Lifetime of metastable helium molecule in intense laser fields

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On the basis of the Floquet formalism linked with the McCurdy-McNutt stabilization technique, metastable states of helium dimer in intense laser fields were investigated. The potential energy curve of helium dimer is found to become attractive when the laser intensity is sufficiently high, and the previous prediction [T. Yasuike and K. Someda, J. Phys. B **37**, 3149 (2004)] based on the Kramers-Henneberger high-frequency approximation is confirmed. Under appropriate laser conditions, the lifetime is found to be sufficiently long to discretize vibrational states, owing to the nonperturbative stabilization effect in photoionization.

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I. INTRODUCTION

It has recently been reported that intense laser fields are capable of changing the characters of atoms and molecules [1–3]. For instance, the linear triatomic molecules such as carbon dioxide and carbon disulfide become bent in intense laser fields [4–6]. Intense laser fields are found to trigger the novel photochemical reaction of aniline-ammonia clusters resulting in drastic rearrangement of chemical bonds [7]. These experimental observations imply that the use of intense lasers can open a new phase in the quantum control of chemical reactions. In this context, the authors have reported the theoretical study predicting a laser-induced chemical bond between two helium atoms [8].

The previous study [8] was based on the Kramers-Henneberger (KH) high-frequency approximation, and there remain open questions in the following two respects; (1) the validity range of the KH high-frequency approximation especially against finite laser frequencies, and (2) the lifetime of the helium diatomic molecule against photoionization, which may be very fast in intense fields. Aiming at clarifying these points, the present paper reports the results of rigorous calculation based on the Floquet formalism without any modeling. Particular attention is focused on the evaluation of lifetime against ionization.

The Floquet Hamiltonian matrix is constructed by the use of quantum chemical computer codes. The McCurdy-McNutt stabilization method [9] is adopted to evaluate lifetimes. The appropriate choice of basis set functions that suits to the stabilization method is investigated. The use of a kind of distributed Gaussians with a spatial scaling parameter is found to produce the reliable values for the lifetime.

The lifetime is evaluated as a function of laser intensity, frequency, and internuclear distance. The favorable combination of laser intensity and frequency that maximizes the lifetime as well as the bonding energy is sought. Under the optimal condition, the helium diatomic molecule is found to

possess a discrete vibrational state which lives for 5.6 fs even in intense laser fields.

II. METHOD

A. Floquet formalism

In the presence of a laser field, the electron motion in a molecule is described, within the Born-Oppenheimer approximation, by the Hamiltonian

$$H = \frac{1}{2}\sum_j \left(\boldsymbol{p}_j + \frac{1}{c}\boldsymbol{A}(t) \right)^2 - \sum_j \sum_a \frac{Z_a}{|\mathbf{r}_j - \boldsymbol{R}_a|} + \sum_{j<k} \frac{1}{|\mathbf{r}_j - \boldsymbol{r}_k|}, \quad (1)$$

where $\boldsymbol{p}_j$ and $\boldsymbol{r}_j$ are the momentum and coordinate of the jth electron, respectively, $\boldsymbol{R}_a$ and Z_a are the position and charge of the ath nucleus, respectively, c is the light velocity, and $\boldsymbol{A}(t)$ is the vector potential. The atomic units are used throughout. The laser field is assumed to be linearly polarized, and the dipole approximation is adopted. These conditions lead to the vector potential $\boldsymbol{A}(t)$ of the form

$$\boldsymbol{A}(t) = \boldsymbol{\epsilon}\frac{cF}{\omega}\cos \omega t, \quad (2)$$

where $\boldsymbol{\epsilon}$ is the polarization vector, F is the strength of the electric field, and ω is the angular frequency of the field. By taking this form of vector potential, the molecular electronic Hamiltonian H has time-periodicity. According to the Floquet theorem [10,11], the solutions of the time-dependent Schrödinger equation

$$i\frac{\partial\Psi}{\partial t} = H\Psi \quad (3)$$

can be represented as the quasienergy state of the form

$$\Psi(t) = e^{-iEt}\Phi(t) = e^{-iEt}\sum_{n=-\infty}^{+\infty} \Phi_n e^{in\omega t}. \quad (4)$$

From Eqs. (3) and (4), one can derive the equation

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$$\left(H(t) - i\frac{\partial}{\partial t}\right)\Phi(t) = E\Phi(t), \qquad (5)$$

which indicates that the function $\Phi(t)$ is an eigenfunction of the Floquet Hamiltonian

$$H_F \equiv H(t) - i\frac{\partial}{\partial t}. \qquad (6)$$

One can rewrite Eq. (5) in terms of the Fourier component Φ_n as follows:

$$\begin{pmatrix} & \vdots & & \\ & H_0 + \hbar\omega & H_{+1} & H_{+2} & \\ \cdots & H_{-1} & H_0 & H_{+1} & \cdots \\ & H_{-2} & H_{-1} & H_0 - \hbar\omega & \\ & & \vdots & \end{pmatrix} \begin{pmatrix} \vdots \\ \Phi_{+1} \\ \Phi_0 \\ \Phi_{-1} \\ \vdots \end{pmatrix} = E \begin{pmatrix} \vdots \\ \Phi_{+1} \\ \Phi_0 \\ \Phi_{-1} \\ \vdots \end{pmatrix}, \qquad (7)$$

where

$$H_\mu = \frac{\omega}{2\pi}\int_0^{2\pi/\omega} H(t')e^{i\mu\omega t'}dt'. \qquad (8)$$

In the present study, we have adopted the velocity gauge, and the explicit forms of Eq. (8) are given by

$$H_n = \begin{cases} \displaystyle\sum_j \frac{p_j^2}{2} - \sum_j \sum_a \frac{Z_a}{|r_j - R_a|} + \sum_{j<k} \frac{1}{|r_j - r_k|} & (n = 0), \\[4mm] \displaystyle\frac{F}{2\omega}\sum_j p_j \cdot \boldsymbol{\epsilon} & (n = \pm 1), \\[4mm] 0 & (n = \pm 2, 3, \ldots). \end{cases} \qquad (9)$$

On the basis of the eigenstates of H_F, one can discuss quasistationary electronic states of the molecule in a laser field.

In the presence of a laser field, the bound states of the unperturbed system H_0 are subject to ionization, and become resonances. As a result, the spectrum of the Floquet Hamiltonian does not contain any real discrete eigenvalues. Under appropriate laser conditions, the bound electronic states become metastable quasibound states, i.e., sharp resonances embedded in ionization continua.

B. McCurdy-McNutt stabilization method

There are several techniques which enable us to evaluate resonance positions and widths as the complex-valued eigenenergies. Among them, the McCurdy-McNutt version of the stabilization method [9] has been employed in the present study. The stabilization method is based on the following idea [12]. The continuous spectrum is discretized when the system is confined in a box. The resultant energy levels originating from scattering states depend directly on the size of the box η. On the other hand, the energies of resonance states should be insensitive to η because the resonance wave functions are spatially localized on the molecule. Instead of the box-boundary condition, a similar situation can be brought by basis set representation to the original scattering problem. When one prepares diffuse basis functions containing a parameter η, which scales the spatial ex-

tension of each, the scattering wave functions are mainly composed of them. The discretized energies for continua depend sensitively on the scaling parameter η, while the resonance energies do not.

We solve the secular equation

$$\det|\mathbf{H}(\eta) - \epsilon\mathbf{I}| = 0, \qquad (10)$$

and obtain energy eigenvalues $\epsilon(\eta)$ as a function of the scaling parameter η. In the graph of $\epsilon(\eta)$ plotted against η, which is called stabilization graph, the lines representing scattering states collide with those representing resonance states. Since they are the solution of the same secular equation, avoided crossings take place between them.

The complex eigenvalues can be obtained based on the complex variational principle [13]. The function $\epsilon(\eta)$ is analytically continued to the complex η plane, and one seeks the complex stationary point η_s defined by

$$\left(\frac{\partial\epsilon(\eta)}{\partial\eta}\right)_{\eta_s} = 0. \qquad (11)$$

The complex-valued eigenenergies are given by the complex stationary values of ϵ,

$$\epsilon(\eta_s) = E_R - \frac{i}{2}\Gamma, \qquad (12)$$

where E_R and Γ are the resonance energy and width, respectively. The stationary points η_s are found in the vicinity of the avoided crossings in the stabilization graph. It should be noted that $\epsilon(\eta)$ has no extremum on the real η axis. The essential feature of the McCurdy-McNutt method is in the procedure of the analytic continuation of $\epsilon(\eta)$. The function $\epsilon(\eta)$ is a root of the secular equation, Eq. (10), and has associated branch-point structures. Therefore the direct analytic continuation of $\epsilon(\eta)$ falls into difficulties. McCurdy and McNutt have surmounted the difficulties by the analytic continuation of the characteristic polynomial rather than $\epsilon(\eta)$ itself.

C. Details of implementation

In order to obtain $\epsilon(\eta)$, the SCF and Floquet CI calculations of He$_2$ were carried out. The employed basis set consists of (1) 6-31G** functions placed at the nuclear position, $z = \pm z_{He}$, and (2) s-type GTOs with the orbital exponent

$$a = \frac{16}{\eta^2} \qquad (13)$$

distributed at the positions

$$z = \pm\left\{z_{He} + \frac{\eta}{4}\left(n - \frac{\phi}{180}\right)\right\}; \quad (n = 1, 2, \ldots, 20), \quad (14)$$

where the parameter ϕ is set equal to 90. We carried out the SCF calculation without a laser field, and resulting MOs were employed in the subsequent Floquet CI calculation.

The scaling parameter η in Eq. (14) determines the minimum wavelength of continuum wave functions. This choice of the scaling parameter is in accordance with the concept of the box stabilization [14], rather than the scaling of the orbital exponent of the basis functions placed at the nuclear positions [15]. The former choice was found to produce more localized avoided crossings in the stabilization graph, and lead to more reliable results than the latter choice.

The additional parameter ϕ governs a relative phase between the wave function localized on the atoms and that of the continuum consisting of the distributed GTOs. In the range of $0 \le \phi \le 80$, a significant ϕ dependence was observed in the one-electron continua obtained by the SCF calculation. The naive choice of $\phi = 0$ was found to be unsuitable for the subsequent Floquet-stabilization calculations as follows: For $90 \le \phi \le 120$, the SCF stabilization graphs, i.e., the MO energies plotted as a function of η, were found to exhibit an isolated avoided crossing which clearly indicates the existence of a resonance in the range of the MO energy of approximately 10.0. The corresponding MO has maximum amplitude in the region of $z = \pm(z_{He} \sim z_{He} + 0.5)$. On the other hand, in the SCF stabilization graphs for $0 \le \phi \le 80$, the avoided crossings were found to be overlapped with each other involving 5–7 MOs so that the resonance is hardly recognized. This implies that the capability of the basis set depends on ϕ. In the subsequent Floquet-stabilization calculations, the scaling parameter η is set in the range of 1.9
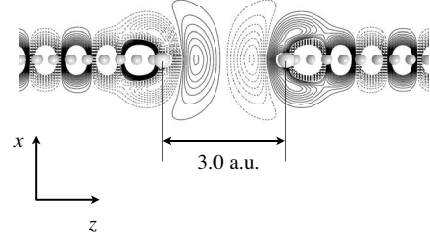

FIG. 1. Contour of the MO with the orbital energy $\epsilon = 8.52$. This MO is occupied in the main configuration of the discretized continuum state which undergoes the avoided crossing with the resonance state in the stabilization graph. The internuclear distance is 3.0 a.u., and the value of η is 2.0. The two large spheres indicate the positions of He nuclei, while small spheres do the positions of the s-type GTOs.

$\le \eta \le 2.1$. It is conjectured that, for these values of η, the basis set with $0 \le \phi \le 80$ is incapable of describing the resonance wave function which should have structures at the close vicinity of the He atoms. Thus the basis set with $0 \le \phi \le 80$ tries to describe the resonance but unsuccessfully, and, as a result, many MOs come to carry the mixed characters of resonance and continuum. Such MOs are harmful in the subsequent Floquet-stabilization calculations, in which we need MOs purely localized on the atoms and those purely representing continuum. In fact, the choice of $\phi = 0$ leads to a useless Floquet-stabilization graph, in which avoided crossings exhibit gaps with different magnitudes depending on η. Accordingly, we employed the basis set with $\phi = 90$, which generates the MOs having well-defined characters so that the resonance and continua are maximally decoupled with each other. The choice of $\phi = 90$ leads to ideal Floquet-stabilization graphs, in which the identical resonance energy can be obtained from a sequence of isolated avoided crossings, as described below.

The resonance found in the SCF-stabilization graph might be interpreted as a shape resonance in the electron scattering by the He-He system. However, we do not discuss further the physical meaning of this resonance because it has no direct relevance to the resonance of ionization of the He-He system in intense fields obtained from the subsequent Floquet-stabilization calculations with $\phi = 90$.

As indicated in Eq. (14), we did not distribute s-type GTOs in between the two nuclei. If we do so, numerical difficulty arises. For instance, if we distribute s-type GTOs on equally spaced grid points $\pm n\eta/4$ $(n = 1, 2, 3, \ldots)$ on the z axis, a pair of the grid points coincides with the nuclear positions $\pm z_{He}$ at particular values of η. At such a value of η, the overlap between an s-type GTO and the 6-31G** functions becomes large, and basis set comes to have severe linear dependency. This leads to numerical instability and prevents us from preparing stabilization graphs. By this reason, s-type GTOs were not placed in between the two nuclei. On the other hand, the 6-31G** basis set of helium involves a p_z function, which helps to construct the wave function in the internuclear region. Figure 1 shows the contour plot of the MO describing a continuum state. It can be seen that the internuclear region is filled with a wave with several nodes. This indicates that the omission of s-type GTOs in the inter-

nuclear region does not harm the physical meaning of the calculation as far as the internuclear distance is not large. Inspection of the MO density confirmed that our basis set remains good for continuum states when the internuclear distance is shorter than 3 a.u. As regards description of the chemical bond formation, the 6-31G** basis set suffices for all internuclear distances.

The MOs are generated by the SCF calculation without laser field. By employing these MOs, the configuration state functions (CSFs) in the zero field are constructed and used as the multielectron basis functions for the matrix representation of the Floquet Hamiltonian. The calculations were carried out by using the modified GAMESS program suite [16]. The matrix representation of $H_{\pm 1}$ is estimated from the velocity form of the transition dipole moment. The laser polarization vector ϵ was set parallel to the molecular axis. The ground and all the singly excited CSFs are taken into account. The single Floquet block contains 97 CSFs, and 15 Floquet blocks ranging from $-7\hbar\omega$ to $+7\hbar\omega$ were typically considered (for $\omega=9.0$ and 10.0). The size of the resulting Floquet Hamiltonian matrix is 1455×1455. Attention is focused on the energy region $-\hbar\omega<E<0$ in order to seek the eigenstate correlating to the ground state of He$_2$ in the null field limit. For the case of small ω (=8.0) and large α, the convergence was deteriorated because of the strong coupling among the field-free states, and 19 Floquet blocks (1843 $\times$1843 Floquet Hamiltonian matrix) were included in calculations.

The full-single Floquet CI employed in the present study is widely accepted as a method providing a good physical picture for molecular dynamical processes in intense fields. As shown in Sec. V, the laser-induced chemical bond is successfully described by the present full-single Floquet CI calculation. On the other hand, ionization by intense lasers may contain various processes such as double excitations producing an electronically excited ion. However, inclusion of such a process in the present Floquet CI calculation is not straightforward for the following reason. As discussed in Sec. VII B, the laser-induced chemical bond is ascribable to the drastic rearrangement of MOs resulting in the formation of unusual bonding and nonbonding MOs. In such a situation, it may not necessarily be justifiable to discuss double excitations with respect to the electron configuration defined in the zero field. Therefore the selection of suitable CSFs for multiply excited CI is not straightforward because our CSFs are defined in the zero field. If one is allowed to discuss the double excitations based on the field-free electron configuration, the corresponding final ionic states are exclusively the Rydberg states of He$_2^+$ due to the absence of vacant valence MOs in the He-He system. Such double excitations are assumed to loose clear distinction from double ionization producing in intense fields, and are not considered in the present calculation.

A typical stabilization graph is shown in Fig. 2. This is quite similar to the one obtained in the benchmark study for a time-periodic simple one-dimensional (1D) system based on the box-size scaling stabilization method [14]. The applicability of the present calculation is thus verified.

In order to determine η_s, a local avoided crossing between a resonance $\epsilon_r(\eta)$ and a discretized continuum $\epsilon_c(\eta)$ is se-
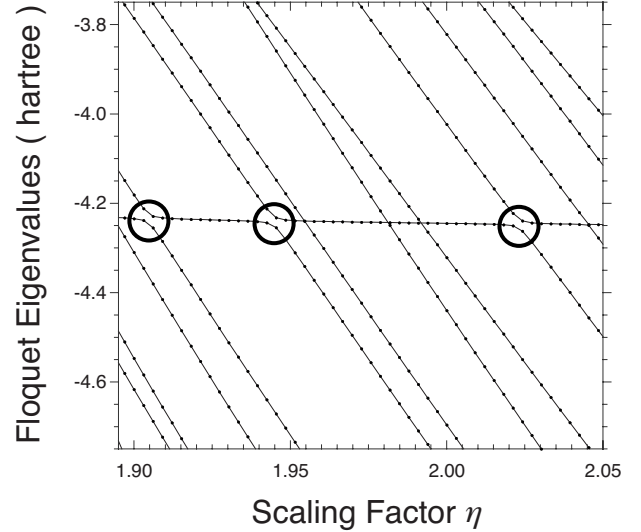

FIG. 2. Stabilization graph, i.e., quasienergy eigenvalues ϵ plotted against the scaling parameter η. The circles indicate the avoided crossing between the resonances and the discretized continua.

lected. These eigenvalues are assumed to be the roots of the second-order characteristic polynomial

$$\epsilon^2 - p_1(\eta)\epsilon + p_0(\eta) = 0, \tag{15}$$

where $p_1(\eta)=\epsilon_r(\eta)+\epsilon_c(\eta), p_0(\eta)=\epsilon_r(\eta)\epsilon_c(\eta)$. The functions, $p_1(\eta)$ and $p_0(\eta)$, are analytic functions of η and can be expanded in the power series of η. In the present study, we construct $p_1(\eta)$ and $p_0(\eta)$ by fitting the data, $\epsilon_r(\eta)+\epsilon_c(\eta)$ and $\epsilon_r(\eta)\epsilon_c(\eta)$, to quadratic polynomials of η. The analytic continuations of $p_1(\eta)$ and $p_0(\eta)$ are self-evidently obtained, and the corresponding $\epsilon(\eta)$ are obtained as

$$\epsilon(\eta) = \frac{p_1(\eta) \pm \sqrt{p_1^2(\eta) - 4p_0(\eta)}}{2}. \tag{16}$$

The complex eigenvalues are obtained as the complex extremum $\epsilon(\eta_s)$ determined by Eq. (11). In the stabilization graph, $\epsilon_r(\eta)$ of a given resonance undergoes several avoided crossings with different curves of $\epsilon_c(\eta)$. According to the principle of the stabilization method, different avoided crossings should lead to the identical values for E_R and Γ. It is confirmed that our stabilization graphs retain that property.

In the following calculations, we used the avoided crossings between the resonance under consideration and the one-photon absorption continuum states, i.e., the continuum states having main configurations in the next $(n=-1)$ Floquet block. Such avoided crossings occur at around $\eta=2$.

The value of $\eta=2$ limits the maximum energy of the discretized continuum to 18 a.u. The photon energy in the present calculation is in the range $8.0\leq\hbar\omega\leq10.0$. It follows that the final channels considered in the calculations are restricted to one and two photon absorption continua. Such a truncation of the final channel is appropriate because the higher-order above-threshold ionization is often negligible in high-frequency conditions [22]. On the other hand, the number of Floquet blocks needed for convergent results was typically 15. This is because the final continuum states in intense
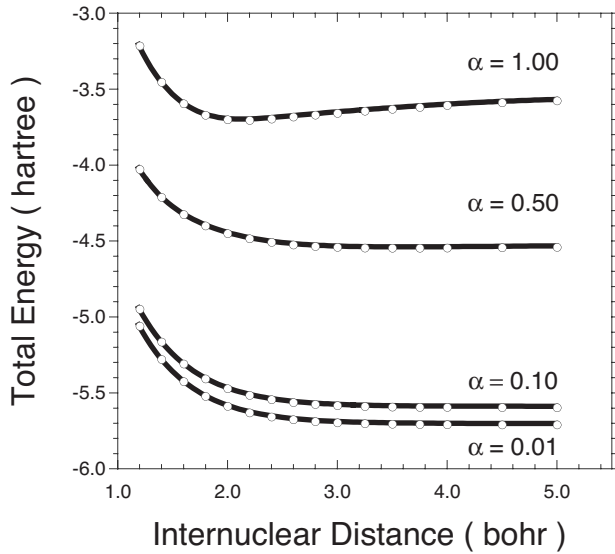
FIG. 3. Potential energy curves for the helium dimer based on the KH approximation.

laser fields are the Volkov states and are superpositions of different photon-number states in the velocity gauge. In fact, it can be shown that the Volkov states for considered laser conditions span 10–15 different photon-number states.

III. POTENTIAL ENERGY CURVES BASED ON THE KH APPROXIMATION

The previous prediction of the laser induced He-He chemical bond was based on the KH approximation [8], the high-frequency approximation in the Kramers-Henneberger frame. The KH Hamiltonian H_{KH} is given by

$$H_{KH} = \sum_j \frac{p_j^2}{2} - \frac{\omega}{2\pi} \int_0^{2\pi/\omega} \sum_{j,a} \frac{Z_a}{|r_j - R_a + \alpha\epsilon \sin \omega t|} dt$$

$$+ \sum_{j<k} \frac{1}{|r_j - r_k|}, \tag{17}$$

where $\alpha \equiv F/\omega^2$ is the ponderomotive radius. The ponderomotive radius is the amplitude of the electron quiver motion in the field and can be an index for the effective coupling strength between matter and light in the high-frequency situation [17,18].

Figure 3 shows the potential energy curves of He$_2$ based on the KH approximation. When $\alpha < 0.5$, the potential curve is repulsive, and no chemical bond is formed. In the case of $\alpha = 1.0$, the potential curve has a well with the minimum at around 2 a.u. The KH approximation thus leads to the conclusion that the formation of the chemical bond requires $\alpha \geq 1.0$. In other words, the amplitude of the laser-induced electron quiver motion should amount to the size of the molecule in order to change the molecular characters drastically.

IV. LIFETIME AND POTENTIAL ENERGY CURVE: SMALL α

Within the KH approximation, the larger α is preferred for the formation of the chemical bond. On the other hand, large
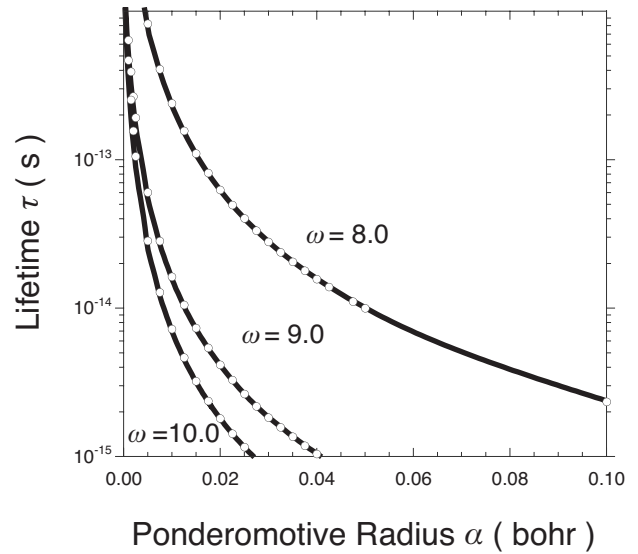

FIG. 4. Photoionization lifetime of He$_2$ ($R=2.4$) as a function of α in the range $0 \leq \alpha \leq 0.01$.

α may cause fast photoionization. In order to clarify the laser-condition dependence of the photoionization lifetime, the Floquet CI stabilization calculation was carried out.

The present system, a helium dimer in a cw laser field, has three independent parameters: the internuclear distance R, the ponderomotive radius α, and the angular frequency of the field ω. We examine the photoionization lifetime $\tau \equiv 1/\Gamma$ as a function of α and ω with the fixed internuclear distance $R=2.4$ a.u., which is a representative value for the bond length in the case that the laser-induced chemical bond is formed [8].

Figure 4 shows the results for small α (<0.1). The value of $\alpha=0.1$, for instance, corresponds to the laser intensities 1.438, 2.303, and 3.510×10^{18} W cm^{-2} for $\omega=8.0$, 9.0, and 10.0, respectively. With increasing laser intensity, the lifetime decreases quickly. The lifetime shorter than 1 fs cannot be evaluated by the present method because the avoided crossings in the stabilization graph become large and overlap with the adjacent ones. The lifetimes less than 1 fs are supposed to be too short to form discrete vibrational states if the adiabatic potential had a well.

In the case of $\alpha=0.01$ and $\omega=10.0$, the lifetime remains on the order of 10 fs, the typical period of molecular vibrations. The result of the Floquet CI stabilization calculation is shown in Fig. 5, together with the KH potential curve. The resonance energies Re(ϵ) accurately agree with the KH potential curve in spite of the finite frequency. Both the curves remain purely repulsive, indicating that the laser intensity corresponding to $\alpha=0.01$ is insufficient to induce any chemical bond. The energy width depends on the internuclear distance only weakly as shown in Fig. 5.

In short, it seems that the laser fields sufficiently strong to induce a chemical bond inevitably destroy the molecule through very fast ionization. However, this simple conjecture turns out to be wrong in the following section. The phenomenon called "stabilization" takes place at stronger fields and makes it possible to keep the molecule live long.
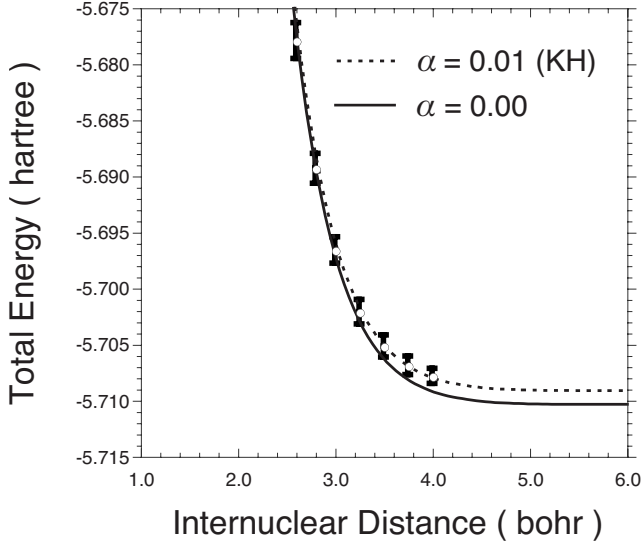
FIG. 5. Potential energy curves for the helium dimer for weaker intensity. The solid curve is the potential energy curve in the null field. The dotted curve is the one with the KH approximation for $\alpha=0.01$. The circles with the error bar represent the Floquet CI stabilization results for the laser condition of $\alpha=0.01$ and $\omega=10.0$. Each error bar indicates the resonance width Γ.

V. LIFETIME AND POTENTIAL ENERGY CURVE: LARGE α

The α dependence of photoionization lifetime for $0.93 < \alpha < 1.09$ is shown in Fig. 6. In all the cases of $\omega=8.0$, 9.0, and 10.0, the lifetime recovers and exhibits a local maximum. The maximum values reach subpicoseconds. Recovery of the lifetime with increasing laser intensity is known as the stabilization effect. It is a nonperturbative effect and has been shown for simple model systems [19–23]. In particular, the corresponding sharp dips in the ionization rate as a function of α have been reported by Yao and Chu [22], and
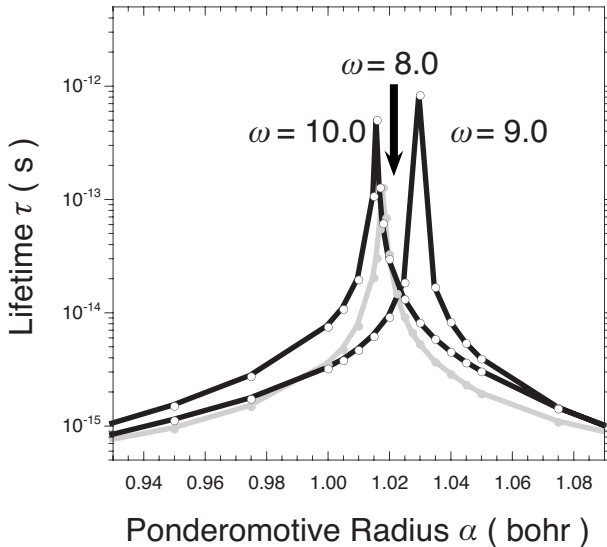

FIG. 6. Photoionization lifetime of He$_2$ ($R=2.4$) as a function of α in the range $0.93 \le \alpha \le 1.09$.
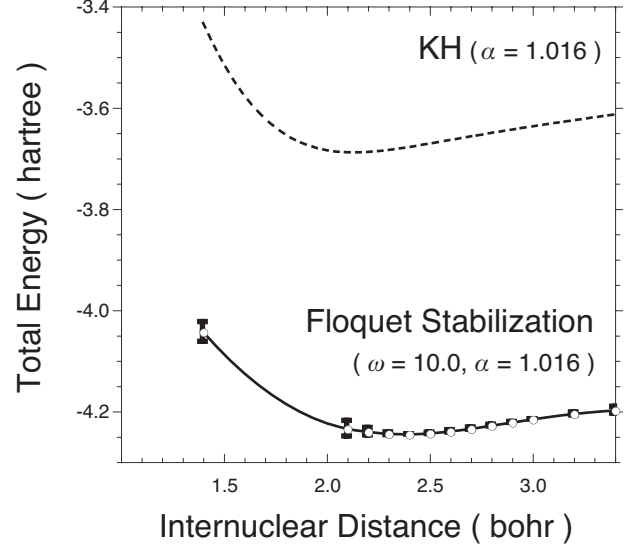

FIG. 7. Potential energy curves of the helium dimer for the laser condition of $\alpha=1.016$ and $\omega=10.0$. The solid curve represents the results with the Floquet CI stabilization method. Each error bar indicates the energy width Γ. The dotted curve is the result of the KH approximation in the corresponding condition ($\alpha=1.016$).

ascribed to a vanishment of an interaction matrix element at particular values of α. The present observation seems to be interpretable by the same mechanism. This point is discussed in Sec. VII A below.

Figure 7 shows the potential energy curve for the case of $\alpha=1.016$ and $\omega=10.0$. The potential curve has a well, indicating the formation of a chemical bond between two He atoms. The potential energy curves obtained with the KH approximation ($\alpha=1.016$) is also shown. Although the potential curve obtained from the KH approximation is shifted from that of the Floquet CI stabilization method, both the curves are attractive. The KH approximation is yet useful for discussing qualitative behavior of the potential energy curve even for finite ω. As shown in Fig. 7, the lifetime strongly depends on the internuclear distance, in contrast to the case of small α. The lifetime τ ranges from $\tau=0.5$ to 1000 fs depending on R.

VI. VIBRATIONAL STATES

Formation of a molecule means the presence of discrete vibrational states. We examine whether the potential curve shown in Fig. 7 holds discrete vibrational levels. Within the Born-Oppenheimer approximation, the nuclear wave function of a metastable electronic state can be described by the stationary Schrödinger equation with a complex-valued potential energy function. The eigenvalues are complex. From their imaginary parts one can obtain the lifetimes of vibrational states.

The vibrational levels and the lifetimes are obtained by diagonalizing the Hamiltonian matrix constructed by the discrete variable representation. The potential shown in Fig. 7 is found to hold eight vibrational states. Table I summarizes the vibrational energy level spacing, the energy widths, and the

TABLE I. Level spacing, energy width, and lifetime for metastable vibrational states of He_2

v	$E_{v+1} - E_v$ (eV)	Γ_v (eV)	τ_v (fs)
0	0.24750	0.11745	5.60
1	0.22403	0.23804	2.76
2	0.19898	0.31083	2.12
3	0.15807	0.36400	1.81
4	0.16854	0.33489	1.96
5	0.16759	0.32145	2.04
6	0.13235	0.38038	1.73
7	-	0.45521	1.45

corresponding lifetimes. Although the lifetime of the electronic state with fixed R exceeds 1000 fs at the equilibrium internuclear distance, the lifetimes of the vibrational states are a few fs in common.

If the level spacing is larger than the energy width, the vibrational level is distinguishable as an isolated peak in the energy spectrum. The existence of an isolated vibrational level is none other than the proof of the He_2 molecule formation. The ground state $v = 0$ satisfies this condition. It is thus shown that helium dimer becomes a covalent-bonding diatomic molecule in high-frequency intense laser fields. On the other hand, even apart from the extreme laser condition, the experimental observation is extremely difficult because the lifetime is less than 1 fs for the region of α between 0.025 and 0.93.

VII. DISCUSSION

A. Stabilization in intense fields

When the interactions between molecules and laser fields are treated by a perturbation theory, the ionization rates are typically proportional to the power of intensity, I^n, where n is the number of photons absorbed. With increasing laser intensity, such a power law breaks down. Several theoretical studies have reported the phenomena in which the ionization rate does not necessarily increase monotonically with laser intensity [19–23]. Such phenomena are called stabilization. The stabilization phenomena studied within the framework of the Floquet formalism can be classified into two types as follows: Type (A); the ionization rate monotonically decreases with increasing laser intensity when the intensity is sufficiently high [19,20]. Type (B); the ionization rate as a function of intensity exhibits sharp dips [22,23]. Physical interpretations for both the types of stabilization can be provided by the Gavrila-Kaminski theory [24]. According to the latter theory, the ionization rate is determined by the matrix element between the bound state of the KH Hamiltonian and the plane wave of the ionization continua in the KH frame. The stabilization of type (A) is ascribable to the asymptotic decrease of the matrix element as a function of the ponderomotive radius α [19]. At the same time, the matrix element exhibits oscillatory behavior as a function of α and vanishes

at particular values of α [22]. Such vanishment causes the stabilization of type (B).

Yao and Chu have presented a simple formula [22] which enables us to estimate the position of the stabilization of type (B). According to the formula, the vanishment of the matrix element occurs when the condition

$$J_n(\alpha k_n) = 0 \qquad (18)$$

is satisfied, where J_n represents the Bessel function of the nth order, and k_n is the wave number of the ejected electron by absorption of n photons. In the derivation, the wave function of the initial bound state is assumed to be delocalized compared with the wavelength of the outgoing wave. The integral of the interaction potential in the KH frame multiplied by the plane wave vanishes at a particular combination of α and the wavelength of the outgoing electron as indicated by Eq. (18).

The observation in the present study, i.e., sharp peak of lifetime as a function of α, is explained by the stabilization of type (B) as follows. In the present case of He_2, the electron binding energy in the KH approximation $E_b(\alpha)$ is given by

$$E_b(\alpha) \sim -0.86 + 0.66\alpha - 0.20\alpha^2 \qquad (19)$$

at around $\alpha = 1$, and this leads to $k_1 = \sqrt{2\{10 - E_b(\alpha)\}}$ for $\omega = 10.0$. Corresponding to the first zero of $J_1(x)$ at $x = 3.8$, the vanishment of $J_1(\alpha k_1)$ occurs at $\alpha = 0.88$. As an order of magnitude estimation, this is in agreement with the peak position $\alpha = 1.016$ of the calculated lifetime shown in Fig. 6. This indicates that the peak in the lifetime is explicable by the stabilization of type (B), i.e., the vanishment of interaction occurring due to mismatch between the interaction potential and the wavelength of the outgoing electron.

B. Formation mechanism of the laser-induced chemical bond

The KH approximation is derived from a time-averaging of the Hamiltonian, and is exact only in the limit of $\omega \to \infty$. However, the present study demonstrated that the KH eigenvalues, ϵ_{KH}, approximate to the resonance energy, $\text{Re}(\epsilon)$, obtained by the Floquet CI stabilization method. In the case of small α shown in Fig. 5, the approximation accuracy is very high. In the case of large α, the disagreement of the absolute values between ϵ_{KH} and $\text{Re}(\epsilon)$ is relatively large, but the shapes of the potential curves shows qualitative accordance. The KH approximation is considered to be useful for qualitative discussions on the behavior of the resonance energy.

Having confirmed the validity of the KH approximation, we can interpret the formation mechanism of the laser-induced He-He chemical bond based on this approximation. According to the previous analysis of the KH molecular orbitals [8], the bond formation is ascribable to the laser-induced deformation of molecular orbitals: In intense laser fields, the energy of the $1s$ atomic orbital becomes high and close to that of the $2p_z$ atomic orbital. By this energy change, not only $1s$ but also $2p_z$ atomic orbitals participate in the formation of the lowest-lying molecular orbitals. As a result of linear combination of two sets of $1s$ and $2p_z$ atomic orbitals, one bonding, two nonbonding, and one antibonding mo-

lecular orbitals are generated. The lowest two molecular orbitals, which are one bonding and one nonbonding, are occupied by four electrons, and the chemical bond is formed. It should be noted that such a simple interpretation is derived by introducing the Kramers-Henneberger frame. Within the normal gauge, the bond formation must be nothing but complicated laser-induced mixing of many electronic states.

C. Floquet CI stabilization method

The advantage of the Floquet CI stabilization method is in that it can be performed by a slight modification of the usual quantum chemical program package. The other methods for estimating the complex eigenvalues, such as the complex basis function method and the absorbing potential method, require the modification of almost all the computing processes to enable the complex-number arithmetics.

The shortcoming is the existence of some arbitrariness in the selection of a local avoided crossing. If the basis set is complete at both the one-electron and many-electron levels, the arbitrariness is expected to be vanish. However, we have met such arbitrariness in practical calculations. Particularly, the arbitrariness was large when the scaling parameter η is introduced as the orbital exponents. The arbitrariness was much reduced when we used the distributed Gaussians described in Sec. II C. By this method, we can obtain a quasi-idealized stabilization graph as shown in Fig. 2.

There is another intrinsic problem. We have employed the second order characteristic polynomial in the step of analytic continuation. The problem arises in the case that there are no localized two-state avoided crossings in the stabilization graph. For such a case, our procedure cannot be applied. By this reason, the data for $1.4 < R < 2.0$ are absent in Fig. 7. Moreover, the same problem occurs in the cases of $\omega < 5.0$, and we cannot discuss such an interesting region of ω. In order to avoid the problem, the use of a higher order characteristic polynomial or the other method, such as the complex-basis function method and the absorbing potential method, should be considered.

D. Possibility of realizing the laser-induced chemical bond

The theoretical formalism employed in the present paper, i.e., the truncated Floquet formalism, is suitable, as well as the KH approximation, for the high frequency laser condition. Since the laser intensity I is given by $I \propto \alpha^2 \omega^4$, the high frequency condition requires the very high intensity in order to achieve a large value of α. The laser condition proposed for the formation of the He_2 molecule is $\alpha = 1.016$, $\omega = 10.0$, which corresponds to $h\nu = 272$ eV, $I = 3.623 \times 10^{20}$ W cm^{-2}. Such a condition is extreme in the present

status of light sources. On the basis of the high harmonic generation technique and the free electron laser, efforts have recently been devoted to the development of high-frequency or intense lasers. The above condition should be realized by the progress of laser technology, but the realization would be in a slightly remote future.

The electrons in the helium atom are strongly bound to the nucleus, and the very intense laser is required to deform the electron clouds. If one uses more polarizable species, the chemical properties of atoms would be more easily changed. For example, neon and argon are good candidates. It is not necessary to deform the electron clouds of the inner shells. It suffices that the laser is sufficiently strong and of sufficiently high frequency only for the valence electrons. The required frequency as well as intensity can largely be reduced.

Besides the extreme laser condition, there is another difficulty in experimental observation of the laser-induced chemical bond. On the way to the laser intensity for stabilization, there is a region where the lifetime is very short as shown in Figs. 4 and 6. Such a region, often called the death valley [19], must be passed if the system is adiabatically excited by a usual pulsed laser with a gradually evolving intensity profile. A possible remedy is the use of a pulsed laser with a sharp rising edge. Such a laser permits a sudden transition from the field-free ground state to the stabilized states with certain probabilities depending on the overlap between wave functions.

VIII. CONCLUSION

The laser-induced chemical bond, predicted on the basis of the KH high-frequency approximation [8], is found to be formed also in laser field of finite frequencies. Although the resultant He_2 molecule undergoes rapid ionization caused by the intense field, the lifetime just manages to be longer than the vibrational period by virtue of the stabilization effect against ionization.

The prediction based on the KH high-frequency approximation is found to be qualitatively good also in the cases of finite frequency. This demonstrates that the validity range of the KH approximation is not restricted only to the limit $\omega \to \infty$ but can be extended down to $\omega \simeq E_b / \hbar$, where E_b represents the electron binding energy. This consequence is in agreement with our previous observation [23].

The KH molecular orbital (KHMO) scheme discussed in the previous paper [8] is expected to retain its validity also in finitely high-frequency situations. The KHMO scheme would be a powerful tool in constructing the new chemical bonding theory which explains the bond hardening or softening [25–29] and molecular structure deformation [4–6] in intense fields.

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