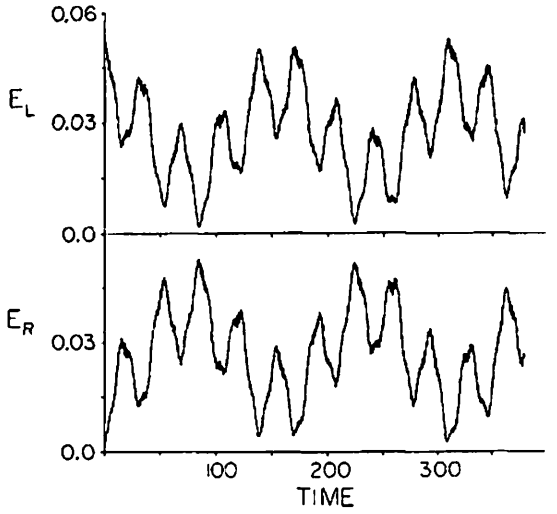

Fig. 3. Same as fig. 1, but with Morse oscillators replaced by harmonic oscillators, each with a force constant given by the Morse oscillator at zero energy.

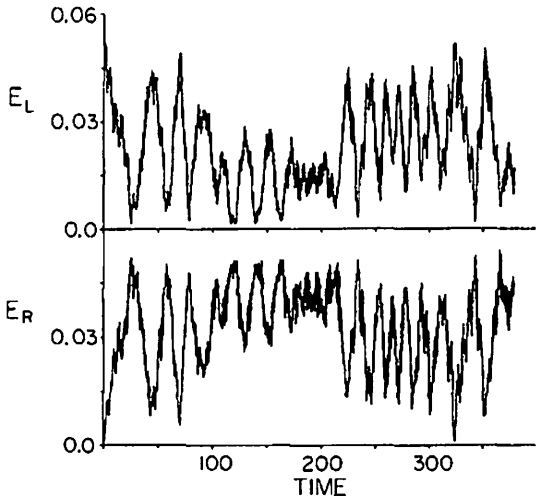

Fig. 4. Same as fig. 1, with mass of Sn decreased by a factor of two.

and the effect on G_{34} is to introduce a cosine term which makes the effective mass of the tin three times as great. When the calculations in fig. 1 were replaced by those with G_{34} containing this cosine term, the average energy in the right-hand side was less than that on the left-hand side by a factor of ten or more.

3. Discussion

The results in fig. 1, as contrasted with those in fig. 2, show the considerable inhibition towards energy transfer through the heavy mass when the initial energy in the left portion is large, even after 400 vibration-

al periods. Energy redistribution among the bonds on the left occurred, in contrast, in a few vibrational periods.

An explanation of the difference between figs. 1 and 2 is provided by the mismatch in the effective frequency (not the fundamental frequency at zero energy), which occurs when one half of the anharmonic C–C–C–Sn–C–C–C molecule has a much higher vibrational energy than the other. It is reflected in the shape of the potential energy contours at high and at low potential energy. Analogous effects occur in the two-oscillator problem [3] and for tetrahedral molecules [4] (judged by the small splitting of symmetric and antisymmetric quantum mechanical energy levels). Our previous results are in agreement with the importance of near-commensurabilities in influencing intramolecular energy transfer [6]. The harmonic oscillator calculations of fig. 3 further support this view: Because of the commensurabilities of vibration frequencies for left and right there was a complete transfer of energy. In collaboration with D. Noid trajectories for fig. 1 with extremely long times are being planned. The regular nature of the motion (perhaps quasi-periodic) suggests that the stability of this state of classical motion might continue for considerably longer times. Indefinitely?

Another source of energy transfer from one side of the molecule to the other is quantum mechanical tunneling. In the case of CH_4 (where the mass ratio is roughly that of Sn/C) the calculated splitting of the symmetric and antisymmetric vibrations was 0.3 cm^{-1} in the state in which the CH has five quanta and the others none [denoted here by (5,0)] (and 0.1 cm^{-1} for $^{13}CH_4$), indicating a calculated energy transfer time of the order of 0.1 ns [4]. (In contrast, in the (2,0) state the splitting was 35 cm^{-1} [4].) Thus, a wave packet of this width with excitation initially localized in one bond as (5,0) would take a time of order of magnitude of 0.1 ns for delocalization. We are currently undertaking quantum mechanical calculations for the present system.

Because of the smallness of the momentum–momentum C–Sn–C coupling term G_{34}, the intramolecular energy transfer can also be treated via perturbation theory, using an "exact" treatment of the separated halves as a starting point. This treatment represents an extension to "group local modes" of ideas previously employed for O–H, C–H and, in general, M–H local modes [3]. The quantization of the separated halves of the molecule can be made either via classical trajectories, by applying our recent 3-D (and 4-D) Poincaré surface of section technique [7], by a variational calculation, and by other methods. Work on this aspect is being undertaken, taking into consideration the actual energy distribution in the chemically activated portion of the molecule.

If verified by further experiments the results suggest a variety of more interesting experiments in the "mode selective" chemistry field. A more detailed report on this work will be presented elsewhere.

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