QUANTUM AND CLASSICAL ENERGY TRANSFER BETWEEN LIGANDS OF A HEAVY METAL ATOM

Steven M. LEDERMAN [a], Vicente LOPEZ [b], Gregory A. VOTH [a] and R.A. MARCUS [a]

[a] *Arthur Amos Noyes Laboratory of Chemical Physics* [1], *California Institute of Technology, Pasadena, CA 91125, USA*
[b] *Departamento Quimica Fisica y Quimica Cuantica, Universidad Autonoma de Madrid, Cantoblanco, 28049 Madrid, Spain*

Received 25 October 1985

Quantum and classical vibrational energy transfer between two ligands separated by a heavy atom are compared for a model system, one ligand being vibrationally excited initially and the other unexcited. Similarities and differences of quantum and classical results are noted. The approximate separability of certain modes simplifies the interpretation.

1. Introduction

There has been recent interest in the effect of a heavy central atom on intramolecular vibrational redistribution [1–5]. Experimental studies on some organometallic compounds have suggested that a heavy metal atom may reduce the energy transfer between the ligands [1], while in another study on a somewhat different system this effect was not observed [2]. Several classical trajectory calculations on models of ligand–metal atom systems have also been reported [3–5]. Studies were made for a non-bending seven-atom chain C–C–C–M–C–C–C [3], an analogous five-atom chain [5], and a much larger system [4]. Analytical results were given for the five-atom system (four coupled Morse oscillators) [5] and compared with trajectory results. A condition that the analysis be applicable or extendable to larger and hence more realistic molecular systems was also described [5].

Quantum and classical dynamical calculations are presented and compared here for the model system studied in ref. [5], the initial state in each case being that of excited "local group modes" described below. The initial classical states are chosen by a semiclassical procedure to permit a direct comparison with the quantum results. The methods used for the calculations are outlined in section 2 and the preliminary quantum and classical results for the model system are reported in section 3. In section 4 these results are discussed. Implications of the quantum–classical comparison for classical trajectory studies of unimolecular reactions are also noted.

2. Theory

We first recall several results obtained in our earlier study [5], where both the C–C–M–C–C system and the C–C–M subsystem were investigated. In this study the C–C bond in one ligand was initially excited (the other bonds had zero-point energy) and energy transfer to the other ligand was examined. The concept of anharmonic collective modes (local group modes) for the C–C–M subsystem was introduced. They were calculated using sixth-order Birkhoff–Gustavson perturbation theory, the unperturbed modes being the (harmonic) normal modes of the C–C–M subsystem. The resonant coupling of the C–C–M and M–C–C modes was then investigated analytically, supplementing the trajectory studies. The local group modes of the C–C–M ligand–metal subsystem were found to be of two quite different types. One such anharmonic group mode was largely, though not entirely, a ligand mode (termed the X mode). For the initial excitations studied it showed little energy transfer at moderate energies to the unexcited ligand but extensive exchange at low energies.

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[1] Contribution No. 7298.

The other (termed the Y mode) was primarily, though not entirely, a C–C versus M vibration. It showed extensive energy exchange with the Y mode of the other ligand in both energy regions.

There are a number of advantages in introducing these X and Y local group modes: (1) There is an approximate separation of variables for these two modes, even when they are coupled to X and Y modes in the second (M–C–C) subsystem [5]. This approximate separation arises because of a frequency gap of the X and Y modes, and occurs except near the "separatrix" of the X motion in C–C–M–C–C [5]. (2) They facilitate the comparison of classical and quantum results, as described later. (3) Their use in the quantum calculation itself is advantageous: Initial quantum calculations using states of local bond mode Morse oscillators, instead of local group mode oscillators, as the basis functions showed convergence difficulties due to the large kinetic coupling between the zeroth-order bond mode Morse oscillator states. To avoid this difficulty, the eigenstates for each subsystem, C–C–M and M–C–C, were first obtained by "prediagonalizing" the couplings in these two subsystems. The new states thus obtained correspond to various excitations of the two local group modes of C–C–M (and similarly for M–C–C). Next, symmetrical and antisymmetrical products of the eigenstates of C–C–M and M–C–C were used as elements of a basis set to represent the Hamiltonian of the total system, which includes the kinetic energy coupling of the two subsystems across the heavy mass M. In this way convergence was obtained more readily for the full system, compared with that when the bond mode basis set was used.

In the quantum calculations the initial non-stationary wavefunction was chosen to be the product of two local group mode wavefunctions, one for each subsystem, which was then propagated in time. The identity of each eigenstate of a subsystem was determined using a classical analysis for local group modes and semiclassical methods. The Hamiltonian and the molecular parameters used were those in ref. [5]:

$$H = \frac{1}{2}\sum_{i,j=1}^{4} g_{ij} p_i p_j + \sum_{i=1}^{4} D\{1 - \exp[-a(r_i - r_i^{e})]\}^2, \quad (1)$$

where the g_{ij} are the usual Wilson G-matrix elements [6] that couple adjacent bonds i and j. The Morse potential parameters are the same as those in refs. [3,5], the r_i are the bond distances and the p_i are their canonically conjugate momenta. From the eigenvalues and eigenvectors of the system C–C–M–C–C and a knowledge of the initial state, all determined as above, the expectation value of the energy in the excited subsystem, C–C–M, was then determined as a function of time. (The kinetic energy coupling term $g_{23}p_2p_3$ across the heavy mass was small and was not included in the energy of the C–C–M subsystem displayed in figs. 1–4.)

Classical trajectories were also calculated to compare with the quantum results. The adiabatic switching method [7] was used to prepare an initial classical state having the desired quantized anharmonic local group mode action variables for the C–C–M and M–C–C subsystems. These initial action variables correspond semiclassically to the initial local group mode quantum numbers of the two uncoupled subsystems in the quantum calculation. Results for the eigenvalues of C–C–M obtained in this way are given in section 3.

Because of the absence of degeneracies, the adiabatic switching method gave excellent results. In particular, the final C–C–M–C–C energy, after the adiabatic switching but before the $g_{23}p_2p_3$ term was introduced, was independent of the initial phase of the trajectory. An initial zeroth-order (harmonic) classical state before adiabatic switching consisted of some excitation of the normal modes of C–C–M (M–C–C) in a harmonic Hamiltonian and had specified action variables. It was used to prepare by adiabatic switching an actual group mode state of C–C–M (M–C–C) having the same action variables. (The fourth- or sixth-order perturbation theory had established earlier the correspondence between the harmonic states of C–C–M and those of the anharmonic C–C–M [5].) The adiabatic switching thus involved the slow conversion of the harmonic potentials to the Morse bond potentials to obtain the desired anharmonic group mode trajectories. Switching times of 50, 100 and 200 C–C vibrational periods (1.9, 3.8 and 7.6 ps) were used and gave essentially the same results for the eigenvalues. The 100-period switching time was used in the calculations reported below.

An ensemble of these trajectories, each prepared by adiabatic switching and having the same initial action variables and a random selection of the four initial phases for the harmonic system, was then used to calculate the ensuing dynamics. Only forty such trajectories were used for the present preliminary calculations in each case. The average energy in the C–C–M subsystem was then computed as a function of time after this C–M–C coupling was initiated.

3. Results

The initial excitation is denoted by (n_X^L, n_Y^L), where the n_X^L and n_Y^L denote the number of quanta in the X and Y group modes in the first subsystem (the "left subsystem") C–C–M. (This description of the states is the one used in table 2 of ref. [5].) The initial state assigned to the X and Y group modes in the second subsystem M–C–C was the ground state $[(n_X^R, n_Y^R) = (0,0)]$. Thus, the initial state of the entire system is a product of the (n_X^L, n_Y^L) state of C–C–M and the (0,0) state of M–C–C. In the figures the energy of the C–C–M in atomic units is plotted versus time in picoseconds. Results were obtained using initial C–C–M states of $(n_X^L, n_Y^L) = (4,0)$, (0,10), and (3,3).

We first report the results of the semiclassical quantization procedure used to identify the local group mode quantum numbers in the quantum calculations and to prepare the corresponding trajectories in the classical calculations. The semiclassical eigenvalues obtained by the adiabatic switching method for these states were 3923.16, 4067.60 and 4161.25 cm^{-1}, respectively, for energies in excess of the zero-point energy, while those obtained [5] by sixth-order Birkhoff–Gustavson perturbation theory were 3923.13, 4067.82 and 4161.34 cm^{-1}. The quantum mechanical eigenvalues which were closest to these semiclassical eigenvalues were 3923.21, 4067.42, and 4161.27 cm^{-1}, respectively [5], and this matching provided a simple identification of the local group mode quantum numbers of these states in the quantum mechanical calculations. The convergence of the quantum calculations themselves was tested by increasing the basis set for C–C–M–C–C from 1764 to 2500 basis functions, and no significant difference in eigenvalues, to twelve places, was found. In addition, no significant difference was found for the various expectation value plots in figs. 1–4.

The quantum and classical results for the C–C–M–C–C system with an initial state of (4,0) for C–C–M are given in fig. 1, and the quantum results for a longer time are given in fig. 2. This excitation represents one of an X-type group mode with a C–C–M energy of 0.021 au or 0.16 D. In figs. 1 and 2 it is seen that in the quantum case there is a periodic transfer of energy from one side of the molecule to the other. The corresponding classical results, also given in fig. 1, show no energy transfer.

In fig. 3 the energy of the C–C–M subsystem is

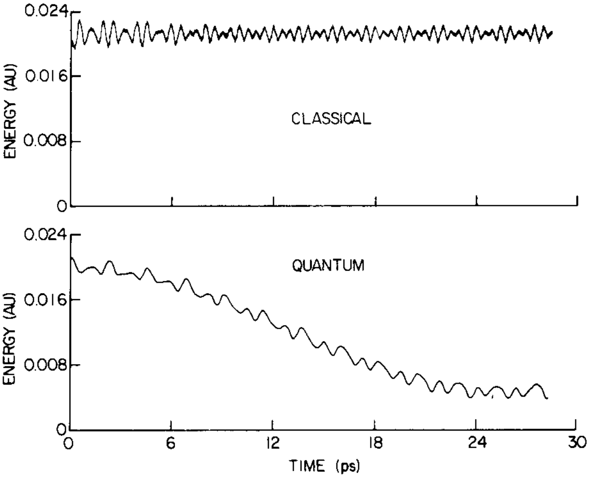

Fig. 1. Energy of C–C–M subsystem in C–C–M–C–C versus time, when the initial excitation is (4,0), and the M–C–C is initially in the state (0,0). Upper curve: classical. Lower curve: quantum.

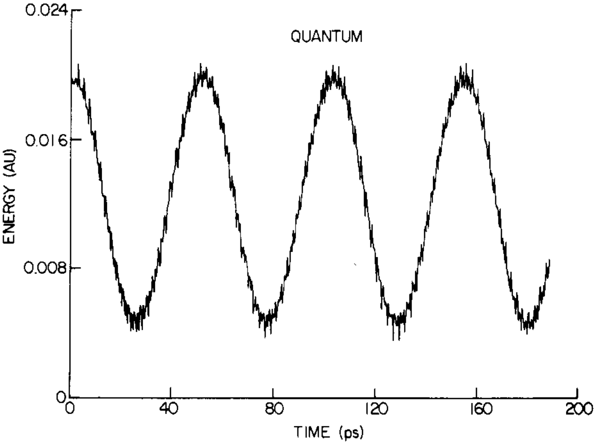

Fig. 2. Quantum results for conditions same as fig. 1 but plotted for a longer time.

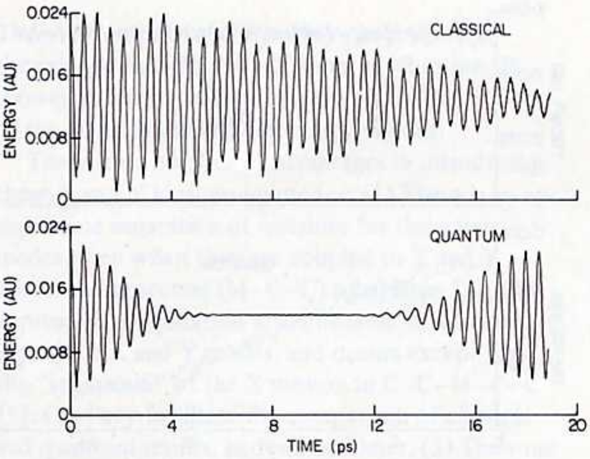

Fig. 3. Same as fig. 1 but for a (0,10) and (0,0) excitation of C–C–M and M–C–C, respectively.

plotted for an initial excitation of (0,10), which corresponds to the excitation of a Y-type group mode of C–C–M. The rate of transfer is much more rapid, both classically and quantum mechanically.

The time behavior of the energy of the C–C–M subsystem for an excitation of the initial state (3,3) is given in fig. 4. This state is a combination state of excited X- and Y-group modes, and shows a behavior characteristic of each (cf. figs. 2 and 3).

The mean energies $\langle H \rangle$ for the wavepackets describing the states with initial excitations of (4,0), (0,10) and (3,3) for C–C–M and (0,0) for M–C–C were calculated to be 2.44×10^{-2}, 2.50×10^{-2}, and 2.55×10^{-2} au, respectively. (H denotes the full Hamiltonian of C–C–M–C–C.) The root mean square deviation $(\langle H^2 \rangle - \langle H \rangle^2)^{1/2}$ of the energies of the initial wave packet was, in each case, relatively small, being 2.6×10^{-4}, 7.2×10^{-4}, and 4.5×10^{-4}, respectively.

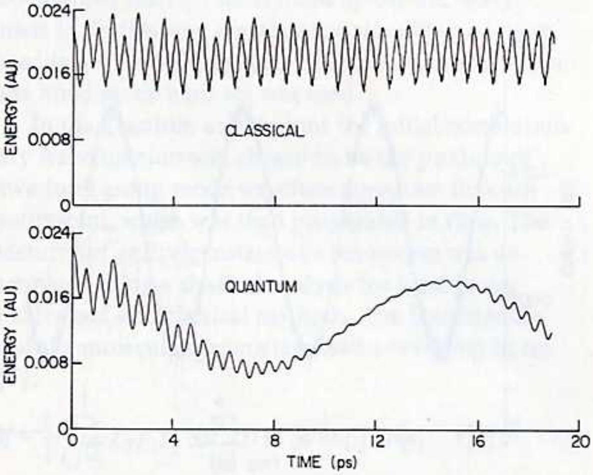

Fig. 4. Same as fig. 1 but for a (3,3) and (0,0) excitation of C–C–M and M–C–C, respectively.

4. Discussion

In the case of the excitation of the (4,0) state in fig. 1, no energy transfer occurs classically for the sample of trajectories used. In contrast, a periodic energy transfer (figs. 1 and 2) occurs quantum mechanically and is apparently due, therefore, to a classically forbidden process ("tunneling"). The period of the energy transfer is seen to be about 50 ps.

The behavior when the initial excitation is (0,10), namely of the Y mode, is seen in fig. 3 to be quite different, although the initial energy is approximately the same. The transfer of energy in both the classical and quantum cases occurs much more rapidly, each with the same period of about 0.5 ps for the high-frequency oscillation. This period agrees well with that computed numerically from the relatively simple classical resonance Hamiltonian derived using perturbation theory in ref. [5] (eq. (13)). The oscillation in energy of C–C–M is approximately from the initial excitation of the C–C–M subsystem to its zero-point energy and then back again. Also seen in the quantum plot in fig. 3 is a damping to a near-stationary value which corresponds to an equal energy on each side of the molecule. Subsequently the amplitude of oscillation again increases and ultimately the slow time behavior observed in this figure will repeat itself. A detailed comparison of the quantum and classical longer time behavior is not appropriate at this time, in virtue of the small sample of classical trajectories.

An initial excitation of the (3,3) state (fig. 4) yields a time dependence in the quantum case for the energy of the C–C–M subsystem whose qualitative appearance is that of a combination of that in figs. 2 and 3. It shows the rapid oscillations of energy found for a Y-mode excitation (fig. 3) and the slower oscillation seen for an X-mode excitation (fig. 2). The classical result itself does not show the slow energy oscillation found in the quantum result (nor did it for the

(4,0) case). The high-frequency oscillation is again similar for the two results. This behaviour for the (3,3) excitation, namely being approximately the superposition of that for the X-mode and for the Y-mode excitation, can be interpreted in terms of the approximate separation of variables used to analyze the classical results in ref. [5].

Further support for an approximate separation of variables in the energy regime examined in the present paper comes from a comparison of the quantum results with those obtained (but not cited in section 3) using smaller basis sets: To compare with the results for the (4,0) excitation in figs. 1 and 2, a basis set was used consisting purely of X-mode excitations for the left and right subsystems, and using the ground state for the Y mode. The results for the energy of C–C–M subsystem versus time were essentially the same as in fig. 2. Indeed, even a five-state basis set having $n_X^L + n_X^R = 4$ provided good agreement with this plot. A similar remark applies to an analogous calculation for an excitation of the (0,10) state in fig. 3 using purely Y-mode excitations and also such excitations with $n_Y^L + n_Y^R = 10$.

The lack of classical energy transfer when the X mode of C–C–M is excited, in contrast to the ready transfer when the Y mode is excited to about the same energy, was explained in ref. [5]: A classical resonance theory was described there and applied to those local group modes and to those of the M–C–C subsystem. The analysis also applies, semiclassically, to the quantum case. However, in the case of a high X-mode excitation, e.g., the (4,0) state, a classically forbidden transfer between two symmetrically related classical tori can occur and permits quantum mechanical energy transfer where it did not occur classically.

The present comparison of classical and quantum results also illustrates a potential shortcoming of classical trajectory calculations of unimolecular processes, a shortcoming sometimes overlooked in such studies when classical tori exist. In fig. 1 an example is given where there is essentially no energy transfer between two parts of a molecule classically (between two tori [5]), but there is a slow transfer quantum mechanically. In this way classical trajectories can give the appearance of less energy redistribution in an isolated molecule than would occur for a wave packet in a corresponding quantum mechanical and hence more realistic calculation. This type of behavior is well known for ABA triatomic systems [8].

If there is an approximate separation of the intraligand and metal–ligand modes in a real molecule (X and Y modes, respectively), energy localization in a ligand may be obtained by an appropriate excitation of the X modes. For example, in the case of alkyl ligands, the X modes would involve the stretching and bending modes of the ligand's carbon and hydrogen atoms. Excitation of X modes of a particular ligand can then be made either via a single-photon high C–H stretching overtone excitation or via an infrared multiphoton excitation of CH bends. (The other ligands could contain D atoms rather than H atoms, to reduce their absorption at the relevant frequencies.) These methods for exciting X modes are suitable, unless some overtone of the metal–ligand Y mode has sufficiently large absorption in the excitation range. It may also be noted that the shorter the excitation pulse, for a given total integrated intensity, the more likely that a localized excitation would cause the excited ligand to react before its energy decays by classical or tunneling processes to the remaining ligands. A direct excitation of the metal–ligand (Y mode) states is perhaps possible using a suitable laser, but would not be useful for the purpose of energy localization and subsequent reaction within one ligand. The main question to be resolved, of course, is whether the Y-mode states are, in real molecules, resonantly coupled to X-mode states, thereby eliminating any separability of the two types of motion.

A more detailed paper amplifying and extending the present results will be submitted for publication, including the extension to larger systems.

Acknowledgement

It is a pleasure to acknowledge the support of the National Science Foundation and of the US–Spain Committee for Scientific and Technological Cooperation. We would also like to acknowledge helpful discussions with Dr. Victor Fairen.

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