Highly multiphoton molecular excitation by an intense laser pulse

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RESEARCH ARTICLE

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Multiphoton excitation of molecules by an intense laser field is treated. When the first excitation energy is much larger than both the photon energy and the transition energy between excited states, excited states are strongly coupled with each other by the photon, even though coupling with the ground state is weak. In such a case, a kind of collective excitation takes places, in which the excitation probability of every excited state is almost linear as functions of intensity on a log–log plot, and the slope is independent of the final state. By taking methane and formaldehyde as examples we numerically study this process.

Keywords: intense field; excitation; fragmentation

1. Introduction

When molecules are irradiated by an intense laser, various dynamical processes are induced. Examples are alignment [1], structural change [2], and ionization followed by high harmonic generation [3] and Coulomb explosion [4]. These processes have been studied for many years since the invention of high power lasers. Electronic excitation by an intense laser [5–7], however, has been studied much less intensively compared to the other processes such as ionization. This is mainly because electronic excitation is regarded to take places with only small probabilities. Most of the neutral molecules have excitation energy much larger than the photon energy of high power laser (1.55 eV is the typical photon energy). This means that electronic excitation of some molecules will require a large number of photons. In other words, characteristic time of electronic motion is faster than the optical frequency, which leads to the validity of adiabatic approximation. As is well known sufficiently intense laser field induces ionization even though adiabatic approximation is valid [8]. On the other hand, excitation can only take places with nonadiabatic effects.

Recently, there have been some studies, both experimentally and theoretically, to discuss the possibilities of excitation processes. Gibson has proposed a possible mechanism of high multiphoton excitation with (nearly) degenerated final states, in which the strong dipole coupling between the degenerated states plays an important role [9,10]. The theory is tested later experimentally showing the reality of this mechanism [11,12]. Kong *et al*. found neutral fragments from methane, ethylene, n-butane, and 1-butane, after irradiating intense laser pulse, indicating that multi-photon excitation to super excited states takes place [13].

In this paper, we report on studies of the multi-photon excitation of a system with many excited states in which the first excitation energy is much larger than both the photon energy and energy spacing among the excited states, schematically depicted in Figure 1. Gibson's model cannot be applied to this system because his model assumes small transition dipole moment between the ground and excited states and that excited states should be necessarily (nearly) degenerated so that Stark shift is negligible. In our system, on the other hand, these assumptions do not hold and Stark shift plays an important role. The basic mechanism of multiphoton excitation for this system is as follows: the number of photon required to excite

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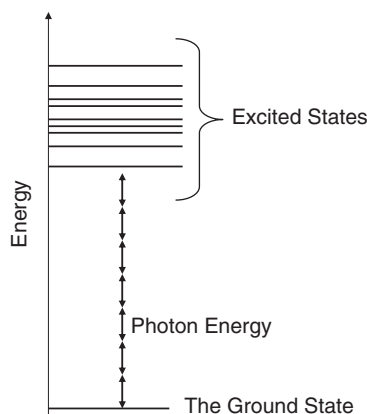*Corresponding author. Email: tera@gate.sinica.edu.tw

Figure 1. Schematic of the energy levels expected to show collective excitation. Here, the first excitation energy is much larger than both the photon energy and the energy spacing among the excited states.

from the ground state is much larger than that required for the transitions between excited states, indicating that the excited states are intensively coupled by photon forming Floquet states before the transition from the ground state takes place. Due to the Stark shift many Floquet states show multiphoton resonance with the ground state within the pulse duration, opening the transition channel from the ground state to the Floquet states. In the case mentioned above, a sort of collective excitation takes place, in which the excitation probabilities of all excited states as functions of the laser intensity are almost linear on a log–log plot, and the slope is independent of the final state. In other words, even at 40 fs, strong laser field excitation involves many electron states.

This paper discusses this type of multiphoton excitation by taking methane and formaldehyde as examples. In the numerical calculation we assume nuclear motion frozen, and ignore Rydberg and continuum states. Even such an approximate calculation agrees with the recent experiment by Kong *et al.*

This paper is organized as follows. In Section 2, basic model of our numerical calculation is introduced. Results of numerical calculation are shown in Section 3 by taking methane and formaldehyde as examples. Our numerical results are analysed utilizing a combination of Floquet formalism and perturbation theory. Concluding remarks are given in Section 4.

2. Formulation

In this study, we consider the dynamics of molecular electronic states under an intense laser field. By taking the dipole approximation and ignoring the rovibrational motion, the total Hamiltonian of the system is given by

$$H(t) = H_0 + V(t). \tag{1}$$

Here, H_0 is the time-independent molecular Hamiltonian, and $V(t)$ is the time dependant interaction. $V(t)$ in the dipole approximation is the product of the laser electric field $E(t)$ and the laser polarization vector $\vec{R}$, namely

$$V(r, t) = E(t)\vec{R} \tag{2}$$

where $E(t)$ is given by

$$E(t) = F(t)\sin(\omega t). \tag{3}$$

Here, ω and $F(t)$ are the carrier frequency and pulse envelope function, respectively. We assume that our target molecule is described by a wavefunction $\Psi(t)$ satisfying the initial condition $\Psi(-\infty) = \Phi_i$. Here Φ_i is the ith eigenfunction of the molecular Hamiltonian $H_0(r)$, namely

$$H_0(r)\Phi_i = E_i\Phi_i, \tag{4}$$

where E_i is the eigen energy of the ith eigen function Φ_i. The excitation probability to the jth excited state P_{ij} is defined by

$$P_{ij} = \left|\langle\Phi_j \mid \Psi(\infty)\rangle\right|^2 \tag{5}$$

where $\Psi(\infty)$ is the wave function at $t = \infty$, obtained by solving the Schrödinger equation given by

$$i\frac{\mathrm{d}}{\mathrm{d}t}\Psi(t) = H(v)\Psi(t), \tag{6}$$

with the initial condition $\Psi(-\infty) = \Phi_i$.

3. Numerical results

In this section, we take methane and formaldehyde molecules as examples of systems. Here, we ignore the nuclear motion, Rydberg states, and continuum states for simplicity.

We made a quantum chemical calculation with single CI method with 6-31-G** basis set to obtain the excitation energy and transition dipole moment matrix elements between the eigen states. For methane, we take 31 states into calculation. The first excitation energy is about 9.61 eV, and the highest eigenstate included has the energy of 15.7 eV above the ground state. We solved the Schrödinger equation Equation (6) by a Runge–Kutta method to obtain the excitation probabilities given by Equation (5).
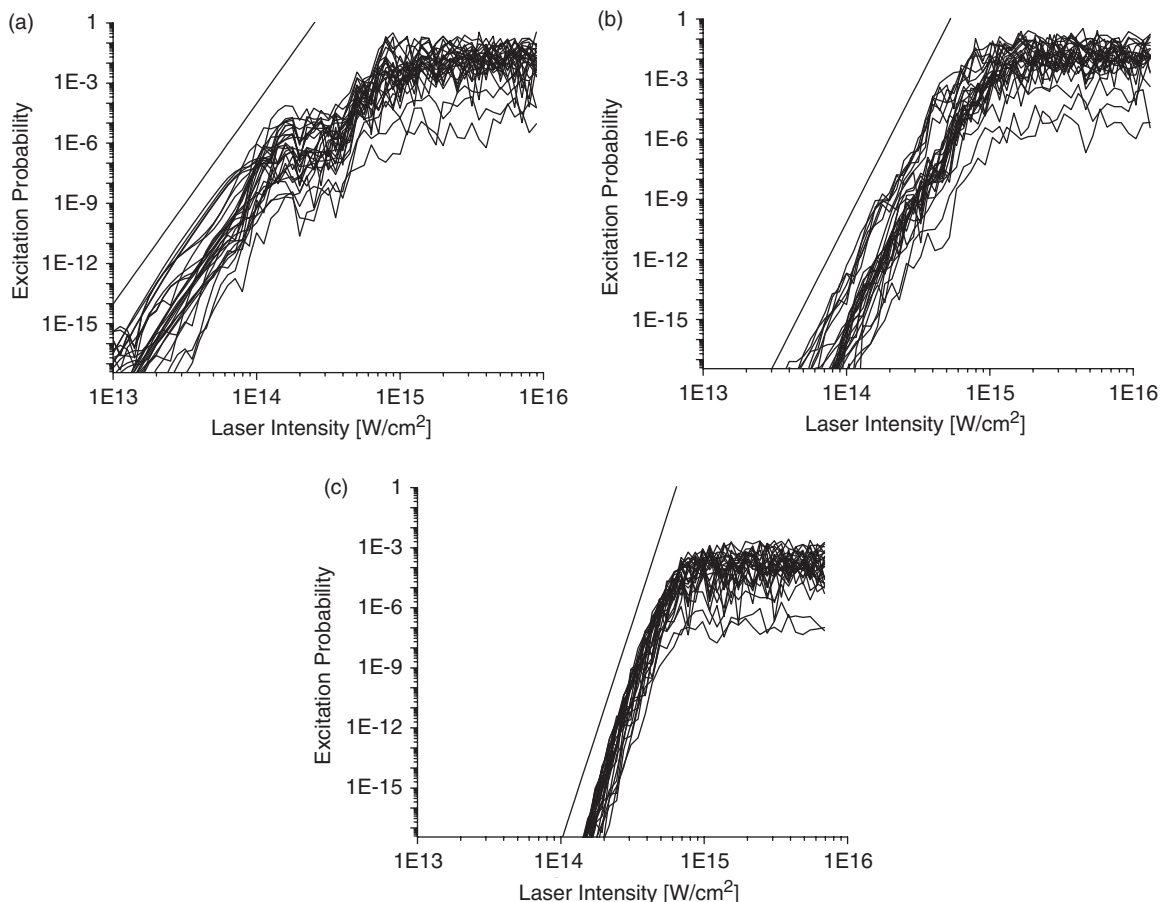
Figure 2. Excitation probabilities to various excited states of methane as functions of laser intensity (thin lines). Here, the laser pulse duration time is 42 fs, and the central frequencies of the laser pulse are (a) 800 nm, (b) 1600 nm, and (c) 3200 nm. Bold lines show the functions (a) I^{10}, (b) I^{14}, (c) I^{22}, respectively.

Figure 2(a) depicts the calculated excitation probabilities of methane as functions of the peak intensity of laser pulse. Here, we assume the Gaussian pulse envelope function with duration time of 42 fs (FWHM). The central wave length taken here is 800 nm. We also assume linearly polarized field with the direction fixed to one of the CH axis. The duration time and the central wave length are taken from the experimental condition in Ref. [13]. In Figure 2(a), we plotted the function I^n with $n = 10$ (the bold line) for comparison. As is easily seen from the figure all the excited states shows roughly the same behavior. In the low intensity region excitation probabilities rise almost linearly on a log-log scale and can be roughly fitted by I^{10}. In the high intensity region, namely $I > 10^{15}$ W/cm^2, the excitation probabilities reach close to unity and the transition probabilities start to saturate.

The low intensity behaviour can be explained by the Floquet formalism together with perturbation theory. To explain this we start from the first order

perturbation theory. According to the first order perturbation theory transition amplitude $\langle \Phi_j | \psi(\infty) \rangle$ is given by

$$\langle \Phi_j \mid \Psi(\infty) \rangle = \delta_{ij} - i \int_{-\infty}^{\infty} dt\, K_{ji}(t) \tag{7}$$

where $K_{ji}(t)$ is defined by

$$K_{ji}(t) = E(t) V_{ji} \exp\left[i\left(E_j - E_i \right) t \right] \tag{8}$$

with

$$V_{ji} = \left\langle \Phi_j | \vec{R} | \Phi_i \right\rangle. \tag{9}$$

In the system schematically depicted in Figure 1, the first excitation energy is much greater than the photon energy, namely $|E_j - E_0| \gg \hbar\omega$. This leads to a small value of the integral in the right hand side of Equation (7) when the initial state is the ground state. Thus we have to include higher order terms.

For that purpose it is convenient to introduce time propagator $S_{jk}(t, t')$ defined by

$$\langle \Phi_j \mid \Psi(t) \rangle = \sum_k S_{jk}(t, t') \langle \Phi_k \mid \Psi(t') \rangle. \tag{10}$$

The perturbative expansion of $S_{jk}(t, t')$ is given by

$$S_{jk}(t, t') = \sum_n S_{jk}^n(t, t') \tag{11}$$

where

$$S_{jk}^n(t, t') = (-i)^n \int_{t'}^t dt_1 \int_{t'}^{t_1} dt_2 \cdots \int_{t'}^{t_{n-1}} dt_n \sum_{m_1, m_2, \ldots, m_n} K_{jm_1}(t_1)$$
$$K_{jm_2}(t_2) \cdots K_{m_n k}(t_n). \tag{12}$$

When the ground state energy is isolated from the others as depicted in Figure 1, $S_{0k}(t, t')$ can be approximately expressed by

$$S_{0k}^n(t, t') = (-i)^n \int_{t'}^t dt_1 \sum_{m \neq 0} K_{0m}(t_1) S_{mk}(t_1, t'). \tag{13}$$

Now, we assume the external field is periodic in time, in other words it is not a pulse but a CW field. If the Hamiltonian is periodic in time with the frequency ω, the propagator is represented in terms of Floquet states [14] given by

$$\Xi_i(t) = \exp[-i\varepsilon_i t] \Omega_i(t) \tag{14}$$

where ε_i is the quasi-energy associated with the ith Floquet state $\Omega_i(t)$ that is periodic in time with the same frequency as the Hamiltonian; namely,

$$\Omega_i(t + 2\pi/\omega) = \Omega_i(t). \tag{15}$$

Floquet states are expanded in a Fourier series given by

$$\Omega_i(t) = \sum_l \sum_n \alpha_{nl}^{(i)} \exp[-in\omega t] \Phi_l. \tag{16}$$

The time propagator $S_{mk}(t, t')$ is now given by

$$S_{mk}(t, t') = \sum_i \sum_n A_{ki} \alpha_{nk}^{(i)} \exp[-in\omega t] \tag{17}$$

where A_{ki} is determined so as to satisfy the boundary condition

$$\Psi(t') = \sum_i A_{ki} \exp[-i\varepsilon_i t'] \Omega_i(t') = \Phi_k. \tag{18}$$

Substituting Equations (17) and (18) into Equation (13) yields:

$$S_{0k}(\infty, -\infty) = \sum_i \sum_n \sum_m (-i)^n A_{ki} \alpha_{nm}^{(i)} V_{0m} \int_{-\infty}^{\infty} dt_1$$
$$F(t_1) \exp[-i(E_0 - \varepsilon_i - n\omega)t_1] \tag{19}$$

The integral in Equation (19) is nonzero when the resonance condition,

$$\varepsilon_i + (n+1)\omega \approx E_0 \tag{20}$$

is satisfied. It should be mentioned that this treatment using Floquet formalism is similar to that used in the study of ATI spectra [15] in which dressed states of Rydberg and continuum played important roles. In our case, Floquet energy has nothing to do with ponderomotive energy because lower excited states and scattered electron have quite different wavefunctions and a transition between the excited states is easily promoted by small number of photons. This contrasts to the Rydberg or continuum states, where Floquet energies are nicely described by ponderomotive shifts.

Since transition energy among the excited states are much smaller than first excitation energy, excited states are strongly coupled to each other while the ground states is coupled with excited states only perturbatively. This strong coupling among the excited states leads to the common tendency of the excitation probability independent of the final states, or collective excitation in other words. The slope on a log–log scale can be explained from the Floquet components $\alpha_{nl}^{(i)}$ in Equation (16). In Figure 3(a), $|\alpha_{nl}^{(i)}|$ is plotted as function of n (photon number) and l (quantum state), where i is chosen so as to satisfy the resonance condition Equation (20) most closely at $n = 0$. Here, central wave length and the laser intensity are respectively taken as 800 nm and 3×10^{13} W/cm². As is easily seen from the figure $\alpha_{nl}^{(i)}$ has large component around $n = 10$ for any excited states, which agrees with our numerical results.

Our result shown in Figure 2(a) should be compared to the experimental result obtained by Kong *et al.* They observed fluorescence from excited neutral fragments after irradiating intense laser field to methane. The laser intensity dependence of CH $(A \to X)$ emission on a log-log scale has a slope of 10 ± 1, from which they assume that 10 photon process is involved in the fragmentation. Assuming that the neutral fragments come only from dissociative excited states that are populated by the laser field and that the dissociation process takes place subsequently, they indicate the possibility that the neutral fragments come from excited neutral parent molecule on the super excited states having the energy around $10\hbar\omega \approx 15.5$ eV above the ground state. Our calculation, however, shows that the excitation probability dependence is $\sim I^{10}$ no matter what the excitation energy is. This leads to the
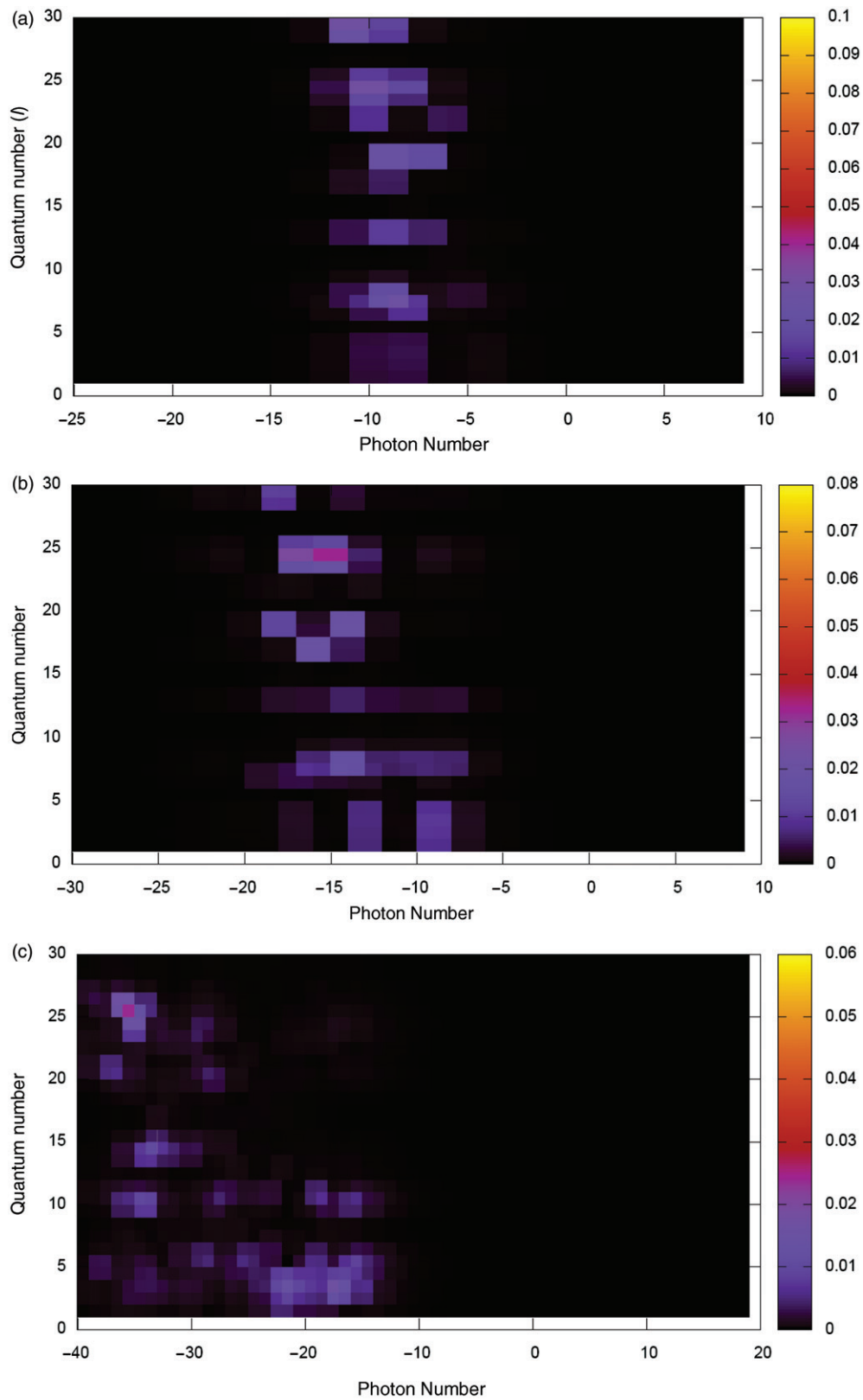
Figure 3. Fourier Floquet components $|\alpha_{nl}^{(i)}|$ (see Equation (16)) as functions of n (photon number) and l (state number). Here, we take i that satisfies most closely the resonance condition Equation (20) at $n = 0$. The laser intensity is taken as $3 \times 10^{13} \text{W/cm}^2$, and the wavelengths are (a) 800 nm, (b) 1600 nm, (c) 3200 nm.

possibility of lower excited states to be a parent state for the fragmentation.

Figure 2(b) and 2(c) depict the intensity dependence of the excitation probabilities with the central laser frequencies (b) 1600 nm and (c) 3200 nm, respectively. Other laser conditions are the same as those of 800 nm case. Both 1600 nm and 3200 nm cases also show a common tendency independent of the final states. The thick lines depict the function I^n with (b) $n = 14$ and (c) $n = 22$, and they describe a rough tendency of the excitation probabilities. The quantity defined by slope on the log-log scale plot (expected photon number) times photon energy namely, $n\hbar\omega = 15.5$ eV (800 nm), 10.9 eV (1600 nm), and 7.92 eV (3200 nm) are not constant and decreases as we increase the wave length. For the 3200 nm case, $n\hbar\omega = 7.92$ eV is even smaller than the first excitation energy. This may indicate that AC Stark effect becomes stonger as we increase the wavelength. Figure 3(b) and 3(c) depict $\alpha_{nl}^{(i)}$ as functions of n and l with the central wave lengths of (b) 1600 nm and (c) 3200 nm, respectively. Figure 3 can roughly explains the wave length dependence of the slope, but there are some discrepancies with our numerical results. For example, $\alpha_{nl}^{(i)}$ distributes more broadly in n for larger wave length, and n distribution depend on l more strongly for lager wave length. These seem to contradict to our numerical results, in which final state dependence of the excitation probability is weak for longer wave length. This may be explained by taking pulse effect into account. Since the Floquet state that satisfies the resonance condition Equation (20) depends on the intensity, we have to consider many Floquet states.

Next we take formaldehyde as another example. The first excited state of this molecule is dipole forbidden, and the excitation energy is about 4 eV. Thus two photon excitation to the first excited state is possible by laser with about 580 nm wave length. In order to excite to the second or a higher excited state by 580 nm laser, more than 5 photons are required if we ignore the AC Stark shift. Even though the energy level structure of formaldehyde is different from that depicted in Figure 1, we expect that the collective excitation takes place in the second or a higher excited states as long as the photon energy is much closer to the transition energy between the excited states higher than the first excited states compared to the second or a higher excitation energy.

Numerical results of the peak intensity dependence of the excitation probabilities are plotted in Figure 4. Here, 31 electronic states are included in the calculation. The duration time and the central
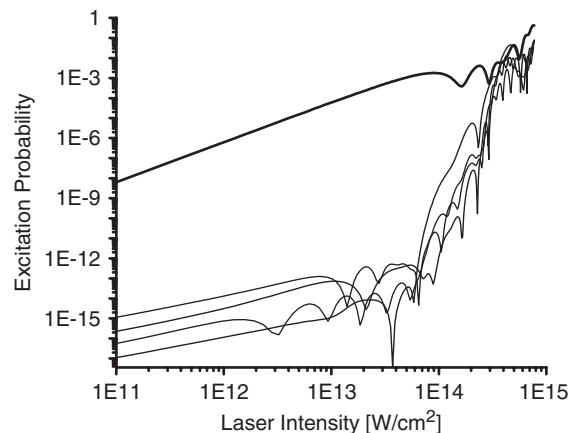

Figure 4. Excitation probabilities to various excited states of formaldehyde as functions of laser intensity (thin lines). Here, the laser pulse duration time is 42 fs, and the central frequency of the laser pulse is 580 nm (close to the two-photon resonance to the first excited state). Bold line shows the excitation probability to the first excited stated.

wave length are 42 fs and 580 nm, respectively. We choose this wavelength to examine if the existence of two photon resonance to the first excited state spoils the collective excitation phenomenon. The direction of the linearly polarized field is fixed at 45 degrees to both the CH bond and the axis perpendicular to the molecular plane. The thick line shows the excitation probability to the first excited state. For low intensity region (say $I < 10^{13}$ W/cm²), only two photon excitation to the first excited state is dominant (the thick line). For $I > 10^{14}$ W/cm², however, multiphoton excitation to higher excited states starts to take place. Excitation probabilities rise almost linearly on a log-log plot having almost common slope of $n = 6$, indicating that the collective excitation is a very general phenomenon that takes place even when the resonant transition is allowed.

4. Concluding remarks

In this paper, we discuss the electronic excitation of molecule by an intense laser field. When the first excitation energy is much larger than both the photon energy and the transition energy among the excited states as depicted in Figure 1, excited states are strongly coupled by photon, and nicely described by a Floquet state. Excitation from the ground state can then be described by a perturbation theory from the ground state to the Floquet states. In such a case, collective excitation takes place, in which the

excitation probability is almost linear on a log–log plot and the slope is independent of the final states. We take methane and formaldehyde as examples to study this collective excitation with numerical calculation. This phenomenon is quite general and expected to take places in various kinds of atoms and molecules. Even though the excited states are easily ionized, we can expect to observe the florescence from the lower excited states.

The experiment by Kong *et al.* is considered as one example. The fluorescence signal from neutral CH fragments from methane shows $\sim I^{10}$ tendency. This may correspond to our collective excitation behavior of $\sim I^{10}$ predicted by both the numerical results and the Floquet coefficients, assuming the neutral fragments are considered as the consequence of excitation to dissociative states. Not only methane but for all the molecules they studied, neutral fragmentations breaking most of the bonds in a molecule were observed. This is reasonable from our point of view because the collective excitation proposed in this paper can take places in various kinds of molecules, and it induces excitation to many different excited states, leading to breaking many different bonds.

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