Localized Vibration-Formation by Driving Raman Active Molecular Vibrations

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This paper presents a new approach to localize molecular vibrations. By analyzing YX₂ type molecules we show that localized vibrations can be created if we stimulate a set of the molecule’s Raman-active normal modes properly by lasers.

Key words: Localized Vibrational Mode; Raman-active Vibrations.

The study on local modes as a molecule’s eigen-vibrations is still an attracting topic [1, 2]. However, a new trend becomes more popular: people are more interested in the vibration properties of molecules under interactions with external laser fields for practical usages such as bond-selective photodesorption [3, 4] and vibrationally mediated dissociation [5–7]. We have already studied the possibility to create localized vibrations by using lasers [8]. Using quantum mechanics we have shown that a set of normal mode vibrational states can be mixed properly into a local mode [8], but we did not treat the molecular vibrational motion directly. In the present paper we consider concretely the couplings between lasers and molecular vibrations in order to solve the molecular vibrational motion problem. Taking YX₂ type molecules as an example, we deal with the vibrational motion directly in the classical picture of forced oscillations and illustrate how a localized vibration can be formed through stimulating a set of Raman-active normal modes by lasers.

In the classical picture, when a molecule is driven by lasers, the molecule may vibrate as forced oscillations. Here we analyze YX₂ (massX > massY) type molecules to explain our idea. We make the following assumptions:

1. The molecular oscillations are as harmonic. The eigen-vibrations of the molecule are normal mode vibrations. The vibrational energy is low.
2. The inter-bond couplings are included. They lift the degeneration existing in the set of vibrational states with the total vibrational quanta \( \nu_{\text{total}} = \text{const.} \); the inter-bond coupling parameters are \( \lambda_i \).
3. Bending vibrations are neglected.
4. Electric dipole interaction dominates in the molecule-laser system.

Hence, we have the following properties:

1. The frequency difference between the adjacent vibrational states in the same set of \( \nu_{\text{total}} \) (\( \nu_{\text{total}} = \text{const.} \)) is equal to 2 \( \lambda_i \) [9], as shown in Figure 1.
2. The molecule has two typical normal modes: the symmetric and asymmetric stretching vibrations. We treat the lowest excited vibrational states with \( \nu_{\text{total}} = 2 \). The normal mode coordinates are denoted as \( q_1 \) and \( q_2 \), as shown in the upper part of Figure 2. They are identified as \( A_1(z) \) and \( B_2(y) \), respectively. \( A_1 \) and \( B_2 \) stand for irreducible representations of the symmetry, while \( z \) and \( y \) denote the polarization directions of the vibrations. The quantum states corresponding to the two stretching vibrations are \( |10 \rangle \) and \( |101 \rangle \), respectively.

For our purpose of forming local modes, we propose a scheme which requires the following conditions:

1. The lasers stimulate vibrations which are Raman-active.
2. The excitations between the different electronic vibrational states are resonant.

With the assumptions and conditions above, the proof of the idea of forming local modes is quite straightforward. The lasers are treated as classical electromagnetic (EM) fields:

\[
E_i = E_{0i} \cos (\omega_{0i} t + \phi_{0i}), \quad i = 1, 2, 3 \ldots
\]  

(1)

Thus the forced oscillations of the molecule are described as

\[
\ddot{q}_i + \nu_i^2 q_i + \nu_{\text{inh}}^2 q_i = F_i(q_i, t), \quad i = 1, 2, 3
\]  

(2)

where \( \nu_{\text{inh}} \) are eigen-frequencies of the vibrations and \( \nu_i \) are decay coefficients. Based on the condition 1 we have

\[
F_i(q_i, t) = \left( \frac{\partial \alpha}{\partial q_i} \right)_{q_i} E^2(t),
\]  

(3)

where \( \alpha \) is the polarizability and \( \left( \frac{\partial \alpha}{\partial q_i} \right)_{q_i} \) the rate of \( \alpha \) with respect to the change in \( q_i \), evaluated normally at the equilibrium position. The lower part of Fig. 2 shows how the polarizability changes corresponding to the two stretching modes. Mode \( A_1 \) is a totally symmetric vibration;
The rate is non-vanishing, so it is Raman-active. Mode $B_1$ however, is normally Raman-inactive since the rate vanishes at the equilibrium position. But due to the condition 2, i.e., we excite this mode via different electronic states where a shift of equilibrium position occurs (see Fig. 1), our scheme takes advantage of Frank-Condon excitation, so that the rate is actually obtained at the shifted position $q_{1\omega'}$ (labeled in the lower part of Figure 2). It can be non-vanishing, too. Therefore we can still stimulate the $B_1$ mode by the Raman coupling mechanism.

By substituting (1) into (3) we have

$$F_i(q_i, t) = \xi_i(q_i) \cos(\Delta \omega t).$$

(4)

The approximation comes from neglecting the higher frequency terms because they do not affect the bond vibrations so much as the lower ones ($\omega_0(\text{field}) \gg \omega_{\text{vib}}(\text{molecule}) \gg \Delta \omega$). Because of resonance excitation, the beat of the applied lasers $\Delta \omega$ is equal to the frequency difference between the two normal frequencies, i.e., $2 \Delta \omega$.

The solutions of (2) are

$$q_i = \frac{\xi_i}{(\omega_{\text{vib}}^2 - \Delta \omega^2) - v_i \Delta \omega \tan \theta_i} \cos(\Delta \omega t + \theta_i)$$

$$= \xi_i \cos(\Delta \omega t + \theta_i),$$

$$\tan \theta_i = -\frac{v_i \Delta \omega}{\omega_{\text{vib}}^2 - \Delta \omega^2}, \quad (i = 1, 2).$$

(5)

Note that the forced vibration is of frequency $\Delta \omega$, which is neither the eigen-frequency of the molecular vibration nor the laser frequency. The molecule is vibrating at the frequency of the laser beat.

Since these two forced vibrations exist simultaneously, the actual motion of the molecule is their combination. If the parameters are carefully chosen so that $\xi_1 = \xi_2$, $\theta_1 = \theta_2$, then from (5) we have

$$r_a = (q_1 + q_2)/2 \approx \cos(\Delta \omega t + \theta);$$

$$r_b = (q_1 - q_2)/2 = 0.$$  

(6)

One single bond is vibrating while the other remains stationary: the combination of two normal modes, as shown in Fig. 2, is just the localized mode we want to prepare.

For the case $\nu_{\text{total}} > 2$ we require more lasers to “mix” more normal modes into a localized vibration. Understandably, the solution to get such a localized mode would be more complicated. But the principle presented here still holds.

In conclusion, with a simple classical mechanics treatment we have clearly shown that a local mode vibration can be produced through resonantly exciting a set of Raman active vibrational modes by lasers.

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