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Intramolecular vibrational dynamical barrier due to extremely irrational couplings*

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The intramolecular vibrational dynamics due to extremely irrational couplings is demonstrated by contrast to the resonance couplings, for the three-mode case of H_2O as an example. The extremely irrational couplings are shown to impose such strong hindrance to intramolecular vibrational relaxation (IVR) that they act as barriers. They restrict the direct action/energy transfer between the two stretching modes, though they allow the transfer between a stretching and a bending modes. In contrast, the resonance is more mediated by the bending mode and leads to chaotic IVR. It is also shown that there is a region in the dynamical space in which resonance and extremely irrational couplings coexist.

Keywords: intramolecular vibrational relaxation, extremely irrational couplings, resonance
PACC: 3425, 3120, 3115

1. Introduction

In nonstatistical intramolecular vibrational relaxation (IVR),[1,2] there are bottleneck barriers that block the energy transfer among the modes. Martens *et al*[3] have proposed that this is related to the extremely irrational ratios among the classical vibrational frequencies in their concept of frequency ratio space and resonance lines. The so-called extremely irrational numbers are $(\sqrt{5}-1)/2\pm$ integers. Hashimoto and Someda[4] have observed that IVR duration between the two O–H stretches (over 1 ps) is much longer than that between the stretch and bend (in 100 fs) in H_2O. This hints that direct vibrational energy flow between the two O–H stretches is hindered. In our previous work,[5,6] we have noticed that there is a region in the dynamical phase space in which resonance and barrier lines coexist. It was also shown that the overlapping of resonance lines is a region full of chaotic motion, in consistence with the famous Chirikov conjecture[7] that the overlapping of resonances will lead to chaos. Furthermore, the barrier region was shown[6] to be composed of periodic and/or quasiperiodic motions which, therefore, block the energy transfer.

In this paper, with the three-mode case of H_2O as an example, the detailed intramolecular dynamical properties due to extremely irrational couplings will be analysed. The physical significance will be emphasized that the barrier caused thereby is more on the energy flow between the two stretches, though they allow the transfer between a stretch and a bending. In contrast, the resonance is, more or less, mediated by the bending mode, i.e. through Fermi resonance. This will certainly lead to dynamical chaos, or statistical IVR. Along with this algorithm, we have first to introduce our algebraic approach.

2. The algebraic approach to the molecular vibrational dynamics

It has been proposed that there is spectroscopic Hamiltonian for the description of molecular vibrational dynamics.[8,9] The spectroscopic Hamiltonian is semi-empirical and is expressed in an algebraic form by the employment of the second quantization representation in which the occupation number and the creation and destruction operators are the basic ingredients. The merit is that when it is projected in the coset phase space,[10] the nonlinear dynamical characters of the molecular system can be well exposed in a classical way. Hence, the spectroscopic Hamiltonian is

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a nice tool to bridge between the quantal and classical aspects of the molecular vibrational dynamics. In the H_2O case, the spectroscopic Hamiltonian which considers the bond modes as Morse oscillators with 1:1 and 2:2 (Darling and Dennison) couplings between the two stretching modes and Fermi coupling among the stretching and bending modes is

$$\begin{aligned} H &= H_0 + H_r, \\ H_0 &= \omega_{\rm s}(n_{\rm s}+n_{\rm t}+1) + \omega_{\rm b}\Big(n_{\rm b}+\frac{1}{2}\Big) \\ &\quad + x_{\rm ss}\Big[\Big(n_{\rm s}+\frac{1}{2}\Big)^2 + \Big(n_{\rm t}+\frac{1}{2}\Big)^2\Big] \\ &\quad + x_{\rm bb}\Big(n_{\rm b}+\frac{1}{2}\Big)^2 + x_{\rm st}\Big(n_{\rm s}+\frac{1}{2}\Big)\Big(n_{\rm t}+\frac{1}{2}\Big) \\ &\quad + x_{\rm sb}(n_{\rm s}+n_{\rm t}+1)\Big(n_{\rm b}+\frac{1}{2}\Big), \\ H_{\rm r} &= K_{\rm st}(a_{\rm s}^{+}a_{\rm t} + {\rm h.c.}) + K_{\rm DD}(a_{\rm s}^{+}a_{\rm s}^{+}a_{\rm t}a_{\rm t} + {\rm h.c.}) \\ &\quad + K_{\rm F}(a_{\rm s}^{+}a_{\rm b}a_{\rm b} + a_{\rm t}^{+}a_{\rm b}a_{\rm b} + {\rm h.c.}), \end{aligned} \tag{1}$$

where the subscripts s, t and b refer to two H–O stretching and the bending modes, respectively; ω, x and K are the coefficients in the unit of $\rm cm^{-1}$. Also, n denotes the action, a^{+} and a are the creation and destruction operators, respectively. For this algebraic Hamiltonian, a matrix can be constructed by the basis states $|n_{\rm s}\rangle|n_{\rm t}\rangle|n_{\rm b}\rangle$. Then, the eigenvalues can be obtained for the fit to the level energies to elucidate the coefficients. This has been done[11,12] and are quoted here for reference: $\omega_{\rm s} = 3890.64$, $\omega_{\rm b} = 1645.25$, $x_{\rm ss} = -82.06$, $x_{\rm bb} = -16.18$, $x_{\rm st} = -13.27$, $x_{\rm sb} = -21.03$, $K_{\rm st} = -42.80$, $K_{\rm DD} = -0.19$, $K_{\rm F} = -14.58$. For this Hamiltonian, it is noted that $N = n_{\rm s} + n_{\rm t} + n_{\rm b}/2$ is a conserved quantity.

The spectroscopic Hamiltonian can be cast in a classical (coset) phase space representation by the Heisenberg correspondence.[13] The final results are obtained with the following replacements:

$$\begin{aligned} &n_{\rm s} = N - n_{\rm t} - n_{\rm b}/2, \quad n_{\rm t} = (q_{\rm t}^2 + p_{\rm t}^2)/2, \\ &n_{\rm b} = (q_{\rm b}^2 + p_{\rm b}^2)/2; \end{aligned} \tag{2}$$

and the coupling terms are

$$\begin{aligned} &K_{\rm st}(2n_{\rm s})^{1/2}q_{\rm t}, \quad K_{\rm DD}n_{\rm s}(q_{\rm t}^2 - p_{\rm t}^2), \\ &K_{\rm F}\{\sqrt{n_{\rm s}}(q_{\rm b}^2 - p_{\rm b}^2) + [q_{\rm t}(q_{\rm b}^2 - p_{\rm b}^2) + 2p_{\rm t}q_{\rm b}p_{\rm b}]/\sqrt{2}\}. \end{aligned} \tag{3}$$

This is a classical coset dynamical space for the quantum levels of the molecular system[9] with $(q_{\rm t}, p_{\rm t}, q_{\rm b}, p_{\rm b})$ as its coordinates. A point in this space corresponds to a vibrational configuration. The equations of motion are

$$\partial H/\partial p_\alpha = {\rm d}q_\alpha/{\rm d}t, \quad \partial H/\partial q_\alpha = -{\rm d}p_\alpha/{\rm d}t. \tag{4}$$

The coupling condition is defined by $K \cdot \omega_0 = 0$ with $\omega_0 = (\omega_{0\rm s}, \omega_{0\rm t}, \omega_{0\rm b})$ and $\omega_{0\alpha} = \partial H_0/\partial n_\alpha$. For the 1:1 and Fermi couplings, $K_1 = (1, -1, 0)$, and $K_2 = (1, 0, -2)$, $K_3 = (0, 1, -2)$. For the extremely irrational couplings, we will have $K_4 = (1, \gamma, -2(\gamma+1))$ and $K_5 = (1, \gamma+1, -2(\gamma+2))$ with $\gamma = (\sqrt{5}-1)/2$ for our analysis. This will be explained below.

3. Numerical analyses and results

Numerical calculation is of a precision up to the 15th digit after the decimal point. In numerical calculation, we set $|K \cdot \omega_0| \le 0.1$ and $N = 15$. For this action, the energy ranges from 38000 to 52000 $\rm cm^{-1}$, which is high enough. Of course, we may have a higher precision, but the time consumption is beyond our tolerance. In fact, we found that the analyses and conclusions based on either $|K \cdot \omega_0| \le 0.1$ or $|K \cdot \omega_0| \le 1.0$ are quite the same.

The three resonance lines in the action space due to K_1, K_2 and K_3 intersect at a point. From the intersection point, it can be assured that there are two coupling lines related to the extremely irrational numbers: $K_4 = (1, \gamma, -2(\gamma+1))$ and $K_5 = (1, \gamma+1, -2(\gamma+2))$ with $\gamma = (\sqrt{5}-1)/2$ that coincide with the intersection point. For short, they are called the barrier lines. This implies that there is a dynamical region in which both the chaotic and barrier motions coexist.[5] These lines and their intersection point in the action space are shown in Fig.1(a).

For dynamical study, we randomly take points from the resonance and barrier lines and follow their trajectories, evolutions of $\Delta\omega_0 = K_i \cdot \omega_0$ and actions as functions of time. For demonstration, only the situations resulting from two initial points in the resonance (K_1) and barrier (K_4) lines, respectively, are shown here. The demonstrations show the typical behaviours of the points in the resonance and barrier lines. The trajectories are shown in Figs.1(a) and 1(b), respectively. It is evident that the trajectories are strongly hindered by the barrier lines. The corresponding evolutions of $\Delta\omega_0$ are shown in Figs.1(c) and 1(d). The initial $\Delta\omega_0$ is zero in both cases. However, for the K_1 case (Fig.1(c)), $\Delta\omega_0$ can be positive and negative. This implies that the corresponding trajectory wanders around the resonance line, though limited by the

barrier lines, as shown in Fig.1(a). For the K_4 case (Fig.1(d)), $\Delta\omega_0$ can only be positive, showing that the corresponding trajectory is hindered as shown in Fig.1(b). Shown in Figs.1(e) and 1(f) are the temporal actions for these two cases. For the K_1 case (Fig.1(e)), action/energy can flow freely among the two stretches and bend modes. However, for the K_4 case (Fig.1(f)), action/energy can only transfer between a stretching and a bending modes. The hindrance to IVR is quite obvious.

The intersecting regions by the resonance and extremely irrational (barrier) couplings, respectively, deserve attention. That by K_1, K_2 and K_3 in the action space is shown in Fig.2(a) and that by K_4 and K_5 is shown in Fig.2(b). It is interesting to note that the region occupied by the resonances is elongated along the bending subspace (± 0.0014) which is about three-fold that in the stretching subspace (± 0.0005). The barrier region is orientated along the two stretching subspaces (± 0.0012) which is about two-fold that of the bending subspace (± 0.0007).

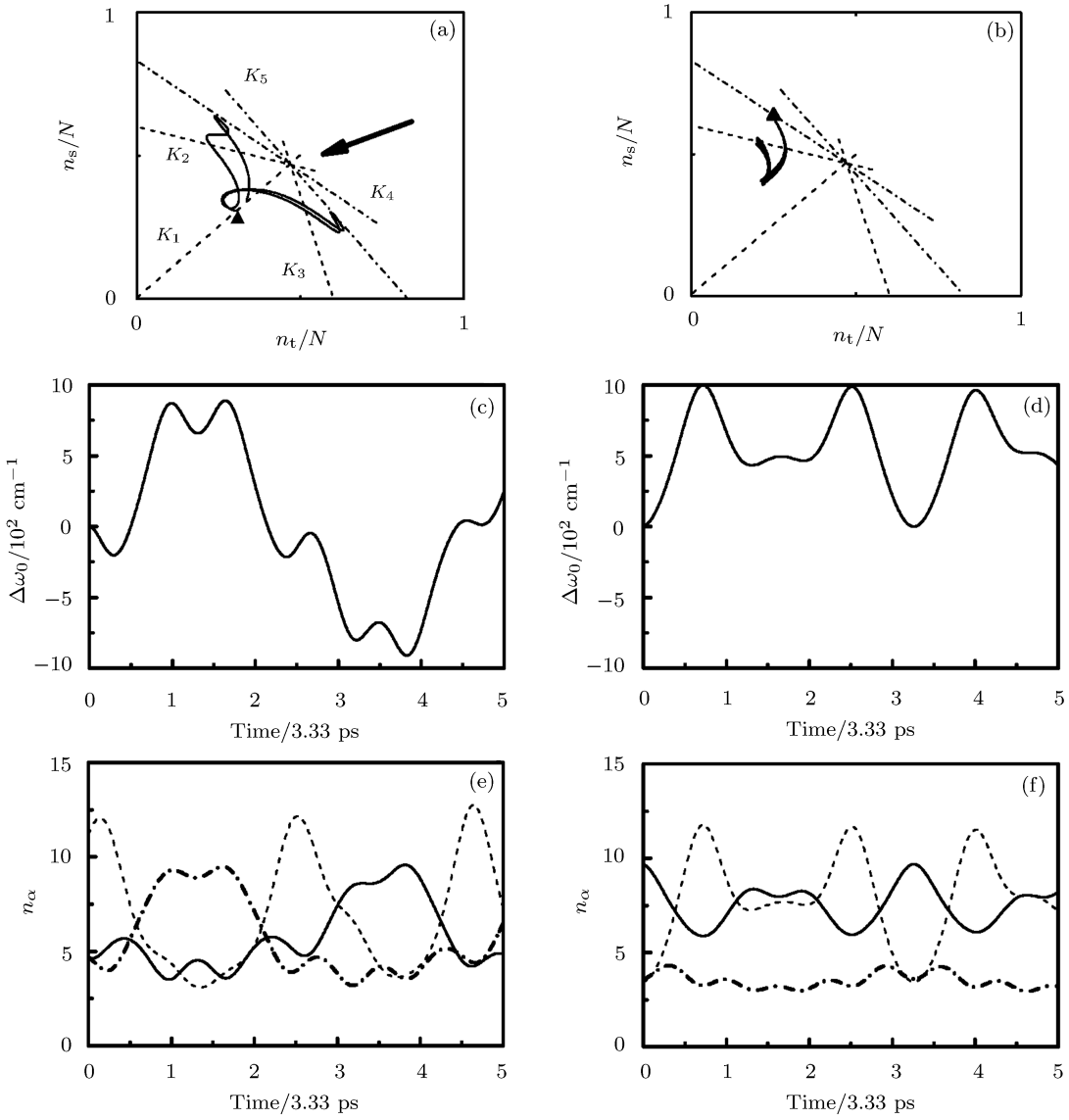


Fig.1. The intersection, indicated by the arrow, of the resonance (K_1, K_2 and K_3) and barrier (K_4 and K_5) lines due to extremely irrational numbers in the action space and the trajectories (the starting points are denoted by ▲) originating from (a) the resonance (K_1) and (b) barrier (K_4) lines. The duration is 16.65 ps. Their corresponding evolutions of $\Delta\omega_0 = K_i \cdot \omega_0$ and actions are shown, respectively, in (c), (e) and (d), (f). In (e) and (f), the solid, dashed and dot-dashed lines are n_s, n_b and n_t, respectively. See text for details.

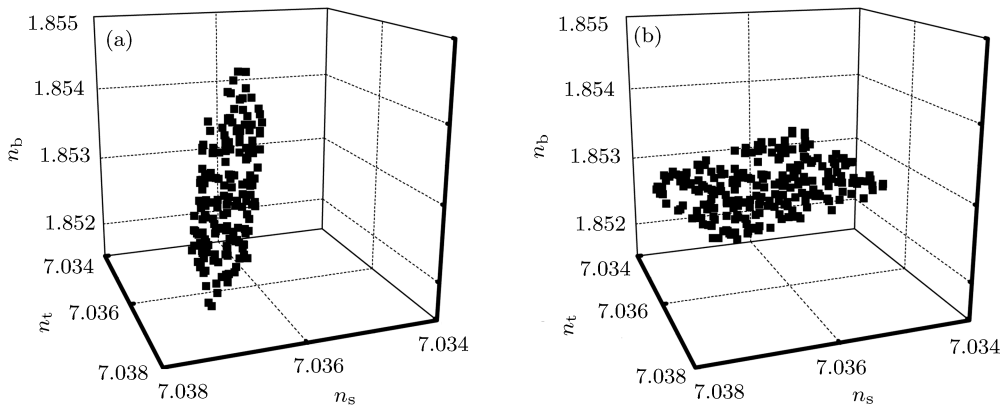


Fig.2. The intersecting regions, labelled by the black squares, (a) by the resonance (K_1, K_2 and K_3) and (b) by the extremely irrational (K_4 and K_5) couplings in the action space.

We have relaxed the condition from $|K \cdot \omega_0| \leq 0.1$ to $|K \cdot \omega_0| \leq 1.0$ and the above relative dimensions remain quite the same. This shows that the geometric shapes as shown above for both the resonance and barrier regions are believable. The physical implication/interpretation of the orientations of these two regions is that the resonance effect, which is prone to IVR, is mediated by the bending motion, while the hindrance by the barrier effect in this region is to suppress the growth of the bending action. Thus, it blocks IVR. From Fig.2, it is observed that there is overlapping between these two (resonance and barrier) regions. However, they are indeed two distinct spaces. Shown in Figs.3(a) and 3(b) are the two trajectories originating from these two spaces, respectively. Again, it is observed that the trajectory from the resonance space can wander more freely than that from the barrier space, which is rather restricted by the barrier lines as evidenced in the action space.

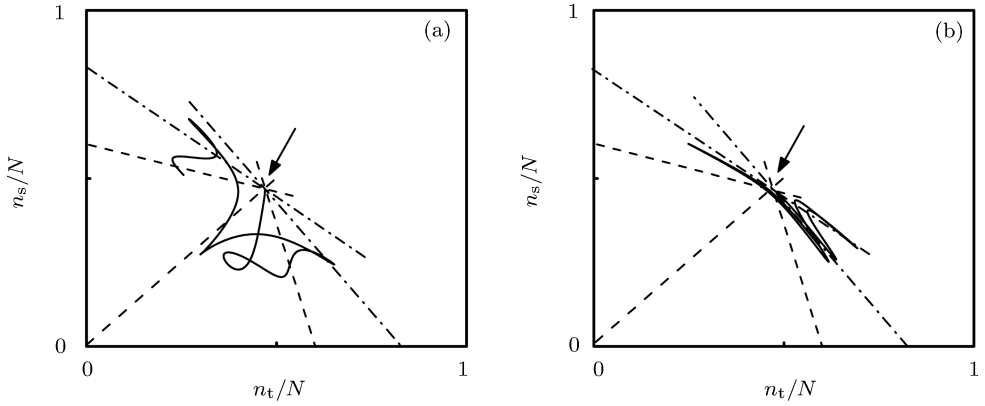


Fig.3. The two trajectories (the starting points are indicated by the arrows), originating from the intersecting regions, (a) by the resonance (K_1, K_2 and K_3) and (b) by the extremely irrational (K_4 and K_5) couplings, as shown in Fig.2.

4. Concluding remarks

The dynamics due to extremely irrational couplings is shown in contrast with that due to resonances, with the three-mode H_2O for the study. The main picture is that the irrational couplings impose hindrance to IVR and act as barriers. They block direct action/energy transfer between the two O–H stretches, though allow the transfer between a stretching and a bending motions. Resonance couplings which lead to chaos of IVR are mainly mediated by the bending mode. There is also a dynamical region in which resonance and extremely irrational couplings coexist.

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