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 YX_2 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 Vibration.

The study on local modes as a molecule's eigen-vibration 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 creat 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 YX_2 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 YX_2 ($\text{mass}_Y \gg \text{mass}_X$) 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 λ_i.
3. Bending vibrations are neglected.
4. Electric dipole interation 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 ν_{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 $|01\rangle$, 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 our idea of forming local modes is quite straightforward. The lasers are treated as classical electromagnetic (EM) fields:

$$E_i = E_{0i} \cos(\omega_{0i}\, t + \phi_{0i}), \qquad i = 1, 2, 3 \ldots \tag{1}$$

Thus the forced oscillations of the molecule are described as

$$\ddot{q}_i + \nu_i\, \dot{q}_i + \omega_{vib_i}^2\, q_i = F_i(q_i, t), \qquad i = 1, 2, \tag{2}$$

where ω_{vib_i} are eigen-frequencies of the vibrations and ν_i are decay coefficients. Based on the condition 1 we have

$$F_i(q_i, t) = \left(\frac{\partial \alpha}{\partial q_i}\right)_{q_{i0}} E^2(t), \tag{3}$$

where α is the polarizability and $\left(\frac{\partial \alpha}{\partial q_i}\right)_{q_{i0}}$ the rate of α with respect to the change in q_i, evaluated normally at the equilibrium position. The lower part of Fig. 2 shows the polarizability changes corresponding to the two stretching modes. Mode A_1 is a totally symmetric vibration;

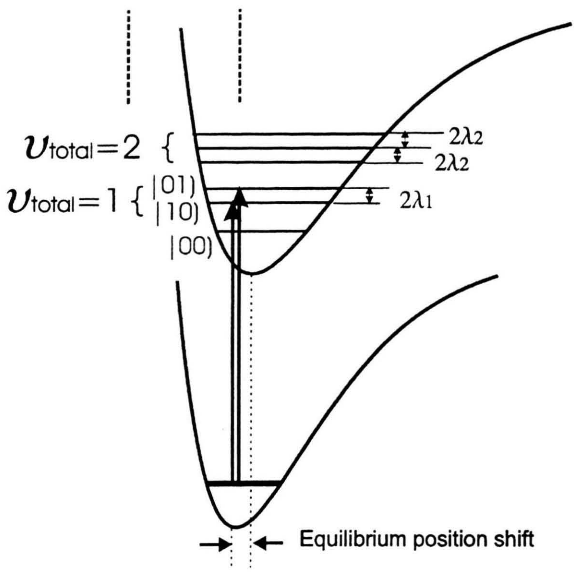

Fig. 1. The resonance excitations of electronic vibrational states.

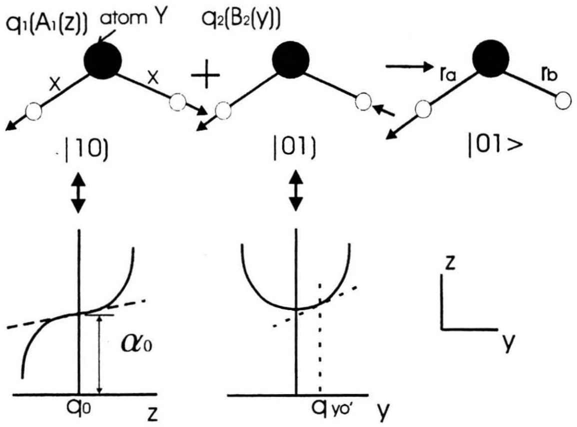

Fig. 2. Combination of two normal stretching vibration modes into a local mode of the YX_2 molecule.

the rate is non-vanishing, so it is Raman-active. Mode B_1 however, is normally Raman in-active 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-Conden excitation, so that the rate is actually obtained at the shifted position $q_{y0'}$ (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

$$F_i(q_i, t) \approx \xi_i(q_i) \cos(\Delta\omega t) . \tag{4}$$

The approximation comes from neglecting the higher frequency terms because they do not affect the bond vibrations so much as the lower ones (ω_{0i}(field)$\gg$ ω_{vib_i}(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., $2\lambda_i$.

The solutions of (2) are

$$\begin{aligned} q_i &= \frac{\xi_i}{(\omega_{vib_i}^2 - \Delta\omega^2) - \nu_i \, \Delta\omega \tan\theta_i} \cos(\Delta\omega t + \theta_i) \\ &= \zeta_i \cos(\Delta\omega t + \theta_i) , \\ \tan\theta_i &= -\frac{\nu_i \, \Delta\omega}{\omega_{vib_i}^2 - \Delta\omega^2} , \quad (i = 1, 2) . \end{aligned} \tag{5}$$

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 $\zeta_1 = \zeta_2$, $\theta_1 = \theta_2$, then from (5) we have

$$\begin{aligned} r_a &= (q_1 + q_2)/2 \propto \cos(\Delta\omega t + \theta) ; \\ r_b &= (q_1 - q_2)/2 = 0 . \end{aligned} \tag{6}$$

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 $v_{\text{total}} > 2$ 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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