Normal-mode selectivity in ultrafast Raman excitations in C_{60}

G. P. Zhang
Department of Physics, Indiana State University, Terre Haute, Indiana 47809, USA

Thomas F. George
Office of the Chancellor and Center for Molecular Electronics, Departments of Chemistry & Biochemistry and Physics & Astronomy, University of Missouri-St. Louis, St. Louis, Missouri 63121, USA

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Ultrafast Raman spectra are a powerful tool to probe vibrational excitations, but inherently they are not normal-mode specific. For a system as complicated as C_{60}, there is no general rule to target a specific mode. A detailed study presented here aims to investigate normal-mode selectivity in C_{60} by an ultrafast laser. To accurately measure mode excitation, we formally introduce the kinetic-energy-based normal-mode analysis which overcomes the difficulty with the strong lattice anharmonicity and relaxation. We first investigate the resonant excitation and find that mode selectivity is normally difficult to achieve. However, for off-resonant excitations, it is possible to selectively excite a few modes in C_{60} by properly choosing an optimal laser pulse duration, which agrees with previous experimental and theoretical findings. Going beyond the phenomenological explanation, our study shines new light on the origin of the optimal duration: The phase matching between the laser field and mode vibration determines which mode is strongly excited or suppressed. This finding is very robust and should be a useful guide for future experimental and theoretical studies in more complicated systems.

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I. INTRODUCTION

Ultrafast Raman spectra represent a major tool to probe dynamics in atoms, molecules,[1,2] chemical, and biological systems. For a simple system like NaI with only one vibrational degree of freedom, it is possible to control the vibrational excitation.[3] But for large systems, no simple rule can be used to selectively target a specific normal mode. A theoretical investigation is very important to the success of the selective mode excitation, but the technical challenges are enormous because the system size often exceeds current computational power. We choose C_{60} as a first example for this purpose since it is large enough to mimic complicated dynamics encountered in larger systems, and yet small enough to be handled numerically.

Because C_{60} has highly-delocalized π electrons, its optical response is very fast. Using a 2.03 eV pump beam and pulse duration of 100 fs, Thomas *et al.* measured the relaxation of photoexcited states in C_{60} by time-resolved optical absorption and found a 1 ps response, and when tuning to the forbidden h_{1u} to t_{1u} transition, they found a 2 ps relaxation.[4] Ishihara *et al.* used a 100 fs, 0.2 mJ, and 628 nm laser to find that the decay times of the self-trapped exciton and polaron are about 570±120 fs and 54±7 ps, but no clear lattice vibration was resolved.[5] A systematic investigation was done by Chergui's group on the ultrafast intramolecular relaxation, where they found that the transient absorption spectra of C_{60} have a characteristic rise time of 200 fs.[6] This study continued the earlier effort by Boucher *et al.*[7] using a pulse duration from 60 to 300 fs and pump and probe energies from 1.57 to 3.14 eV. Farztinov *et al.* showed that the relaxation rate has a pronounced spectral dependence.[8]

Dexheimer *et al.*[9] used a 12 fs laser to investigate the dynamics in C_{60} and revealed that there is a periodic oscillation in the transmittance change associated with the A_g modes. This is a clear example that lasers with shorter pulses can resolve those intrinsic lattice vibrations. However, this finding contradicts the results of Hohmann *et al.*[10] and Bhardwaj *et al.*,[11] who found that it is the H_g mode that dominates the relaxation process. Our previous study[12] clarified that the reason for such difference is the laser pulse duration.

Motivated by the above experimental and theoretical investigations, in this paper we provide a comprehensive investigation into normal-mode selectivity under influence of an ultrafast laser field. We first introduce the kinetic-energy method for the normal-mode analysis, which is exact and overcomes the difficulty with the high anharmonicity of the normal-mode vibration upon the laser excitation. We then investigate the possibility to selectively excite Raman modes in C_{60}. We find that such selectivity is normally difficult to achieve if we excite the system resonantly since strong electron excitations complicate normal-mode excitation. However, the off-resonant and weak excitation can be used to selectively excite a few normal modes. The key is to select an appropriate laser pulse duration that matches the normal-mode periods. Going beyond a phenomenological explanation, we gain important insights into this optimal pulse duration by comparing the time evolutions of the laser field and kinetic energy of the normal modes. If the field and normal-mode vibration reach their maxima at the same time, the mode gains energy substantially from the laser; otherwise, the mode is basically silent. Our findings will be important for future experimental investigations since duration-based control is very robust and does not sensitively depend on the incident laser frequency, provided that the frequency is away from the resonance.

The rest of the paper is arranged as follows. The theoretical scheme is presented in Sec. II followed by the kinetic-energy-based normal-mode analysis in Sec. III. Resonant and off-resonant Raman excitation are presented in IV. We conclude the paper in Sec. V.

II. THEORETICAL FORMALISM

A dynamical simulation of ultrafast Raman mode excitations at the *ab initio* level is still very challenging for large systems such as C_{60}. At present, to our knowledge, there is no such study which includes the electrons, lattice and laser field. We have decided to use a tight-binding model to simulate C_{60},[13–15]

$$H_0 = -\sum_{ij,\sigma} t_{ij}(c^{\dagger}_{i,\sigma}c_{j,\sigma} + \text{H.c.}) + \frac{K_1}{2}\sum_{i,j}(r_{ij}-d_0)^2 + \frac{K_2}{2}\sum_i d\theta^2_{i,5} + \frac{K_3}{2}\sum_i (d\theta^2_{i,6,1} + d\theta^2_{i,6,2}), \quad (1)$$

where $c^{\dagger}_{i,\sigma}$ is the electron creation operator at site i with spin $\sigma(=\uparrow\downarrow)$.[12] We only include one π orbital for each site, which consists of the sp^2-sp^3 hybridization. A similar Hamiltonian has successfully been used by other research groups[16] to treat C_{60} and polymer chains such as polyacetylene.[17] The first term on the RHS represents the electron hopping, where $t_{ij} = t^0 - \alpha(|\mathbf{r}_i - \mathbf{r}_j| - d_0)$ is the hopping integral between nearest-neighbor atoms at $\mathbf{r}_i$ and $\mathbf{r}_j$, and $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$. Here t^0 is the average hopping constant, and α is the electron-lattice coupling constant. The last three terms on the RHS are the lattice stretching, pentagon-hexagon and hexagon-hexagon bending energies, respectively. Since two hexagons are adjacent to each other, the summation contains two terms. By fitting the energy gap, bond lengths of two kinds and 174 normal-mode frequencies, You *et al.*[14] have determined the above parameters as $t^0 = 1.91$ eV, $\alpha = 5.0$ eV/Å, $K_1 = 42$ eV/Å^2, $K_2 = 8$ eV/rad^2, $K_3 = 7$ eV/rad^2 and $d = 1.5532$ Å. These parameters will be fixed in our calculation. To find the equilibrium position of C_{60}, we minimize the total energy $\mathcal{E}$ with respect to the atom positions, or $\partial\mathcal{E}/\partial\mathbf{r} = 0$. After we obtain the atomic equilibrium position, we can compute the normal-mode frequencies and eigenvectors by diagonalizing the force matrix.[14]

The dynamical properties are simulated by including the laser field, which is described by $H_I = -e\Sigma_{i\sigma}\mathbf{E}(t)\cdot\mathbf{r}_i n_{i\sigma}$, where $n_{i\sigma}$ is the electron number operator and $|\mathbf{E}(t)| = A\cos[\omega(t-t_0)]\exp[-(t-t_0)^2/\tau^2]$.[18] Here A, ω, τ, e, t, and t_0 are the field amplitude, laser frequency, pulse duration or width, electron charge, time and time delay, respectively. We numerically integrate the Liouville equation for the electron density matrices,[12,18,19]

$$-i\hbar\frac{\partial\langle\rho^{\sigma}_{ij}\rangle}{\partial t} = \langle[\rho^{\sigma}_{ij}, H]\rangle, \quad (2)$$

where $H = H_0 + H_I$, $\rho^{\sigma}_{ij} = c^{\dagger}_{i\sigma}c_{j\sigma}$ is the density matrix operator, and $\langle\ \rangle$ represents the expectation value. The quantum effect of normal modes is certainly important, but it is very challenging. As a first step, we treat the carbon atoms classically as before by solving Newton's equations for each carbon atom.[19,20] Such a treatment is justified since the quantum effect of a carbon atom's vibration is small compared with the electronic excitation. The semiclassical treatment is formally used in the Car-Parrinello method,[21] melting in metals,[22] and simulation in rhodopsin,[23] clusters[24] and solids.[17] Information about the lattice dynamics is obtained from the displacements and velocities of each carbon atom.

III. KINETIC-ENERGY-BASED NORMAL-MODE ANALYSIS

We would like to see how those normal modes absorb energy from light. In contrast to the electronic part where once we know the charge density $\rho_{ij}(t)$ we can analyze properties easily, the lattice dynamics is more difficult to treat. At first, it may appear convenient to use the normal-mode energy $\{E_\nu\}$ as an absolute measure to determine which mode is strongly excited, where $\{E_\nu\}$ is the sum of the normal-mode kinetic energy $\{E^\nu_{ke}\}$ and potential energy $\{E^\nu_{pe}\}$. Here $\{E^\nu_{ke}\} = m\dot{Q}^2_\nu/2$ and $\{E^\nu_{pe}\} = m\omega^2_\nu dQ^2_\nu/2$, where the normal-mode velocity $\dot{Q}_\nu$ is computed by $\dot{Q}_\nu = \Sigma_i \mathbf{Z}(i,\nu)\cdot\mathbf{v}_i$, the normal-mode displacement dQ_ν is computed by $dQ_\nu = \Sigma_i \mathbf{Z}(i,\nu)\cdot(\mathbf{r}_i - \mathbf{r}^0_i)$, and m is the mass of carbon atoms. The summation Σ_i is taken over all the atoms i, and $\{\mathbf{Z}(i,\nu)\}$ is the normal-mode eigenvector of the force matrix. We use boldface $\mathbf{Z}$ to denote that this vector has three components along the x, y, and z axes. $\mathbf{v}_i$ is the velocity of atom i, and $(\mathbf{r}_i - \mathbf{r}^0_i)$ is the displacement of atom i, where $\mathbf{r}_i$ and $\mathbf{r}^0_i$ are the final and initial positions of atom i, respectively. Within the harmonic approximation, the potential energy can be accurately decomposed into $\{E_\nu\}$.

However, with the presence of laser excitation, the harmonic approximation is not enough. In particular, high-order terms become significant,

$$V(\{\mathbf{r}\}) = V(\{\mathbf{r}_0\}) + \sum_i \left[\frac{\partial V}{\partial r_i}\right]_{eq}\Delta r_i + \frac{1}{2!}\sum_{ij}\left[\frac{\partial^2 V}{\partial r_i \partial r_j}\right]_{eq}\Delta r_i \Delta r_j + \text{high-order terms}, \quad (3)$$

where the first term is the static potential energy, and the second term is zero at the equilibrium position. We find that those high-order terms can be larger than the second-order term, and the harmonic expansion is not accurate. In Fig. 1(a), we present one example. The laser field amplitude is 0.01 V/Å, the frequency is 0.1 eV, and the pulse duration is 20 fs. The solid line represents the exact potential change (the new potential energy minus the static potential energy), and the dashed line shows the potential energy computed from the summation over the normal-mode potential energy $\Sigma_\nu E^\nu_{pe}$. One sees that even with such a weak laser field, the deviation is substantial. There are two additional difficulties associated with the above expansion in Eq. (3). First, the potential energy computed by summation over those normal modes is always positive since ω^2_ν is positive, while in the exact expansion, the potential energy change can be negative since the electron may take away the energy from the lattice. Second, the second term on the RHS of Eq. (3), which

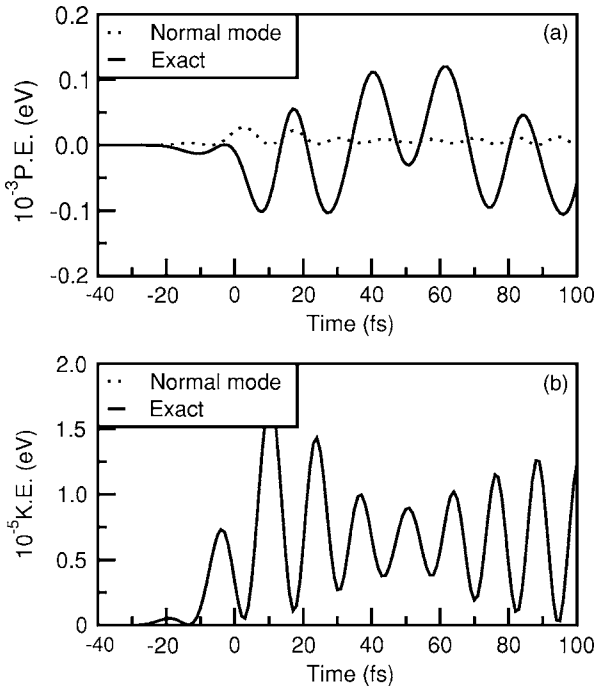

FIG. 1. (a) Comparison of the normal-mode-expanded potential (dotted line) and exact potential (solid line) energy as a function of time. From −40 to −30 fs both are the same, but with the arrival of the laser field, the deviation becomes substantial. (b) Comparison between the exact kinetic energy and normal-mode-expanded kinetic energy. Two lines overlap completely. Here $A=0.01$ V/Å, $\omega=0.1$ eV, and the pulse duration is 20 fs.

should be zero at the equilibrium, is nonzero with the presence of the laser field, but the normal-mode frequencies and eigenvectors are computed at the equilibrium position without the external laser field. These three major difficulties call for an alternative method.

One way to eliminate the above difficulties is to use the instantaneous normal-mode analysis.[25] This method requires the diagonalization of the force matrix at those pre-selected time instants. Since the potential expansion is done away from equilibrium, some of the eigenfrequencies become imaginary. These imaginary modes are supposed to decay into real modes when the equilibrium is reached. In C_{60}, we prefer to choose a different method without explicit diagonalization of the force matrix at each time step. Our method is to expand the kinetic energy. The reason is simple: All the kinetic energy only has one quadratic term, and there is no approximation to the expansion of the total kinetic energy in terms of the normal-mode kinetic energy,

$$K=\sum_{\nu} K_{\nu}=\sum_{\nu} \frac{m}{2}\dot{Q}_{\nu}^{2}, \tag{4}$$

where K_{ν} is the kinetic energy for mode ν. Numerically, we compare the total kinetic energies with and without the normal-mode expansion and find they are indeed the same [see Fig. 1(b)], where the exact and normal-mode-expanded kinetic energies overlap completely with each other. The kinetic-energy-based normal-mode analysis has several appealing advantages. It is valid for any laser intensity, frequency and pulse duration. This scheme does not rely on the equilibrium condition either, and is not limited to molecular systems. We expect this method could be readily used in liquids, solutions, solids and biological materials, where high anharmonicity appears. We should note that the normal-mode kinetic energy can not be directly probed by experiments, but such an analysis contains the same information as that in the time-resolved absorption spectra, and more importantly provides experimentally inaccessible insight into those mode excitations. And the practical application[12] shows that the results are also consistent with the experimental observations.

IV. EXCITATION IN RAMAN-ACTIVE A_g AND H_g MODES

We are interested in mode selectivity in normal-mode excitations. Two laser parameters, laser frequency and pulse duration, can be used for this purpose.[26] In C_{60}, there are two Raman-active A_g and eight H_g modes.[27] Raman excitation is a second-order optical process and is directly connected with the electronic excitation. This can be seen clearly from the equation[28]

$$\frac{\partial^2 Q_{\alpha}}{\partial t^2}+\omega_{\alpha}^2 Q_{\alpha}=\sum_{ij}\left(\frac{\partial \chi_{ij}}{\partial Q_{\alpha}}\right)A_i A_j, \tag{5}$$

where χ is the electronic susceptibility and A is the electric field strength. One notices that if there is no change in the susceptibility, there is no Raman mode excitation. Therefore, the overall excitation of the Raman modes directly depends on whether the electronic states are strongly excited or not. In the case of weak laser and off-resonant excitation, the Raman excitation is very weak.

A. Resonant excitation

In order to have a strong excitation, we tune the laser frequency to the first dipole-allowed transition of 2.75 eV. We find that both electron and normal modes are excited strongly. Figure 2 shows the resonant excitation results as a function of laser pulse duration for two different laser intensities, 0.01 V/Å [Figs. 2(a) and 2(b)] and 0.05 V/Å [Figs. 2(c) and 2(d)]. For a weak laser, the vibrational excitation is relatively simpler. From Fig. 2(a), we notice that the $A_g(1)$ mode dominates almost all the regions except for very short laser pulse duration. This breathing mode has the optimal pulse duration of 50 fs. The physical reason for this optimal duration is not obvious since both the electron and lattice are strongly excited and lattice vibrations proceed on both the ground- and excited-state potential surfaces, but our finding is in good agreement with the strong laser intensity results.[16] This result is also consistent with our previous finding for the absorbed total energy change with the laser intensity, where the nonlinear dependence is found.[20] Figure 2(b) illustrates that the $H_g(1)$ mode acquires the second largest kinetic energy, but its kinetic energy $K_{H_g(1)}$ is about 10 times smaller than $K_{A_g(1)}$. However, what is interesting is that those $H_g(1)$ modes increase with the laser pulse duration all the way up

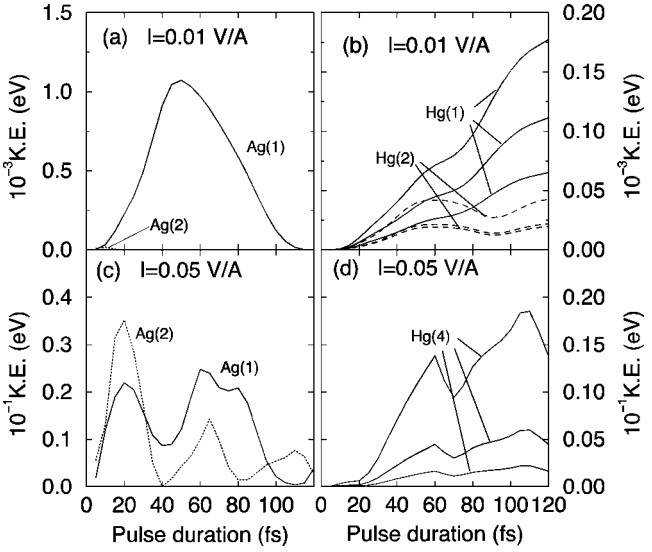

FIG. 2. Resonant excitation with the laser intensity of 0.01 V/Å for (a) and (b) and intensity of 0.05 V/Å for (c) and (d). The laser frequency is 2.75 eV, which corresponds to the first-dipole-allowed transition from the HOMO to LUMO+1. The kinetic energies for the A_g modes are shown in (a) and (c), while the kinetic energies for the H_g modes are in (b) and (d). The mode selectivity is difficult to achieve.

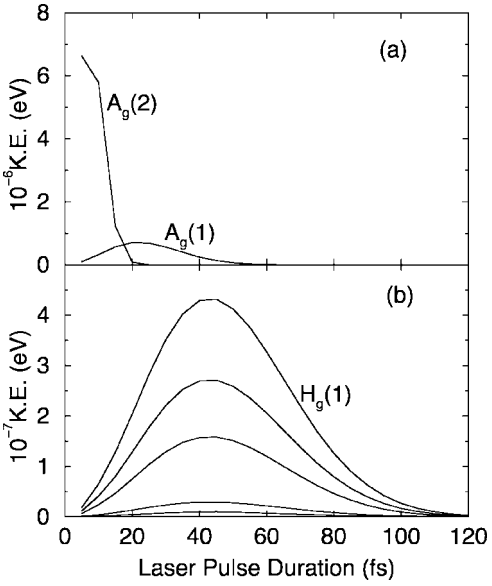

FIG. 3. Selectivity of Raman modes by the pulse duration for the off-resonant excitation. The laser frequency is 1.95 eV, which is away from any dipole-allowed transition, and the intensity is 0.05 V/Å. (a) $A_g(1)$ and $A_g(2)$ kinetic energies, where the $A_g(1)$ mode has an optimal duration at about 22 fs. $H_g(1)$ modes' kinetic energy, where five degenerate modes show a common optimal duration.

to 120 fs, while the A_g modes decrease after the optimal pulse duration. The $H_g(2)$ mode acquires the third largest kinetic energy; it decays after duration 60 fs and then increases after 100 fs. All the other high-frequency modes have at least three orders of magnitude smaller kinetic energy than the $A_g(1)$ and $H_g(1)$ modes.

From Eq. (5), we notice that the field intensity also affects the mode excitation. We increase the laser intensity from 0.01 to 0.05 V/Å. For the same pulse duration, both the $A_g(1)$ and $A_g(2)$ modes are strongly excited and have a local maximum at about $\tau=20$ fs and 60 fs, respectively [see Fig. 2(c)]. Compared with $K_{A_g(2)}$, $K_{A_g(1)}$ is smaller at a shorter duration but is larger at a longer duration. Figure 2(d) shows the dependence of the kinetic energy for the H_g mode on the duration. In contrast to the low-intensity case where the low-frequency mode $H_g(1)$ acquires most of the kinetic energy, here the $H_g(4)$ mode dominates and gains a substantial kinetic energy. Other than this, the overall change is similar to that of the $H_g(1)$ mode. Another consequence of the increasing laser intensity is that at strong intensity, K_{A_g} is about twice as large as $K_{H_g(1)}$, while for weak excitation, K_{A_g} is about five times larger than $K_{H_g(1)}$. This points out a common feature that the intensity evens out the difference between the A_g and H_g modes in terms of the absorbing power of the kinetic energy. This finding, however, also demonstrates that it is difficult to selectively excite a few normal modes accurately. So we next explore the off-resonant excitations.

B. Selectivity off resonance

From the above study, it is clear that resonant excitations lack mode specificity. It is indeed true that even in a two-level model system, it has been proposed that off-resonant excitation without substantial electron excitation population change is more effective to target a few modes. In a real and large system like C_{60}, the situation is similar and more complicated since many degrees of freedom are involved. We choose the laser frequency as 1.95 eV and the intensity as 0.05 V/Å. From the above resonant excitation, we know the normal modes have a strong dependence on the laser pulse duration. We present a comprehensive investigation of such a dependence. Figures 3(a) and 3(b) show the dependence of the A_g and H_g modes on laser pulse duration. Different from resonant excitations, different modes dominate different regions. For instance, the A_g modes dominate the shorter duration while the H_g mode dominates the longer duration. As pointed out previously, this is the origin of the differences between the Dexheimer's[9] and Hohmann's experiments.[10] This also justifies that the kinetic-energy-based analysis is very accurate and efficient. If we look at these dependences more closely, we find that each mode has its distinctive optimal duration. This is encouraging since it shows the possibility of exciting a specific mode according to the length of the laser pulse duration. In addition, Fig. 3(b) shows five degenerate $H_g(1)$ modes absorb energy differently, but their optimal laser pulse duration stays the same. This means that the optimal laser pulse duration depends only on the normal mode's intrinsic period, which provides the basis for mode specific excitation.

If we compare the off-resonant results with the resonant results, we find there are several differences. First, in the resonant excitation with a weak laser pulse such as $I=0.01$ V/Å, only the A_g modes have an optimal duration, but the H_g modes do not, and their kinetic energies basically

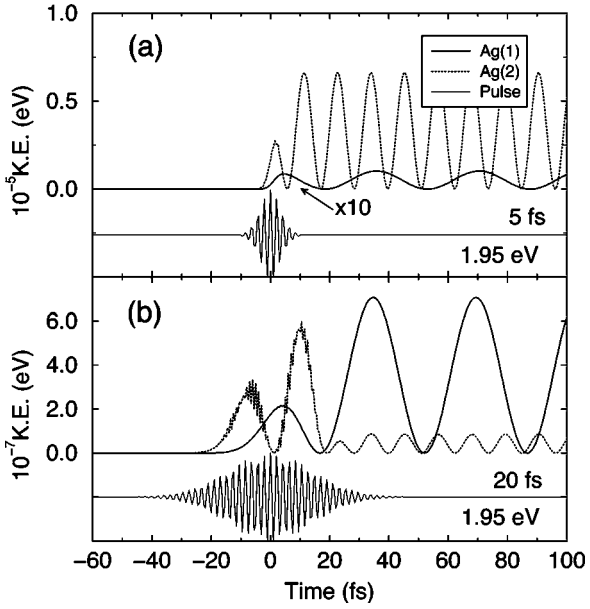

FIG. 4. Origin of the optimal pulse duration with a laser frequency of 1.95 eV: (a) laser pulse duration, 5 fs; (b) duration, 20 fs. The solid and dotted lines represent the $A_g(1)$ and $A_g(2)$ modes, respectively. The laser pulse (the thin solid line) is shown at the bottom of each graph. Whether a mode dominates depends on whether the normal mode can phase match the laser field.

increase with the laser pulse duration. By contrast, for the off-resonant excitation, the A_g and H_g modes show a similar dependence on the pulse duration. Second, in the resonant excitation the laser intensity has a huge impact on the dependence. The $A_g(1)$ and $A_g(2)$ modes dominate in two separate regions of the duration: one is from 5 to 40 fs, and the other is from 40 to 100 fs. The $H_g(4)$ mode dominates over $H_g(1)$ and $H_g(2)$. In the off-resonant case, the intensity (below 0.2 V/Å) does not change the dependence as shown in our previous study.[12] What is even more important is that in the off-resonant excitation the laser frequency has a very weak effect on the pulse duration dependence. If we compare Fig. 3 with Fig. 2(a) in Ref. 12 where the incident laser energy is 0.69 eV, the dependence is similar. Such a robust dependence on the pulse duration is promising and deserves further investigation. In our previous study we proposed a phenomenological explanation for the optimal duration, and here we go beyond this to gain new physical insight. In particular, we want to know how the laser energy of different pulse durations is absorbed into different modes.

C. Physical origin of the optimal pulse duration

To gain insight as to how the laser pulse duration affects the mode excitation, we use two different laser pulse durations off resonance, 5 fs in Fig. 4(a) and 20 fs in Fig. 4(b). For both pulse durations, the frequency is 1.95 eV, and the laser intensity is 0.05 V/Å. We start with Fig. 4(a). One sees that with arrival of the laser pulse (thin solid line), the normal modes are excited immediately (solid and dotted lines), but the kinetic energies absorbed into each mode are different: $A_g(1)$'s kinetic energy is tiny (we enlarge the solid line by 10 times for a better view), but the $A_g(2)$ mode absorbs a large portion of kinetic energy. Now, if we compare the change in kinetic energy of the A_g mode with the shape of the laser pulse, we find that the $A_g(2)$ mode closely follows the leading edge of the laser pulse and is almost in phase with the laser field. But $A_g(1)$ is almost out of phase with the pulse: when the field reaches its maximum, the $A_g(1)$ mode only starts to oscillate and lags behind the field, which leads to a suppression in its kinetic energy.

Next, we want to see what happens if we increase the laser pulse duration to 20 fs while keeping the rest of parameters unchanged. The results are shown Fig. 4(b). This time, the $A_g(1)$ mode is in phase with the electric field oscillation. Both the field and the $A_g(1)$'s kinetic energy reach their respective maximums at the same time. Consequently, the $A_g(1)$ mode acquires a substantial portion energy from the light. By contrast, the $A_g(2)$ mode is out of phase with the field, and the field's maximum is the kinetic energy's minimum of the $A_g(2)$ mode, which explains why the $A_g(2)$ mode does not obtain a large portion of the kinetic energy for this particular pulse duration. Such a strong phase dependence has previously been observed in molecular systems[29] and has been used to selectively control the normal-mode excitations.[12] Since changing laser pulse duration has been possible for a long time, we expect our results may motivate future experimental studies to use the laser pulse duration to control the vibrational excitations. Since our finding is very robust, it may suit for different experimental conditions as well.

V. CONCLUSIONS

In conclusion, we have investigated the possibility to selectively excite Raman vibrational modes in C_{60}. We have found that the Raman modes can be selectively excited by a given laser pulse duration and off resonance, not on resonance. On resonance, the excitation becomes noticeably intensity dependent and loses mode specificity. We expect that these findings can be detected experimentally. Pump-probe experiments with a short pulse of 12 fs have already probed the rapid oscillations of the A_g modes.[9] Even shorter pulses are now routinely available. Therefore, our study should motivate further experimental investigations.

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