Missing Rung Problem in Vibrational Ladder Climbing

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We observed vanishing of the transition dipole moment, interrupting vibrational ladder climbing (VLC) in molecular systems. We clarified the mechanism of this phenomenon and present a method to use an additional chirped pulse to preserve the VLC. To show the effectiveness of our method, we conducted wavepacket dynamics simulations for LiH dissociations with chirped pulses. The results indicate that the efficiency of LiH dissociation is significantly improved by our method compared to conventional methods. We also revealed the quantum interference effect behind the excitation process of VLC.

Controlling molecular reactions as desired is one of the ultimate goals of chemistry. Compared to conventional macroscopic reaction control methods using temperature and pressure, proposed methods that directly control the quantum state of molecules using the electric field of a laser are expected to achieve dramatically improved efficiency and selectivity of reactions [1–3]. Such techniques, first proposed by Brumer and Shapiro in the 1980s [1], are called “coherent control”, and with the advent of femtosecond pulsed lasers and the development of laser shaping technology have been the subject of numerous studies and continue to attract considerable attention [4–6]. A promising coherent control method is vibrational ladder climbing (VLC) [7], which employs a cascade excitation process in molecular vibrational levels under chirped infrared laser pulses with time-dependent frequencies corresponding to the vibrational excitation energy levels. VLC can focus an input laser pulse energy on a specific molecular bond. Thereby, it is expected to realize highly efficient bond-selective photodissociation [8]. VLC has been studied intensively both experimentally and theoretically. Experimentally, the vibrational excitation by VLC in diatomic molecules (NO [9], HF [10]) and amino acids [11] have been reported. Recently, Morichika et al. succeeded in breaking molecular bonds in transition metal carbonyl WCO6 with a chirped infrared pulse enhanced by surface plasmon resonance [8]. Unfortunately, there are few experimental reports of successful bond breaking by VLC, which remains a challenge. In early theoretical works, Liu et al. and Yuan et al. studied the classical motion of driven Morse oscillators [12–14]. They analyzed the excitation and dissociation dynamics of diatomic molecules under a chirped electric field using the action-angle variable, and found the condition for efficient excitation [12, 13]. Regarding the quantum aspects, a pioneering work by Friedland et al. [15] focused on quantum and classical excitation processes, specifically quantum ladder climbing and classical autoresonance, and proposed parameters to characterize the quantum and classical phenomena [15, 16]. Based on the characterization parameters, quantum and classical comparisons were made in various systems [17–20] such as plasma systems [21] and superconducting circuits [22]. The excitation condition proposed by Duan et al. [22] and the characterization parameters proposed by Friedland et al. depend on the physical properties of the system such as the potential energy surface (PES) and the dipole moment. Thereby, these properties determine the characteristic of the VLC. However, most of the theoretical treatments were based on simple model functions of these properties such as Morse potentials and linear dipole moments [12, 15, 23–25].

In this study, we performed wavepacket dynamics simulations of VLC based on the PES and the dipole moment computed by a highly accurate ab-initio quantum chemistry method. The results of the simulations revealed a problem that has not previously been recognized in VLC: VLC is interrupted by the existence of a level with a nearly zero adjacent transition dipole moment (TDM), i.e., vanishing of the TDM. We call this problem the missing rung problem (MRP) as it is like a rung missing in the middle of a ladder. To clarify the issue in more detail, the absolute values of TDMs for the diatomic molecules LiH and HF are shown in the lower panels of Fig. 1(b) and (c), respectively. It can be seen that the TDMs of the 16th level of LiH and the 12th level of HF have nearly zero values, which indicate “missing rungs” in the vibrational levels.

To understand the cause of the MRP, we start by considering a harmonic oscillator. The vibrational wavefunctions of the harmonic potential $|\phi_i\rangle$ are described by Hermite polynomials, and their parities are different between adjacent levels, as described in Fig. 1(a). Assuming an odd function for the dipole moment, the TDM between adjacent levels $\mu_{i,i+1}=\langle \phi_i | \mu | \phi_{i+1}\rangle$ becomes an integral of an even function, which yields a nonzero value (i.e., an allowed transition). The well-known infrared selection rule $\Delta \nu = \pm 1$ corresponds to this result [26]. On the other hand, if we assume an even function for the dipole moment, the adjacent TDM $\mu_{i,i+1}$ becomes an integral of an odd function, which yields zero (i.e., a forbidden transition), as shown in the lower panel of Fig. 1(a).

Based on the above discussions, we consider two realistic molecular systems, LiH and HF, where the shapes
of the vibrational wavefunctions of molecules are similar to those of a harmonic potential except for a distortion due to the anharmonicity of the PESs, as shown in Figs. 1(b) and (c). Therefore, the nature of the parity of the wavefunctions is approximately conserved, whereas the parity of molecular dipole moments is not as simple as in the above discussion for the harmonic potential. Near the equilibrium distance, the dipole moment can be regarded as being linear (i.e., odd function-like). Thereby, the TDM $\mu_{i,i+1}$ increases monotonically as the vibrational level increases, as for the harmonic model. As the bond length increases, however, nonlinearity of the dipole moment appears. The dipole function takes maxima (i.e., is even function-like) and then decreases asymptotically to zero. This behavior results from the relaxation of the molecular polarization, which always occurs for charge neutral heteronuclear diatomic molecules. As the edge of the distribution of the $i$th vibrational level of the wavefunction reaches the maxima of the dipole function, the TDM $\mu_{i,i+1}$ begins to decrease due to the even-function nature of the dipole function. Then the TDM has a near-zero value, as can be seen in Fig. 1(b) and (c) for LiH and HF, respectively. No missing rung will appear in the VLC simulations based on the assumption of the linear dipole function and is likely to give an unrealistic result. Since the position of the missing rung sensitively depends on the shape of the PES and dipole function (see Supplemental Material), highly accurate quantum chemistry methods are required to identify its exact position.

To verify the existence of the missing rung by numerical experiments, we conducted wavepacket dynamics simulations for the LiH molecule. The time evolution of the wavepacket $\Psi(x,t)$ under a laser electric field $E(t)$ is expressed by the following time-dependent Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \Psi(x,t) = H(x,t)\Psi(x,t), \quad (1)$$

where the Hamiltonian $H(x,t)$ is defined by

$$H(x,t) = H_0(x) - \mu(x)E(t) \quad (2)$$

$$H_0(x) = -\frac{\hbar^2}{2M_{\text{red}}} \frac{\partial^2}{\partial x^2} + V(x). \quad (3)$$

$M_{\text{red}}$ in $H_0(x)$ is the reduced mass of LiH. The potential energy $V(x)$ and the dipole moment $\mu(x)$ were calculated by the multireference averaged quadratic coupled-cluster (MR-AQCC) method [27]. Details of these computations are described in the Supplemental Material. We employ a Gaussian pulse as the electric field $E(t)$ of the pulsed
where $E_0$ is the maximum electric field intensity, $\alpha$ is the Gaussian spreading parameter, $t_0$ is the center time of the pulse, and $\omega(t)$ is the time-dependent frequency. The time variation of $\omega(t)$ is assumed to be a linear chirp, and parametrized by the two dimensionless parameters $\gamma_1$ and $\gamma_2$ as follows,

$$\omega(t) = \omega_0 \left\{ -(\gamma_1 + \gamma_2) \cdot \frac{t - t_0}{4\sigma} + 1 + \frac{\gamma_1 - \gamma_2}{2} \right\}$$

where $\sigma = 1/\sqrt{2\alpha}$ is the standard deviation of the Gaussian pulse envelope. Equation 5 means that $\omega(t)$ is a linear function through two points, $\omega(t_0 - 2\sigma) = \omega_0(1 + \gamma_1)$ and $\omega(t_0 + 2\sigma) = \omega_0(1 - \gamma_2)$. The reference frequency $\omega_0$ was set to the transition frequency between the ground state and the first excited state ($\omega_0 = (E_1 - E_0)/\hbar$). Based on the above formulation, the VLC process for the LiH molecule was simulated by computing the time evolution of wavepackets initially set to the ground state using the second-order Suzuki–Trotter decomposition method. Here, we discuss the parameter ranges of $E_0$ and $\alpha$ that determine the shape of the pulses. As mentioned in the introduction, there are two types of excitation process mechanisms induced by chirped lasers: quantum ladder climbing and classical autoresonance. Since MRP is a quantum issue that apparently appears when the vibrational levels can be regarded as discrete, the parameter range should be chosen so that quantum ladder climbing occurs. Therefore, using the characterization parameters proposed by Friedland et al. [16], we estimated the parameter range for quantum ladder climbing (see Supplementary Material for details). The parameter range was determined to be $E_0 = 2.0-20\text{[MV/cm]}$ and $\alpha = 10^{-8}-10^{-7}\text{[fs}^{-2}]$. For this parameter range of $E_0$ and $\alpha$, a grid of 20×20 points on logarithmic scales was defined and wavepacket dynamics simulations were carried out for each grid point. The chirp parameters $\gamma_1,\gamma_2$ were optimized by Bayesian optimization so as to maximize the degree of excitation and the dissociation probability. The degree of excitation was evaluated by the expectation value of the occupied states, and the dissociation probability was evaluated by a time-integration of the probability density flux of the wavepacket that reaches the dissociation limit. The details of the wavepacket simulations and optimizations are described in the Supplementary Material.

Figure 2(a) and (b) shows the results of the wavepacket dynamics simulations with optimized chirp parameters. The color map in Fig. 2(a) shows the dissociation probabilities get larger with larger electric fields ($\propto E_0$) and longer pulse widths ($\propto 1/\sqrt{\alpha}$). This result is a natural consequence of the fact that greater dissociation is promoted by a higher pulse energy. The color map in Fig. 2(b) shows the vibrational state that has the largest occupation number (excluding the ground state) after each of the simulations. It can be seen that there is a wide plateau consisting of the 15th and 16th states. The missing rung of LiH is located around the 16th state, indicating that the wavepacket was trapped there due to the missing rung during the VLC. This result shows that the MRP hinders photodissociation by VLC. Since the MRP occurs for all molecular bonds with polarization, it is important to solve the MRP to achieve photodissociation by VLC.

FIG. 2: Color maps of the results of the single pulse method and the DSP method (explained later in the paper). (a) Dissociation probabilities and (b) vibrational state with the largest occupation number for the single pulse method. (c) Dissociation probabilities for the DSP method. The blue dots represent the grid points where the wavepacket simulations were conducted. The yellow boxed area in (a) and (b) represents the parameter range chosen for the DSP method.
Here, we propose the double-stepping pulse (DSP) method as a solution for the MRP. In addition to a conventional pulse for the adjacent transitions ($\Delta \nu = \pm 1$), the DSP method uses a secondary pulse to achieve transitions of $\Delta \nu = \pm 2$, i.e. double stepping, between levels around the missing rung. Based on the previous discussion, when the dipole function has an even function property around the missing rung, transitions between levels with different parity ($\Delta \nu = \pm 1$) are forbidden, while transitions between levels with the same parity ($\Delta \nu = \pm 2$) are allowed, and vice versa when the dipole function has an odd function property (see Supplementary Material). Thereby, the DSP is complementary to a conventional pulse for successful VLC.

To show the effectiveness of our method, we conducted wavepacket dynamics simulations of the DSP method. For the main pulse for the transitions of $\Delta \nu = \pm 1$ we chose pulse parameters for which almost no dissociation occurred using a single pulse ($E_0 = 3.0 - 9.0$[MV/cm], $\alpha = 1.0 \times 10^{-8} - 2.0 \times 10^{-8}$[fs$^{-2}$], $9 \times 6$ grid points on logarithmic scales, as shown in the yellow boxed area in Figs. 2). For the DSP, the pulse parameters $E_0 = 3.0$[MV/cm], $\alpha = 8.0 \times 10^{-8}$[fs$^{-2}$] were used. Here, we have to optimize the chirp parameters for two pulses, the main pulse and the DSP, and the delay time between the two pulses ($\Delta t_0 = t_0^{\text{main}} - t_0^{\text{DSP}}$). Hence, we have to optimize five parameters, $\gamma_0^{\text{main}}, \gamma_0^{\text{DSP}}, \gamma_0^{\text{DSP}}$, and $\Delta t_0$. Since the computational cost of handling five variables in Bayesian optimization is high, the CMA-ES [28] evolutionary optimization method was used for the parameter optimization (see Supplementary Material for details). The reference frequency of the DSP is set to the transition frequency between the 15th and 17th levels, (Fig. 3(a)), the wavepacket is successfully excited to the dissociation limit. Figure 3(c) shows the electric fields and time-dependent frequencies used for the above simulations with the most energy efficient pulses in the DSP method. The pulse parameters of the main pulse are $E_0 = 5.95$[MV/cm], $\alpha = 1.27 \times 10^{-8}$[fs$^{-2}$]. (b) Snapshot of the excitation process with only the main pulse, with the same parameters as in (a). (c) Upper panel: electric field intensities of the main pulse, the DSP and the overall field. Lower panel: corresponding time-dependent frequencies of the main pulse and the DSP in (a). The red and blue dashed lines represent the transition frequencies for $\Delta \nu = \pm 1$ (red) and $\Delta \nu = \pm 2$ (blue).

FIG. 3: (a) Snapshot of the excitation process with the most energy efficient pulses in the DSP method. The pulse parameters of the main pulse are $E_0 = 5.95$[MV/cm], $\alpha = 1.27 \times 10^{-8}$[fs$^{-2}$]. (b) Snapshot of the excitation process with only the main pulse, with the same parameters as in (a). (c) Upper panel: electric field intensities of the main pulse, the DSP and the overall field. Lower panel: corresponding time-dependent frequencies of the main pulse and the DSP in (a). The red and blue dashed lines represent the transition frequencies for $\Delta \nu = \pm 1$ (red) and $\Delta \nu = \pm 2$ (blue).
lation shown in Fig. 3(a). It clearly shows that the DSP is focused on the 15th and 16th excitation frequencies which are around the missing rung.

However, the above discussions were limited to phenomenological cases. To understand the mechanism of the DSP method microscopically, we propose an analysis method that clarifies the dynamics of the vibrational levels under electric fields. Under an arbitrary electric field $E(t)$, the time evolution of the probability amplitude $c_j$ of the $j$th level, is expressed by the following equation,

$$i\hbar \frac{\partial c_j}{\partial t} = \epsilon_j c_j - \sum_{k \neq j} \mu_{j,k} E(t) c_k,$$  

(6)

where $\epsilon_j$ is the eigenenergy of the $j$th level and $\mu_{j,k}$ is the TDM of the $j$th and $k$th levels. Approximately, the variation of the probability amplitude $\Delta c_j$ during $\Delta t$ can be written as

$$\Delta c_j \simeq -i\frac{\epsilon_j \Delta t}{\hbar} c_j + i\frac{\Delta t}{\hbar} \sum_{k \neq j} \mu_{j,k} E(t) c_k.$$  

(7)

Figure 4(a) illustrates the meaning of Eq. 7. The first term of the right hand side of Eq. 7 does not change the norm of $c_j$ since it merely rotates $c_j$ in the complex plane. On the other hand, the second term, which cause mixing the second term changes the norm of $c_j$. Therefore, the contribution to the norm of $c_j$ can be quantified through rotating $\Delta c_j$ by the argument of $c_j$, $\theta_j = \arg c_j$, and taking its real part. The summation of the second term in Eq. 7 represents the contributions to $c_j$ from each level. We define $\Delta C_j^{(k)}(t)$ as the time integration of the contribution to the $j$th level from the $k$th level, indicating the net contribution of the $k$th level to the $j$th level norm up to time $t$. It is written as

$$\Delta C_j^{(k)}(t) = \int_{-\infty}^{t} \text{Re} \left( i\mu_{j,k} E(t') \frac{c_k(t')}{\hbar} \exp(-i\theta_j(t')) \right) dt'.$$  

(8)

A positive value of Eq. 8 means that the $k$th level acts to increase the norm of the $j$th level, and a negative value means that it acts to decrease it. By calculating $\Delta C_j^{(k)}(t)$ for each level, it is possible to analyze which vibrational level has the dominant contribution to the excitation process of a given level. Furthermore, by calculating $\Delta C_j^{(k)}(t)$ for each electric field component $E\text{Main}(t)$ and $E\text{DSP}(t)$, we can distinguish the contributions of each pulse.

Figure 4(b) shows the occupation number of the 12th, 13th, and 14th vibrational levels (levels lower than the missing rung) and the contribution from the other levels calculated by Eq. 8 for the simulation of the DSP method shown in Fig. 3(a). It can be understood that the cascade excitation of a wavepacket, i.e. the VLC, is the result of quantum interference of the positive contribution from the lower level and the slightly delayed negative contribution from the upper level. Note that these transitions are caused by contributions from adjacent levels, which agree with the process of quantum ladder climbing described by successive Landau–Zener transitions [16]. It is also worth noting that even though the electric field of the DSP is present during the transition of these levels, it does not contribute at all to the changes in occupation numbers. This indicates that the excitation processes at levels lower than the MRP region are all induced by the main pulse.

Next, we show the results for the vibrational levels of the 15th, 16th, 17th, and 18th (levels around the missing rung) in Fig. 5. Figure 5(a) shows the result with DSP shown in Fig. 3(a) and Fig. 5(b) shows the result without DSP shown in Fig. 3(b). Comparing the time variations of the occupation number for the 15th level, it can be seen that without the DSP, the positive contribution of the 14th level is not sufficiently canceled by the negative contribution from the 16th level, and most of the wavepacket remains in the 15th level. Whereas with the DSP, the additional negative contribution from the 17th level caused by the DSP significantly decreases the occupation number of the 15th level. In the contribution to the 17th level in Fig. 5 there are slight contributions from other levels without the DSP. On the other hand, there is an apparent positive contribution from the 15th level with the DSP, which excites wavepackets to higher levels. Such an interlevel excitation can also be seen between the 16th and 18th levels for the DSP method. These results confirm the interpretation of the MRP and the mechanism of the DSP method.

The proposed contributions reveal that the DSP
method utilizes quantum interference effectively to solve the MRP. Such quantum interference effects are one of the most important features of coherent control [29–31]. Another indication of quantum interference is the effects of the phases of the electric fields. It is found that the dissociation probability changes significantly as the relative phase changes (see Supplemental Material). This implies that the phases of the electric field and that of the vibrational levels are coupled, and they play an important role in the dynamics of quantum interference. Thus, quantum interference is deeply related to the DSP method.

In summary, we simulated photodissociations by VLC based on the PES and dipole moment computed by a highly accurate quantum chemistry method. We found the MRP, which causes an interruption of VLC, and revealed that the MRP is caused by the disappearance of the adjacent TDM at a specific vibrational level. As a solution to this problem, we proposed the DSP method that uses additional pulses to induce a $\Delta \nu = \pm 2$ transition, and verified its effect on the MRP by wavepacket dynamics simulations. We note that the DSP method not only enhances the dissociation probability but is also more energy-efficient than the single pulse method. We also clarified the detailed mechanisms of the VLC and DSP method. The excitation process of the VLC is caused by quantum interference between the positive contribution from the lower level and the negative contribution from the upper level and the DSP plays an essential role in the excitation process to higher levels. The MRP is considered to be a ubiquitous problem in VLC because it originates in the parity of the vibrational wavefunction and the dipole function. The MRP may be why there are few experimental reports of VLC-induced molecular bond breaking, and we believe that our findings may pave the way to VLC-induced photodissociation and, ultimately, to the versatile control of chemical reactions.

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I. QUANTUM CHEMISTRY COMPUTATIONS

The potential energy curves and dipole moments of the LiH and HF molecules were calculated using the multi-reference averaged quadratic coupled-cluster (MR-AQCC) method [1]. First, complete active space self-consistent field (CASSCF) calculations [2] were carried out and the obtained CASSCF wavefunctions were adopted as reference functions for the MR-AQCC calculations. For LiH, the molecular orbitals derived from the Li 2s and H 1s atomic orbitals were selected as active orbitals. The CAS was constructed by distributing two electrons over these two orbitals. In the MR-AQCC calculations, the electrons in Li 1s were additionally correlated. For HF, the molecule was placed on the z-axis. Accordingly, the H 1s and F 2pz orbitals were relevant for the formation of the H-F bond. The molecular orbitals derived from these atomic orbitals were selected as active orbitals in the CASSCF calculations; two electrons involved in these orbitals were treated as active electrons. The electrons in the orbitals originating from F 1s, F 2s, F 2px, and F 2py were also correlated in the MR-AQCC calculations. The basis set used was Dunning’s aug-cc-pVQZ [3–5]. All the calculations were carried out using the GAMESS program [6, 7]. The calculated spectroscopic parameters and dipole moments are summarized in Table I. Here, the spectroscopic parameters were estimated by fitting the potential energy curve with a quadratic function. The calculated parameters were in good agreement with the corresponding experimental values [8]. The results suggest that the potential energy curves and dipole moments are reliable over the entire range. The CASSCF and MR-AQCC potential energy curves and transition dipole moments are compared in Fig. 1. The CASSCF results were quite different from the MR-AQCC results because of the lack of dynamical correlations. As a result, the missing rung in which the transition dipole moment is close to zero appeared at different states. The results suggest that calculations using a high-level method are necessary to estimate the exact position of the missing rung.

II. DOUBLE-STEPING TRANSITION

Here, we show the transition dipole moments (TDMs) of $\Delta \nu = \pm 2$. Figures 2(a) and (b) show the TDMs of $\Delta \nu = \pm 1$ transitions and $\Delta \nu = \pm 2$ transitions of LiH and HF molecules. It is clearly seen that the increase and decrease of these values are opposite, which can be explained by the parities of wavefunctions and the dipole moment.
III. WAVEPACKET DYNAMICS SIMULATIONS

Non-relativistically, the time evolution of quantum systems can be described by the time-dependent Schrödinger equation,

\[ i\hbar \frac{\partial}{\partial t} \psi(x, t) = H(t)\psi(x, t). \]  

The formal solution of the Schrödinger equation with the time-independent potential \( V(x) \) can be written as

\[ \psi(x, t) = e^{-i \frac{H(x)}{\hbar} t} \psi(x, 0), \]

where \( U(t) = e^{-i H(x)/\hbar} \) is the time evolution operator. However, we have to consider the time-dependent Hamiltonian \( H(x, t) \) that describes the system under the laser electric field \( E(t) \),

\[ H(x, t) = -\frac{\hbar^2}{2M} \frac{\partial^2}{\partial x^2} + V(x, t), \]

where \( V(x, t) = V(x) - \mu(x)E(t) \). To treat the time-varying potential \( V(x, t) \), we set \( t = Ndt \) and express the time evolution operator as the product of \( N \) operators in time increments of \( dt \),

\[ U(t) = \prod_{j=0}^{N} U_j(dt), \]
FIG. 2: Absolute values of TDMs for $\Delta \nu = \pm 1$ and TDMs for $\Delta \nu = \pm 2$ for the (a) LiH molecule and (b) HF molecule. The TDMs are calculated based on the PESs and dipole moments calculated by MR-AQCC.

where

$$U_j(dt) = e^{-i H(x,j dt) dt}$$

Several methods of applying an exponential operator to a wave function have been developed [9], including methods based on a Taylor expansion and the Chebyshev-polynomial method. However, the Suzuki–Trotter decomposition method [10] is often used because of the good balance between computational cost and speed. We also use the Suzuki–Trotter decomposition method for the time-evolution computation. The second-order Suzuki–Trotter decomposition can be written as

$$U_j(dt) \sim e^{-i T dt \frac{\hbar}{2}} e^{-i V(x,j dt + dt/2) dt \frac{\hbar}{2}} + O(dt^3).$$

An error arises because $T$ and $V$ are non-commutative. Here, $T$ is diagonal in wavenumber space and $V$ is diagonal in real space, so in the second-order Suzuki–Trotter method, when applying $e^{-i T dt \frac{\hbar}{2}}$, the wave function is expressed in wavenumber space using a fast Fourier transformation (FFT) and $e^{-i V(x,j dt + dt/2) dt \frac{\hbar}{2}}$ is applied to the wave function, which returns to real space notation by an inverse FFT. When $e^{-i T dt \frac{\hbar}{2}}$ is applied again, the wave function is expressed in wave number space using the FFT again. Using the above procedure, the time-evolution computation can proceed without expanding the exponential function operator. By repeating these calculations $N$ times, the wave function at the desired time $t$ can be obtained.

For the simulations of LiH dissociation by chirped laser pulses, $dt = 1.0$ [a.u.] is used. The simulation time $t$ depends on the shape of the chirped laser pulses, $t = 8\sigma$, where $\sigma$ is the standard deviation of the Gaussian envelope for the pulse laser. We take an evenly spaced isotropic grid of $2^{10}$ elements for $x$ in the range $x = 1.5–15.0$ [bohr].

A. Dissociation probability

Here, we describe how to calculate the dissociation probability. The wavefunctions that reach the right edge of the grid represent the state of bond-dissociation. Therefore, the probability densities $|\psi(x_{right-edge})|^2$ represent the dissociation probability. It is convenient to use the probability density flux,

$$J(x,t) = \frac{\hbar}{2iM}(\psi^*(x,t)\nabla \psi(x,t) - (\nabla \psi(x,t))^* \psi(x,t)) = Re(\psi(x,t)^* \frac{\hbar}{iM} \nabla \psi(x,t)).$$
\( \frac{\hbar}{iM} \nabla \psi(x, t) \) can be transformed as the following,
\[
\frac{\hbar}{iM} \nabla \psi(x, t) = \frac{\hat{p}\psi(x, t)}{M} = \text{IFFT}(k\psi(p, t))/M,
\] (8)
where IFFT means an inverse FFT. Thereby we can quickly compute \( \frac{\hbar}{iM} \nabla \psi(x, t) \) because we have the wavefunction in wave number space \( \psi(p, t) \) and can therefore use the Suzuki–Trotter decomposition method for the time-evolution computation. The time integral of the probability density flux at the right edge of the grid after a sufficiently long simulation time gives the dissociation probability in this case:
\[
P_{\text{dissociation}} = \int_{t_0}^{t} J(x_{\text{right-edge}}, t') dt'.
\] (9)

**B. Complex absorbing potential**

An absorption potential with a negative pure imaginary value was set to prevent the wavefunction from reaching the grid boundary. Here, we used the complex absorption potential of a 4th order function,
\[
V_{\text{absorbing}}(x) = -i\xi x^4
\] (10)
where \( \xi = 1.0 \) is used in this study. The norm of the wave function reaching the region where this function has a significant value decays. This prevents reflections at the edge and the consequent unwanted interference. We placed the potential just after the flux calculation point.

**IV. RANGE OF LASER PARAMETERS**

Since the MRP is a quantum problem that appears when the vibrational levels can be regarded as being discrete, we have to choose laser parameters (\( E_0 \): maximum electric field intensity, \( \alpha \): Gaussian spreading parameter) that reproduce the excitation process where quantum phenomena are dominant. Here, we provide a rough estimation of the laser parameter range where quantum ladder climbing occurs, using the parameters proposed by Friedland et al. to distinguish between quantum ladder climbing and classical autoresonance [11].

The excitation process is characterized by three time scales,
\[
T_R = \sqrt{\frac{2m\hbar \omega_0}{\epsilon}}, \quad T_S = \frac{1}{\sqrt{\Gamma}}, \quad T_{\text{NL}} = 2\omega_0/\Gamma
\]
where \( m \) is the reduced mass, \( \omega_0 \) is the eigenfrequency, \( \beta \) is the anharmonicity of the system, \( \epsilon \) is the magnitude of external field, and \( \Gamma \) is the chirp rate.

To obtain the values of \( \omega_0 \) and \( \beta \) of LiH, the excitation frequency is fitted with the following equation:
\[
\omega_{n,n+1} = \omega_0 [1 - 2\beta(n+1)].
\] (11)
The fitting gives \( \omega_0 = 0.0068 \) [a.u.], \( \beta = 0.0176 \).

\( \epsilon \) corresponds to the product of the electric field and the linear dipole moment. Although the dipole moment of LiH is nonlinear, in the range 2–5.5 [Bohr], it is linearly approximated to be \( \mu(x) = 0.354x + 1.086 \). The effective external field magnitude \( \epsilon_{\text{eff}} \) is estimated as \( \epsilon_{\text{eff}} = 0.354E_0 \). The chirp rate \( \Gamma \) is taken as the value when \( \gamma_1 = \gamma_2 = 0.5 \), namely \( \Gamma = \omega_{0-1}/4\sigma \).

Based on these values, \( T_R, T_S, \) and \( T_{\text{NL}} \) are calculated. The parameters that distinguish the quantum case from the classical case \( P_1, P_2 \) are expressed as follows,
\[
P_1 = \frac{T_S}{T_R},
\] (12)
\[
P_2 = \frac{T_{\text{NL}}}{T_S}.
\] (13)

The conditions under which phase-locked ladder climbing occurs are as follows,
\[
P_2 > P_1 + 1,
\] (14)
\[
P_1 > 0.79.
\] (15)

Figure 3 shows the calculated value of \( P_2 - (P_1 + 1) \) for the parameter ranges \( E_0 = 10^{-1} - 10^2, \alpha = 10^{-9} - 10^{-6} \). The parameter range that satisfy the conditions Eq. 15 is colored in red. From Fig. 3, ladder climbing is considered to
FIG. 3: Characterization parameter $P_2 - (P_1 + 1)$ calculated in the ranges $E_0 = 10^{-1}–10^2$, $\alpha = 10^{-9}–10^{-6}$. The parameter range corresponding the quantum ladder climbing is colored red. The blue boxed area represents the parameter ranges we chose.

occur in the parameter range $E_0 = 2.0–20$ [MV/cm], $\alpha < 10^{-7}$ [fs$^{-2}$]. It is not possible to make $\alpha$ arbitrarily small due to the vibrational relaxation time. We refer to the vibrational lifetime of the CO stretching measured by Kemlin et al. [12] and assume a time scale for vibrational relaxation of a few tens of ps, which corresponds to the parameter range $\alpha = 10^{-8}–10^{-7}$[fs$^{-2}$]. Based on the above estimation, we set the parameter ranges as $E_0 = 2.0–20$ [MV/cm], $\alpha = 10^{-8}–10^{-7}$[fs$^{-2}$] (blue boxed area in the Fig. 3). Note that a more detailed discussion is required for an actual system to obtain a more accurate characterization.

V. OPTIMIZATION OF THE CHIRPED LASER PULSE PARAMETERS

Here, we describe the details of the optimization methods of chirped laser parameters. We adopted the following linear chirped frequency as the time-dependent frequency $\omega(t)$ of the laser pulse,

$$\omega(t) = \omega_0 \left\{ - (\gamma_1 + \gamma_2) \cdot \frac{t - t_0}{4\sigma} + 1 + \frac{\gamma_1 - \gamma_2}{2} \right\}.$$  \hspace{1cm} (16)

Equation 16 is parameterized by the two dimensionless parameters $\gamma_1$ and $\gamma_2$. These chirp parameters significantly affect the excitation process of VLC. To achieve a more effective excitation, we optimized these parameters using a combination of machine learning and a wavepacket dynamics simulation. We used machine learning to update the parameters based on the evaluated values of the parameters obtained by the wavepacket dynamics simulation.

For a single pulse, the two parameters $\gamma_1$ and $\gamma_2$ are optimized in a range restricted to [0, 1] so as to represent the downchirp. This parameter space is divided into a 100 $\times$ 100 grid (i.e. 0.01 steps), and the optimal parameter is searched from these grid points by the optimization method.

The chirp parameters are optimized for each of 400 different pulses, thus a fast and efficient optimization method is required. In addition, since the effects of the parameters on the excitation process cannot be evaluated analytically, this system is regarded as a black-box. As a fast black-box optimization method, we employed Bayesian optimization. Bayesian optimization enables efficient exploration and optimization in parameter space leveraging predictive models such as Gaussian process regression, which is a powerful method for black-box optimization [13]. We used Gpy [14],
an open source library in Python, for the implementation of Bayesian optimization. In the optimization, we adopted
Gaussian process regression with the RBF (radial basis function) kernel as the predictive model for the parameter
space, and employed the UCB (upper confidential bound) as the acquisition function. The iteration number for
updating parameters was set to 50.

The objective function was set to be the sum of the excited and dissociated wavepackets. Although we aim to
find parameters that give efficient photodissociation, for some pulse parameters whose energy is not sufficient to
cause dissociation, an objective function with only an amount of dissociation will result in insufficient optimization.
Therefore, by including an amount of an excited wavepacket in the objective function in addition to the dissociated
wavepacket, it is possible to obtain optimized parameters that realize efficient excitation. The amount of dissociated
wavepacket is evaluated by integrating the absorbed wavepacket described in the previous section. The degree of
excitation is evaluated by the expected value of the occupied states $|\langle \phi_i | \psi(x, t) \rangle|^2$, as follows,

$$
P_{\text{excited}} = \sum_{i=0}^{n_{\text{dissoc}}} \left( \frac{i}{n_{\text{dissoc}}} \right) |\langle \phi_i | \psi(x, t) \rangle|^2,$$

(17)

where $n_{\text{dissoc}}$ is the highest level in the bound state, $n_{\text{dissoc}} = 23$ in the case of LiH. The expected value of the level is
normalized by $n_{\text{dissoc}}$ in order to balance the amount of dissociation, whose value range is $[0, 1]$. Based on the above
settings, optimization of the chirp parameters was performed for a single pulse.

In the case of the DSP method, there are five parameters to be optimized, the chirp parameters of the main pulse and
the DSP, $\gamma_{\text{Main}}, \gamma_{\text{DSP}}, \gamma_{\text{Main}}$, and $\gamma_{\text{DSP}}$, and the delay time between the main pulse and the DSP ($\Delta t_0 = t_0^{\text{DSP}} - t_0^{\text{Main}}$).

Since the computational cost of Bayesian optimization increases in proportion to the cube of the number of variables
[15], it is difficult to handle five variables in Bayesian optimization. Thus, CMA-ES [16] was used for optimization.
CMA-ES adaptively updates and optimizes the covariance matrix of the multivariate normal distribution that
generates candidate solutions based on the evaluation values of the candidates. It is known that CMA-ES is a robust
method that can be optimized even in noisy high-dimensional parameter spaces [17, 18].

In the optimization using CMA-ES, the number of generations was set to 150 and the number of individuals to 16
for each generation. The objective function was set to be only the dissociated wavepacket because a certain amount
of dissociation can be expected by adding the DSP. The initial values $\gamma_{\text{Main}}, \gamma_{\text{Main}}^{\text{DSP}}$ are inherited from the optimal
parameters for the single pulse case. The value range of the parameters is not restricted, allowing the parameters to
be negative. Negative parameters give the possibility of upchirping or the DSP reaching ahead of the main pulse.

VI. ESTIMATION OF ENERGY EFFICIENCY

To determine the energy efficiency of photodissociation by VLC, the energy of the laser pulse and the amount of
dissociated molecules have to be estimated. Here, we show a rough estimation of these values. First, we explain how
to estimate the energy of a pulse. The electric field of a Gaussian pulsed laser $E(t)$ is determined by the maximum
electric field intensity $E_0$ and the Gaussian spreading parameter $\alpha$ as follows,

$$
E(t) = E_0 \exp(-\alpha^2(t-t_0)^2) \cos(\omega(t)(t-t_0)).
$$

(18)

The irradiance $I$[W/cm²] of a pulsed laser is expressed using the maximum electric field intensity $E_0$[V/cm], as follows
[19],

$$
I = \frac{c\epsilon_0 n}{2} E_0^2,
$$

(19)

where $c$, $\epsilon_0$, and $n$ are the speed of light the dielectric constant, and refractive index of the vacuum, respectively. The
energy of a pulse $e$[J] is expressed by the irradiance $I$[W/cm²], pulse width $T$[s], and cross section of the pulse $S$[cm²]
as follows,

$$
e = STI \simeq 0.002 \cdot \frac{E_0^2 S}{\sqrt{\alpha}},
$$

(20)

where the pulse width $T$[s] is defined as the full width at half maximum of the Gaussian pulse, $T = 2\sqrt{2\log 2} \sigma \simeq
2.23/\sqrt{2\alpha}$. In the case of a single pulse, the total energy required to cause VLC is calculated by Eq.20. In the case of
the DSP method, two pulses, the main pulse and the DSP, are required for VLC. We assume that the optical system
for the implementation of the DSP method is like that used in pump-probe spectroscopy with a single light source.
Assuming that there is no energy loss in such an optical system, the total energy required for VLC become the sum of
the main pulse and the DSP energy. Since this is a very rough estimate, it is considered that more energy is required for the DSP method in practice.

Next, we explain the calculation method for the amount of dissociated molecules. The amount of molecules \( N_{\text{all}} [\text{mol}] \), present in the region of the pulse cross section \( S [\text{cm}^2] \), can be written as \( N_{\text{all}} = \rho S \), where \( \rho [\text{mol/cm}^2] \) is the areal density of the molecules. Assuming that the laser pulse causes dissociation with a dissociation probability \( d \), the amount of dissociated molecules \( N_{\text{dissoc}} [\text{mol}] \) is given by

\[
N_{\text{dissoc}} = N_{\text{all}} d = \rho S d.
\]  

(21)

For simplicity, we assume that \( \rho = 1 [\text{mol/cm}^2] \).

From Eqs. 20 and 21, the energy efficiency \( P [\text{mol/J}] \) of photodissociation by VLC can be estimated as follows,

\[
P = \frac{N_{\text{dissoc}}}{e} \approx 478 \cdot \frac{d\sqrt{\alpha}}{E_0^2}.
\]  

(22)

Based on the above formulation, we estimated the energy efficiency for the results of the single-pulse case and DSP method, respectively.

![FIG. 4: Calculated energy efficiencies for (a) a single pulse and (b) the DSP method](image)

Figure 4 shows the calculated energy efficiency of each case. It can be seen that the DSP method shows a higher energy efficiency than the single pulse case. The maximum energy efficiency for a single pulse is 0.193 [\text{mol/J}], while that for the DSP method is 0.763 [\text{mol/J}], which is about four times higher. This result shows the superiority of the DSP method with respect to energy efficiency.

VII. EFFECT OF RELATIVE PHASE

In the optimization of the parameters of the DSP method, the relative phase between the electric field of the main pulse and that of the DSP was fixed at zero. This is because the relative phase changes significantly with changes in the parameters, such as the chirp parameters, making it difficult to optimize it simultaneously with those parameters. However, the effect of the relative phase is not negligible, since it affects the time evolution of the probability amplitudes of the vibrational levels. In this section, we discuss the effect of the relative phase between the main pulse and DSP on the photodissociation by the DSP method.

For the 54 pulses considered in the DSP method with optimized parameters at a relative phase of zero, we performed a wavepacket dynamics simulation by varying the relative phases from 0 to 2\( \pi \).
Figure 5 shows the relationship between the dissociation probability and relative phase. Figure 5 shows that the relative phase has a significant effect on the dissociation probability. The change in relative phase affects the phase of the probability amplitude of the vibrational levels and changes the interference between them, which leads to a change in the dissociation probability, shown in Fig.5. Therefore, this result can be attributed to the quantum interference effect between the vibration levels.

In addition, it is notable that the relationship between the dissociation probability and the relative phase is approximately cosine functional. Since the optimization was performed with the relative phase fixed at zero, the optimized parameters were considered to have been chosen to maximize the dissociation probability at a phase of zero. The fact that the dissociation probability becomes minimum at a relative phase of $\pi$, that is the antiphase to the case of zero, is a characteristic result in interference phenomena. Since the excitation process results from the complex interference between many vibrational levels, it is not obvious that such a cosine functional relationship appears between the dissociation probability and relative phase. A complete interpretation of these results will require a more detailed discussion.
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