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Photodissociation path in H_2^+ induced by nonuniform optical near fields: Two-step excitation via vibrationally excited states

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In this paper, effects of the spatial nonuniformity of an optical near field (ONF) on the molecular photodissociation process are presented. The dissociation dynamics of H_2^+ was theoretically investigated by solving a non-Born-Oppenheimer Schrödinger equation. It was found that in addition to two dissociation mechanisms, which are one-photon and three-photon processes induced by uniform laser light excitation, the nonuniform ONF opens another dissociation path: two-step excitation mediated by vibrationally excited states. The nonuniformity of the ONF causes a transition between vibrational states that is forbidden according to conventional selection rules, leading to the dissociation path. The dependences of photodissociation on the intensity and nonuniformity of the ONF were calculated and the results validated the two-step dissociation mechanism.

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I. INTRODUCTION

Molecular dissociation processes induced by intense laser pulses are important to understanding and controlling photochemical reactions [1]. A number of experimental and theoretical studies on laser-molecule interactions have been conducted that focused on H_2^+, which is the simplest system having general properties of molecules. Theoretical studies [2–4] have clarified that there are several dissociation mechanisms of H_2^+, such as bond softening induced by a three-photon process, resonant excitation, and Coulomb explosion (for further details, see Ref. [5] and references therein). These mechanisms have been experimentally observed by utilizing pulsed lasers [6,7]. However, nonlinear light-matter interactions, including the dissociation of H_2^+, generally require laser pulses with high peak intensities ($> 10^{13}$ W/cm^2).

A promising approach to solve this problem is to utilize plasmon resonances of metal nanostructures. When the frequency of incident light is in tune with the plasmon resonance frequency [8], the intensity of the optical near field (ONF) generated around a metal nanostructure is enhanced by two or more orders compared with the incident light [9]. Kim *et al.* [10] experimentally demonstrated high harmonic generation, which is a nonlinear phenomenon used for attosecond pulse generation [11] and tomographic imaging of molecular wave function [12], caused by a relatively weak-pulsed laser field (10^{11} W/cm^2) by increasing the intensity of the ONF generated in bowtie-shaped gold nanostructures. Although the ONF was introduced primarily to enhance the absolute intensity of the field in their study, another essential and inherent feature of the ONF that has evoked interest is its spatial nonuniformity. Indeed, several theoretical works [13–15] inspired by the above-mentioned experiment [10] have shown that a nonuniform light field generates even harmonics that are absent in uniform laser excitation and increases the cutoff frequency. Considering that the nonuniformity of light has such great influences on high harmonic generation, nonuniform light is expected to give rise to novel physical phenomena in photodissociation processes aided by metal nanostructures.

In this paper, we present a theoretical investigation of the dissociation process of H_2^+ induced by a nonuniform ONF, by solving a non-Born-Oppenheimer time-dependent Schrödinger equation. We demonstrate that the nonuniform ONF dissociates H_2^+ through a different path from those induced by uniform laser lights, i.e., a two-step transition mediated by vibrationally excited states in the electronic ground state. This dissociation path arises because the nonuniformity of the ONF can lead to the excitation of higher-order vibrational states that is forbidden according to conventional selection rules based on uniform photoexcitation. Further, we show the dependences of dissociation on the intensity and nonuniformity of the ONF, which validates the two-step photodissociation mechanism.

II. THEORY AND COMPUTATIONAL METHODS

A reduced dimensional model [16] was employed to represent the electron-nucleus system of H_2^+. The model describes the system in terms of two coordinates R and z, which represent the distance between the nuclei and the distance from the midpoint of the nuclei to the electron, respectively. The static Hamiltonian of the model, $\hat{H}_0$, is written as

$$\hat{H}_0(z,R) = -\frac{1}{2\mu_z}\frac{\partial^2}{\partial z^2} - \frac{1}{2\mu_R}\frac{\partial^2}{\partial R^2} - \frac{1}{\sqrt{(z-R/2)^2+\alpha}} - \frac{1}{\sqrt{(z+R/2)^2+\alpha}} + \frac{1}{\sqrt{R^2+\beta}}, \quad (1)$$

where $\mu_R = m_p/2$ and $\mu_z = 2m_p m_e/(2m_p + m_e)$ are reduced masses calculated from the proton mass m_p and the electron

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mass m_e. Screening parameters α and β introduced to avoid the divergence of potential are set to be 1.0 and 0.03, respectively. The eigenstates of $H_2{}^+$ are obtained by diagonalizing Eq. (1).

To investigate the photodissociation dynamics of $H_2{}^+$, we solved the time-dependent Schrödinger equation (in atomic units)

$$i\frac{\partial}{\partial t}\Psi(z,R,t) = [\hat{H}_0(z,R) + \hat{V}_{ext}(z,R,t)]\Psi(z,R,t), \qquad (2)$$

where $\hat{V}_{ext}$ represents the potential of external optical excitation. In this calculation, we modeled the electric field amplitude of the nonuniform ONF by using a linear function,

$$E(z) = E_0(1 + 2\epsilon z), \qquad (3)$$

where E_0 is the field amplitude at the midpoint of the nuclei, and ϵ, defined as $E'(z)/2E(0)$, represents the extent of the nonuniformity. Although the ONF is often approximated as an electric dipole radiation, we used Eq. (3) for the following two reasons: (i) Since the electric field generated by an electric dipole diverges at the dipole position, the dipole should be placed outside of the computational grid. However, this makes the distance between the dipole and $H_2{}^+$ too large to observe the effect of a nonuniform field when a sufficiently large simulation box is considered. (ii) We can directly investigate the effect of nonuniformity by performing calculations with various values of ϵ because it represents the extent of nonuniformity. The electric field amplitude in Eq. (3) corresponds to the Taylor expansion of a nonuniform field to the first order. Therefore, an arbitrary nonuniform field can be represented by Eq. (3), although the effects of higher-order terms, such as $z^2, z^3, \ldots$, are ignored in this study. By integrating Eq. (3) and multiplying the time-dependent term, $\hat{V}_{ext}$ is obtained as

$$\begin{aligned}\hat{V}_{ext}(z,R,t) &= \left[\int_0^z dz' E(z') - \int_0^R dz' \left\{E\left(\frac{z'}{2}\right) - E\left(-\frac{z'}{2}\right)\right\}\right]\sin(\omega t) f(t) \qquad (4)\\ &= E_0[z(1+\epsilon z) - \epsilon R^2]\sin(\omega t) f(t), \qquad (5)\end{aligned}$$

where ω is the angular frequency of the field, and $f(t)$ is a trapezoidal envelope function defined by

$$f(t) = \begin{cases} \sin^2\left(\frac{\pi t}{2T_1}\right) & (0 \leqslant t < T_1)\\ 1 & (T_1 \leqslant t < T_2)\\ \sin^2\left\{\frac{\pi[t-(2T_2-T_3)]}{2(T_3-T_2)}\right\} & (T_2 \leqslant t < T_3)\\ 0 & (T_3 \leqslant t), \end{cases} \qquad (6)$$

where the parameters are set to be $T_1 = 10$, $T_2 = 30$, and $T_3 = 40$ fs. The first and second integrals in Eq. (4) represent the potentials exerted on the electron and nuclei, respectively. Note that $\hat{V}_{ext}$ depends on the coordinate R only when the field is nonuniform, i.e., $\epsilon \neq 0$. The R dependence of the potential arises because the forces exerted by the nonuniform ONF on each nucleus are different.

The time-dependent Schrödinger equation was solved by using an improved Crank-Nicolson scheme [17] with a time spacing of $dt = 0.0005$ fs. The spatial grids were defined by $|z| \leqslant 80$ a.u. and $0 \leqslant R \leqslant 15$ a.u. with spacings of $dz = 0.2$ a.u. and $dR = 0.05$ a.u. During the time evolution, a mask function with the shape of $\cos^{\frac{1}{6}}$ was introduced at the boundaries of both the z and R coordinates to absorb the emitted wave packets. The wave packets absorbed by the mask function at the z and R boundaries are regarded as ionized and dissociated, respectively.

III. RESULTS AND DISCUSSION

The calculated Born-Oppenheimer potential energy surface of $H_2{}^+$, shown in Fig. 1(a), contains a bound ground state ($1\sigma_g$) and a repulsive excited state ($2\sigma_u$). There are 20 vibrational states belonging to the $1\sigma_g$ state and we consider the vibrational ground state $v = 0$ as the initial state in the time-dependent calculation.

Figure 1(b) shows the dissociation spectra for different values of light intensity I_0 and nonuniformity ϵ. There are three spectral patterns at approximately 2.0, 3.6, and 8.0 eV for light intensity higher than 10^{12} W/cm^2, which can be attributed to three dissociation mechanisms. The peak at 8.0 eV is derived from the usual one-photon resonant absorption, as shown by the purple arrow in Fig. 1(a). Since this absorption is a linear optical process, the peak at 8.0 eV appears even at low light intensity. Moreover, the dissociation saturates at $I_0 = 10^{13}$ W/cm^2 because the dissociation spectra are calculated by

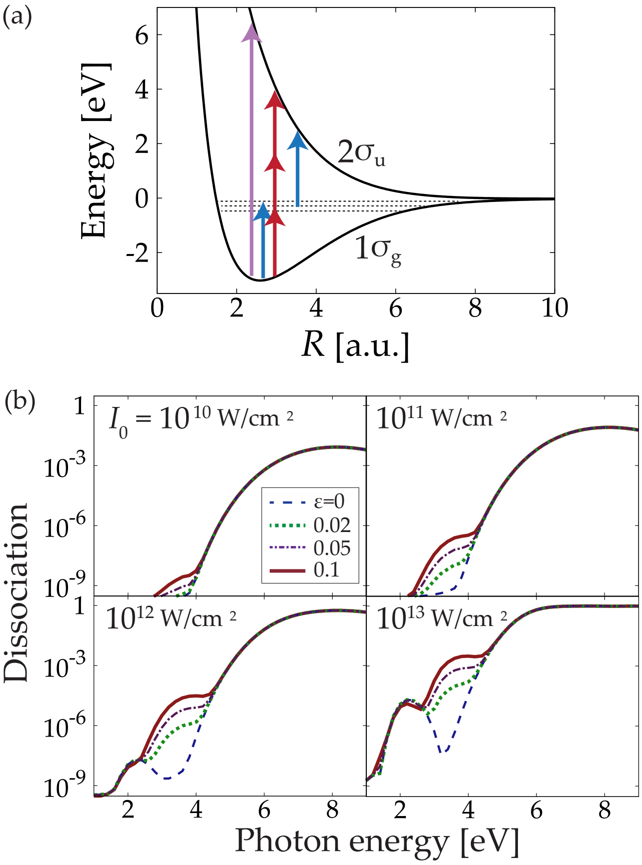

FIG. 1. (a) Born-Oppenheimer potential energy surface of $H_2{}^+$. The red, blue, and purple arrows represent three dissociation paths. (b) Dissociation spectra of $H_2{}^+$ for light intensities $I_0 = \{10^{10}, 10^{11}, 10^{12}, 10^{13}\}$ W/cm^2 and field nonuniformity $\epsilon = \{0, 0.02, 0.05, 0.1\}$.

integrating the wave packets absorbed by the mask function; thus, the upper limit of the spectrum is $\iint dz dR\ |\Psi|^2 = 1$. The peak at 2.0 eV originates from a three-photon process, as shown by the red arrows in Fig. 1(a). This process has been of particular interest in the research area of intense laser field and molecular interactions. Indeed, numerous theoretical and experimental studies have been conducted [2–7] to investigate the dissociation process induced by a Ti:sapphire laser. The spatial nonuniformity of light does not influence the two dissociation paths, as is indicated from the same pattern of the spectra for various ϵ. Therefore, the conventional description of the light-matter interaction based on the electric dipole approximation is sufficient to explain the dissociation though these two paths. However, the peak at 3.6 eV is due to the spatial nonuniformity of the ONF. Although the spectrum for uniform laser light ($\epsilon = 0$) shows no peak at this photon energy, a peak appears at higher ϵ and grows rapidly with the increase of ϵ. As will be described later, the peak at 3.6 eV originates from the two-step transition mediated by vibrationally excited states, represented by the blue arrows in Fig. 1(a).

The nonuniform ONF gives rise to a different dissociation path because of its ability to break down the conventional optical selection rules. It has been known that the nonuniform ONF induces electric quadrupole transitions, which are forbidden under the electric dipole approximation [18–22]. Similarly, the nonuniform field can induce vibrational excitation processes that are forbidden according to the optical selection rule based on uniform laser-light excitations. A transition matrix element between vibrational states, denoted as v and v', is calculated by

$$\langle v'|\ \hat{V}_{ext}\ |v\rangle = \iint dz dR\ \phi^*_{v'}(z,R)\hat{V}_{ext}(z,R)\phi_v(z,R), \quad (7)$$

where ϕ_v represents the wave function of the vibrational state $|v\rangle$. By substituting $\hat{V}_{ext}$ given by Eq. (5) into Eq. (7) except for the time-dependent part, the matrix element is divided into three integrals:

$$\begin{aligned}\langle v'|\ \hat{V}_{ext}\ |v\rangle = {} & E_0 \iint dz dR\ \phi^*_{v'}(z,R) z \phi_v(z,R) \\ & + \epsilon E_0 \iint dz dR\ \phi^*_{v'}(z,R) z^2 \phi_v(z,R) \\ & - \epsilon E_0 \iint dz dR\ \phi^*_{v'}(z,R) R^2 \phi_v(z,R), \quad (8)\end{aligned}$$

where the second and third terms are proportional to ϵ, which implies that only the first term is obtained for a uniform field. Since ϕ_v for all v which belongs to the $1\sigma_g$ state is an even function of z, the first integral of Eq. (8) becomes zero. In contrast, the second and third terms are, in general, nonzero. Therefore, the dependence of the transition matrix element on the nonuniformity of the field is $\langle v'|\ \hat{V}_{ext}\ |v\rangle \propto \epsilon$; thus, the dependence of the transition rate from v to v', $T_{v\rightarrow v'}$, is given by

$$T_{v\rightarrow v'} \propto |\ \langle v'|\ \hat{V}_{ext}\ |v\rangle\ |^2 \propto \epsilon^2. \quad (9)$$

This dependence indicates that a nonuniform ONF with a finite ϵ causes the transition from the vibrational ground state to excited states. Subsequently, the transition from the vibrationally excited states to the $2\sigma_u$ state occurs followed by dissociation, as shown by the blue arrows in Fig. 1(a).

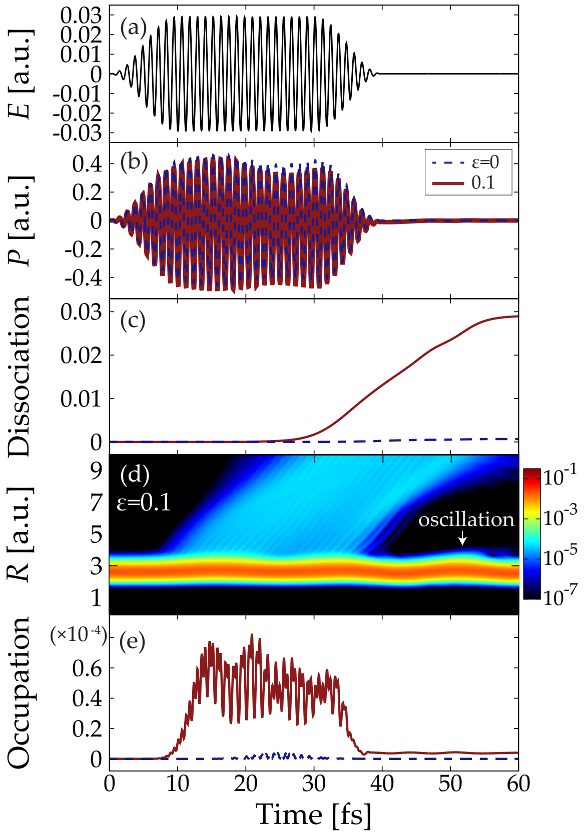

FIG. 2. (a) The electric field amplitude of the incident pulse applied to the system. (b),(c),(e) Time-dependent dissociation dynamics caused by uniform ($\epsilon = 0$, red solid line) and nonuniform ($\epsilon = 0.1$, blue dashed line) fields: (b) induced electric dipole moment, (c) dissociation probability, and (e) occupation probability of the vibrationally excited state $|v = 18\rangle$. (d) A contour plot of radial probability density for the nonuniform excitation.

Next, we show the dissociation dynamics for $I_0 = 3 \times 10^{13}\ \mathrm{W/cm^2}$ and $\omega = 3.6$ eV, for both uniform ($\epsilon = 0$) and nonuniform ($\epsilon = 0.1$) fields. The incident pulse shape for the given parameters is shown in Fig. 2(a), while Fig. 2(b) demonstrates the electric dipole moment $P(t)$ of H_2^+. Since the value of $P(t)$ is mostly determined by the absolute light intensity at the center of H_2^+, $P(t)$ induced by uniform and nonuniform fields show similar features. Figure 2(c) shows the dissociation probabilities evaluated from the wave packets absorbed by the mask function at $R = 10$ a.u. and reveals that only the nonuniform field dissociates H_2^+. Figure 2(d) presents the contour plot of the radial probability density $\int dz|\Psi(z,R,t)|^2$ for the nonuniform field excitation in a log scale. The density emitted from 10 to 35 fs corresponds to dissociated wave packets, the probability of which is plotted in Fig. 2(c). Figure 2(e) shows the occupation probability of a vibrationally excited state ($v = 18$) for both the uniform and nonuniform fields. The occupation of the other vibrational states indicates similar dynamics to that of $v = 18$. Note that the emission of the wave packets [Fig. 2(d)] occurs in coincidence with the increase in the occupation of the vibrationally

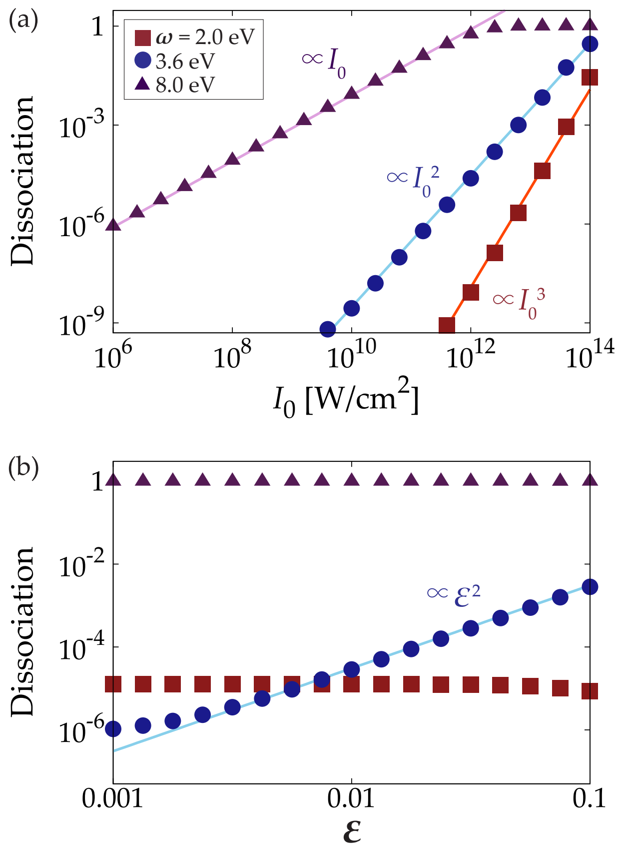

FIG. 3. Dependence of dissociation caused by nonuniform light with photon energies of 2.0 eV (red squares), 3.6 eV (blue circles), and 8.0 eV (purple triangles) on (a) light intensity I_0 and (b) field nonuniformity ϵ.

excited state [Fig. 2(e)], not with laser irradiation [Fig. 2(a)]. This coincidence clearly indicates that the dissociated packets are emitted from the vibrationally excited states. Furthermore, the small oscillation (or undulation) of the radial probability density in the range of $R \sim 3$ a.u. and $t \gtrsim 15$ fs observed in Fig. 2(d) implies that H_2^+ is vibrationally excited by the nonuniform field. These dynamics characteristics, i.e., the dissociation coincident with the occupation of the vibrationally excited states and the oscillation of the radial probability density, support the dissociation mechanism based on the two-step transition mediated by the vibrationally excited states in the presence of the nonuniformity of the ONF.

Figure 3 shows the dependences of the dissociation amount on the intensity and nonuniformity of light at photon energies of 2.0, 3.6, and 8.0 eV inducing the three different dissociation mechanisms. Figure 3(a) shows the dependence of dissociation on the light intensity I_0, at $\epsilon = 0.1$. The dissociation dependences corresponding to photon energies of 8.0, 3.6, and 2.0 eV are fitted to be proportional to I_0, $I_0{}^2$, and $I_0{}^3$ because they correspond to one-, two-, and three-photon processes, respectively; thus, the dissociation mechanisms for each photon energy are confirmed. Figure 3(b) indicates the dependence of dissociation on the field nonuniformity ϵ, at $I_0 = 10^{12}$ W/cm^2. While the dissociations for 2.0 and 8.0 eV are independent of the nonuniformity, that for 3.6 eV is proportional to ϵ^2, which is consistent with Eq. (9), as explained below. The dissociation process by the nonuniform ONF consists of two transitions: (i) from the vibrational ground state to vibrationally excited states and (ii) from vibrationally excited states to the $2\sigma_u$ state. Since transition (ii) is electric dipole allowed, its rate is almost independent of ϵ. Therefore, the dependence of the dissociation rate on ϵ is determined by transition (i), and hence is proportional to ϵ^2 according to Eq. (9).

In this paper, we presented the theoretical investigation of the effect of field nonuniformity, focusing on the dissociation process of $H_2{}^+$. Moreover, we claim that the nonuniformity of the ONF has a significant effect on general chemical reactions because the principle of excitation of vibrational states presented in this paper is universal. Recently, the activation of photochemical reactions using metal nanostructures has been intensively explored [23]. Electric field enhancement [24] and heat generation [25] caused by plasmon resonance, or electron transfer from metal to molecules [26], are mainly considered as the effects of metal nanostructures on chemical reactions. In addition to these effects, the nonuniformity of the ONF generated around metal nanostructures would play a role in activating molecular dissociation and subsequent chemical transformations. This physical process would enable the spatial and spectral control of photochemical reactions by a novel mechanism.

IV. SUMMARY

In conclusion, we have investigated the effect of spatial nonuniformity of the ONF on the photodissociation of $H_2{}^+$. The calculated dissociation spectra reveal that in addition to the one-photon and three-photon processes induced by a uniform laser field, the spatial nonuniformity of the ONF opens up a different dissociation path, which is a two-step transition mediated by vibrationally excited states. The dissociation mechanism involves the transitions between vibrational states induced by the nonuniform ONF that are forbidden in the case of uniform light excitation. The amount of dissociation caused by the two-step transition was shown to be proportional to the square of ϵ, which is the parameter that represents the nonuniformity of the field. This dependence was validated by the fact that the transition rate between any vibrational states is also proportional to ϵ^2, as derived by means of a simple analysis. We exemplified the dissociation induced by the ONF excitation in $H_2{}^+$, which is the simplest molecular system; however, the essential physical dynamics derived in this study is not limited to the $H_2{}^+$ system. The field nonuniformity effect demonstrated here will have a significant influence on various molecular systems. Our findings pave the way for the spatial control of photochemical reactions using ONFs around metal nanostructures.

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[1] R. J. Levis, G. M. Menkir, and H. Rabitz, Science **292**, 709 (2001).
[2] P. H. Bucksbaum, A. Zavriyev, H. G. Muller, and D. W. Schumacher, Phys. Rev. Lett. **64**, 1883 (1990).
[3] A. Giusti-Suzor, X. He, O. Atabek, and F. H. Mies, Phys. Rev. Lett. **64**, 515 (1990).
[4] A. Giusti-Suzor and F. H. Mies, Phys. Rev. Lett. **68**, 3869 (1992).
[5] J. H. Posthumus, Rep. Prog. Phys. **67**, 623 (2004).
[6] K. Sändig, H. Figger, and T. W. Hänsch, Phys. Rev. Lett. **85**, 4876 (2000).
[7] P. M. Paul, E. S. Toma, P. Breger, G. Mullot, F. Augé, Ph. Balcou, H. G. Muller, and P. Agostini, Science **292**, 1689 (2001).
[8] L. Novotny and B. Hecht, *Principles of Nano-Optics* (Cambridge University Press, Cambridge, 2012).
[9] P. Mühlschlegel, H. J. Eisler, O. J. F. Martin, B. Hecht, and D. W. Pohl, Science **308**, 1607 (2005).
[10] S. Kim, J. Jin, Y.-J. Kim, I.-Y. Park, Y. Kim, and S.-W. Kim, Nature (London) **453**, 757 (2008).
[11] A. D. Bandrauk, S. Chelkowski, and H. S. Nguyen, Intl. J. Quantum Chem. **100**, 834 (2004).
[12] J. Itatani, J. Levesque, D. Zeidler, H. Niikura, and H. Pépin, Nature (London) **432**, 867 (2004).
[13] M. F. Ciappina, J. Biegert, R. Quidant, and M. Lewenstein, Phys. Rev. A **85**, 033828 (2012).
[14] I. Yavuz, E. A. Bleda, Z. Altun, and T. Topcu, Phys. Rev. A **85**, 013416 (2012).
[15] J. Luo, Y. Li, Z. Wang, Q. Zhang, and P. Lu, J. Phys. B **46**, 145602 (2013).
[16] K. C. Kulander, F. H. Mies, and K. J. Schafer, Phys. Rev. A **53**, 2562 (1996).
[17] N. Watanabe and M. Tsukada, Phys. Rev. E **62**, 2914 (2000).
[18] J. R. Zurita-Sánchez and L. Novotny, J. Opt. Soc. Am. B **19**, 1355 (2002).
[19] S. Tojo, M. Hasuo, and T. Fujimoto, Phys. Rev. Lett. **92**, 053001 (2004).
[20] R. Filter, S. Mühlig, T. Eichelkraut, C. Rockstuhl, and F. Lederer, Phys. Rev. B **86**, 035404 (2012).
[21] P. K. Jain, D. Ghosh, R. Baer, and E. Rabani, Proc. Natl. Acad. Sci. USA **109**, 8016 (2012).
[22] A. M. Kern and O. J. F. Martin, Phys. Rev. A **85**, 022501 (2012).
[23] S. Linic, U. Aslam, C. Boerigter, and M. Morabito, Nat. Mater. **14**, 567 (2015).
[24] S. Kuhn, U. Hakanson, L. Rogobete, and V. Sandoghdar, Phys. Rev. Lett. **97**, 017402 (2006).
[25] J. Qiu and W. D. Wei, J. Phys. Chem. C **118**, 20735 (2014).
[26] J. Yan, K. W. Jacobsen, and K. S. Thygesen, Phys. Rev. B **84**, 235430 (2011).