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Femtosecond photodissociation of molecules facilitated by noise

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We investigate the dynamics of diatomic molecules subjected to both a femtosecond midinfrared laser pulse and Gaussian white noise. The stochastic Schrödinger equation with a Morse potential is used to describe the molecular vibrations under noise and the laser pulse. For weak laser intensity, well below the dissociation threshold, it is shown that one can find an optimum amount of noise that leads to a dramatic enhancement of the dissociation probability. The enhancement landscape, which is shown as a function of both the noise and the laser strength, exhibits a global maximum. A frequency-resolved gain profile is recorded with a pump-probe setup which is experimentally realizable. With this profile we identify the linear and nonlinear multiphoton processes created by the interplay between laser and noise and assess their relative contribution to the dissociation enhancement.

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I. INTRODUCTION

The efficient dissociation of a molecular bond by the application of ultrashort laser pulses is a long sought after goal in photochemistry [1,2]. However, to achieve significant molecular dissociation with coherent ultrashort laser pulses is difficult due to the anharmonicity of the molecular vibrations [3]. Very high intensities of the laser field are therefore required to produce significant dissociation, despite the lower value of the dissociation energy compared to the ionization potential. For such strong laser fields molecular tunnel ionization often masks the dissociation process [4,6].

Alternative strategies have been proposed to enhance the dissociation yield for weaker laser pulses. For instance, the approach using the linearly (or circularly) polarized chirped laser pulses have been proposed. Here, the frequency is designed to match the vibrational ladder of a specific molecule, thereby facilitating the ladder climbing of the molecule and eventually its dissociation [5]. These ideas have been confirmed in the experiments, using chirped femtosecond midinfrared (MIR) laser pulses. A large population transfer to higher vibrational levels has been achieved with diatomic molecules (HCl, NO, etc.) as well as in some polyatomic molecules [$\mathrm{Cr(CO)_6}$] [7–9]. Furthermore, the optimally tailored pulses by a closed loop control have also been used quite recently to dissociate a specific molecular bond in a polyatomic molecule; it was possible to control, in particular, the branching ratio between two possible reaction channels [10].

Following a completely different approach to achieve the molecular dissociation, it has been proposed recently that one can instead use incoherent random kicks [11]. In the same spirit, there has been a growing interest in understanding the role of random fluctuations on the quantum dynamics of atomic and molecular systems [13–15]. However, the molecular dissociation processes due to the simultaneous application of a laser and a noise source have so far not been considered. In doing so, we expect the coherent laser pulse to become more efficient when submerged in a small amount of noise. It is indeed well known that in some classical as well as quantum nonlinear systems (e.g., bistable systems), the noise can lower the nonlinear threshold via the stochastic resonance (SR) effect [16,17]. It is also worth mentioning here that SR also exists in some nonlinear chemical reactions [12,16], but has not been demonstrated in the crucial process of molecular (photo) dissociation on a femtosecond time scale yet.

Here, we propose an approach to control the molecular dissociation by irradiating diatomic molecules by a femtosecond MIR laser pulse in the presence of noise. We show how and to what extent the presence of noise can reduce the dissociation threshold of diatomic molecules due to its nonlinear interaction with the laser pulse. This approach can be applicable to both polar and nonpolar molecules and is readily possible to use in experiments.

We begin the main text of this work in Sec. II with a brief description of the molecular Hamiltonian including a coherent laser pulse and a stochastic term. In Sec. III we describe the fast-Fourier-transform (FFT) split-operator method to solving the stochastic Schrödinger equation with absorbing boundary conditions and focus on the relevant physical observable of interest. Our results for the role of noise in the molecular photodissociation and other interesting features of the effect are discussed in Sec. IV. Finally, Sec. V concludes the paper with some perspectives.

II. THEORETICAL APPROACH

The total molecular Hamiltonian for the diatomic molecule under time-dependent external fields is given by (atomic units are used unless stated otherwise)

$$H(t) = H_0 - x\xi(t) - xF(t), \tag{1}$$

where $H_0 = p^2/2m + V(x)$ describes vibrational motion of the molecule with reduced mass m in the Morse potential [18]

$$V(x) = -D_e + D_e[1 - \exp(-\beta x)]^2, \tag{2}$$

with well depth D_e and length scale β. The eigenenergies E_n of the Morse oscillator H_0 are given by

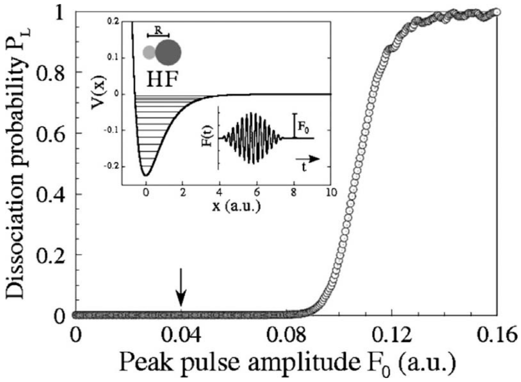

FIG. 1. Dissociation probability P_L as function of the laser peak amplitude F_0 over long time t $(t \gg T_p)$ with $\omega=0.007$ a.u., $\delta=0.0$, and $T_p=30\pi/\omega$. The arrow indicates the value of $F_0=0.04$ a.u. for which $P_L \sim 0$ is far less than the dissociation threshold. The inset shows the corresponding 15 optical cycle laser pulse $F(t)$ (light solid line) and the schematic pictures of a diatomic molecule HF (two nuclei separated by R, with R_0 being the equilibrium internuclear distance) and the Morse potential $V(x)$ (thick solid line), with $x=R-R_0$.

$$E_n = \hbar\omega_e(n+1/2)[1-B(n+1/2)/2], \quad 0 \le n \le [j], \tag{3}$$

where ω_e is the harmonic frequency and $n_b=[j]+1$ is the number of bound states with

$$j = 1/B - 1/2, \quad B = \hbar\beta(2mD_e)^{-1/2}, \quad \hbar\omega_e = 2BD_e. \tag{4}$$

The laser field is a nonresonant MIR femtosecond pulse,

$$F(t) = f(t)F_0 \sin(\omega t + \delta), \tag{5}$$

where ω denotes the angular frequency, and the effective peak amplitude F_0 as well as the noise term $\xi(t)$ (see below) contain the molecular dipole gradient [11]. We choose a smooth pulse envelope $f(t)$ of the form

$$f(t) = \sin^2(\pi t/T_p), \tag{6}$$

where T_p is the pulse duration of typically 15 optical cycles (see inset of Fig. 1).

The noise term $\xi(t)$ is a zero-mean Gaussian white noise having the following properties:

$$\langle \xi(t) \rangle = 0, \tag{7}$$

$$\langle \xi(t)\xi(t') \rangle = 2D\delta(t-t'), \tag{8}$$

where D is the noise intensity [19].

III. TIME EVOLUTION AND OBSERVABLES

A. Quantum stochastic propagation

The full time-dependent stochastic Schrödinger equation is

$$i\hbar \frac{\partial|\psi(t)\rangle}{\partial t} = H(t)|\psi(t)\rangle. \tag{9}$$

The time evolution under Eq. (9) with the Hamiltonian given in Eq. (1) is nondeterministic due to its stochastic nature. A solution taking into account the external fields perturbatively is not possible, because the fields of interest are so strong that they influence the dynamics substantially. Hence we have to numerically solve the full time-dependent stochastic Schrödinger equation (9). The solution is accomplished by averaging over a sufficient number of deterministic solutions under different specific realizations r of the noise.

For a given realization r, the solution of the stochastic Schrödinger equation amounts to solving the standard time-dependent Schrödinger equation,

$$|\psi_r(t)\rangle = U_r(t,t_0)|\psi(t_0)\rangle, \tag{10}$$

starting from an initial state $|\psi(t_0)\rangle$ at time t_0. The stochastic evolution operator $U_r(t,t_0)$ is written as a product of operators propagating over a small time interval Δt,

$$U_r(\Delta t) = \exp\left(-i\int_t^{t+\Delta t} H(x,t)dt\right). \tag{11}$$

This short-time propagator can be formulated explicitly by evaluating the integral in the exponent in the Stratonovitch sense [19], leading to

$$U_r(\Delta t) = \exp\{-i[H_0(x) - xF(t)]\Delta t\}\exp(ix\sqrt{2D\Delta t}\xi_t), \tag{12}$$

where ξ_t is a Gaussian distributed random number of unit variance. The representation of Eq. (12) illustrates how the coherent evolution of the system (with laser) acquires an additional random phase in the form of a momentum kick whose strength is random due to ξ_t but scales with the amplitude of the noise $\sqrt{2D\Delta t}$ over the time interval Δt. The short-time propagator given by Eq. (12) can be easily realized numerically using the FFT split-operator approach with absorbing boundary conditions [20].

B. Dissociation probability

We use the dissociation probability as a measure for the nonlinear coupling of energy from the external fields to the molecule. It can be most conveniently expressed as a complement of the probability to find the molecule at time t in any of its bound states, which reads for a given realization r

$$P_d^r(t) = 1 - \sum_{\nu=0}^{N_b-1} |\langle \psi_\nu | \psi_r(t) \rangle|^2, \tag{13}$$

where for the initial state $|\psi_0(t=0)\rangle$ we take the ground state of the Morse potential with energy E_0 [Eq. (3)]. Typically we will average over a large number of realizations (N_r about 100) to calculate the average dissociation probability over long time $t_\infty \gg T_p$,

$$P = \frac{1}{N_r}\sum_{r=1}^{N_r} P_d^r(t_\infty). \tag{14}$$

In the following, we shall consider different physical situations, such as when the molecule is subjected to (i) the laser pulse alone (denoted by subscript L), (ii) the noise alone (N), or (iii) a combination of both fields ($L+N$).

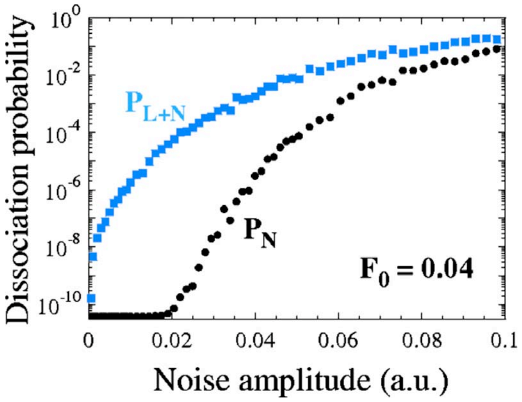

FIG. 2. (Color online) Average dissociation probability of the molecule for noise only P_N (square) and for the simultaneous application of the laser pulse and the noise P_{L+N} (circle). The total number of realization $N_r=100$ and the laser peak amplitude is kept fixed at $F_0=0.04$ a.u.

IV. RESULTS AND DISCUSSIONS

A. Femtosecond photodissociation under noise

Photodissociation of diatomic molecules by a femtosecond laser pulse is a highly nonlinear processes, as can be seen in Fig. 1 for a 15 cycle MIR pulse at $\omega=0.007$ a.u. The dissociation probability P_L versus the peak field amplitude F_0 exhibits a prototypical S-shape curve with a thresholdlike behavior. High intensities (i.e., F_0^2 values) are necessary for dissociation by a laser pulse alone. However, the addition of a weak amplitude noise to a subthreshold laser pulse may lead to substantial dissociation. As we have shown before, such a combination is quite efficient for an optimum choice of the noise amplitude in achieving ionization of an atom [13] resembling the phenomenon of stochastic resonance [16,17].

We choose a laser pulse of peak amplitude $F_0=0.04$ a.u., for which the dissociation probability is extremely small, $P_L<10^{-10}$ (see Fig. 1). Keeping this laser pulse unchanged, we add a small amount of noise to it. Figure 2 shows the average dissociation probability P_{L+N} versus the noise amplitude $\sqrt{D}$ (squares). One can clearly see that by adding a small amount of noise, P_{L+N} rises rapidly, well beyond the increase induced by the noise alone (P_N, circles) which is applied for the same time T_p as the laser pulse.

The enhancement by noise can be quantified with the parameter

$$\eta=\frac{P_{L+N}-P_0}{P_0}, \tag{15}$$

with $P_0=P_L+P_N$, which is plotted in Fig. 3. By construction, $\eta\rightarrow 0$ if one of the two fields, laser or noise, is much larger than the other. However, for a specific noise amplitude, here at $\sqrt{D}=0.02$, a dramatic enhancement of the order of 10^5 is observed.

B. Net enhancement landscape

Having kept the laser amplitude fixed so far to a subthreshold value ($F_0=0.04$ a.u.), we now investigate the enhancement factor as a function of both laser and noise amplitudes. As can be seen in Fig. 4, $\eta(\sqrt{D},F_0)$ shows a global maximum. Additional calculations have revealed that the shape of $\eta(\sqrt{D},F_0)$ is quite robust for different range of parameters, such as carrier-envelope phase δ, pulse duration T_p, and even for different values of the laser frequency ω in the infrared (IR) regime. Hence the enhancement landscape from Fig. 4 can be used as a guide to identify the range of enhancement possible in experiments on molecular photodissociation under noise.

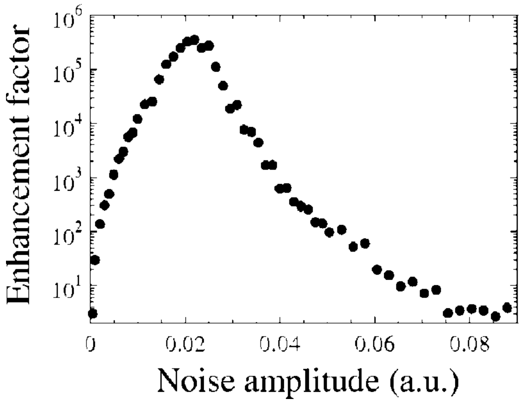

FIG. 3. Factor of enhancement η vs the noise amplitude $\sqrt{D}$ for the 15 cycle long MIR pulse with $F_0=0.04$ a.u. and $\omega=0.007$ a.u.

C. Frequency-resolved enhancement profile for HF

In order to shed light on the mechanism underlying the stochastic enhancement of dissociation we take a closer look at the frequency resolved enhancement profile for the case of HF. This will reveal which frequencies provide the gain within the broadband noise and will in turn clarify the nonlinear photo processes responsible for the enhancement.

For this purpose, we record the frequency-resolved molecular gain (FRMG) $G(\omega)$ employing a pump-probe type of setting *without* noise. We consider the HF molecule to be driven by the MIR laser pulse of $F_0=0.04$ a.u. and ω

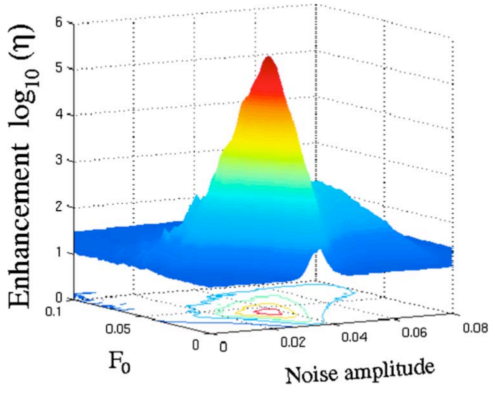

FIG. 4. (Color online) Enhancement landscape $\eta(\sqrt{D},F_0)$ vs the peak pulse amplitude F_0 and the noise amplitude $\sqrt{D}$. Other parameters are kept fixed as in Fig. 3. Contour lines of equal enhancement are also shown on the $(\sqrt{D},F_0)$ plane.

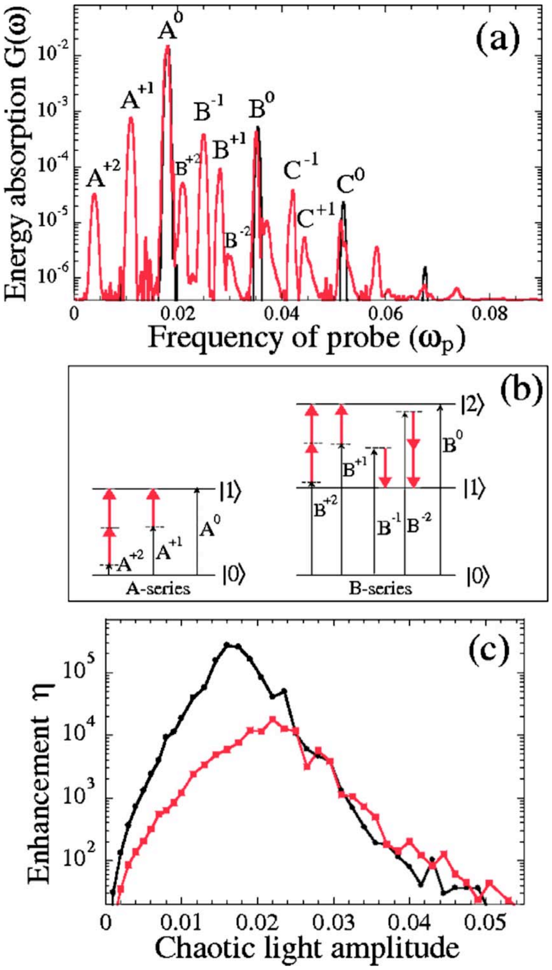

FIG. 5. (Color online) (a) Frequency-resolved gain $G(\omega)$ for the driven HF molecule measured using a simultaneous pump-probe setting without noise. $G(\omega)$ for the bare molecule is also shown (black curve) for comparison. (b) Various single-photon and mutiphoton transitions corresponding to the peaks in $G(\omega)$ are classified as A series, B series, and C series that involve first two, three, and four vibrational levels of HF, respectively. Thick red arrow denotes the pump photon ($\omega = 0.007$ a.u.) and thin black arrow is for tunable weak probe pulse. Pulse bandwidth here is negligible compared to the photon energies. (c) Enhancement curve for the chaotic light with a perforated spectrum of hole widths 0.004 a.u. is compared with the broadband light of BW=1.0 a.u..

$=0.007$ a.u. (pump pulse) and replace the noise by a probe pulse of amplitude F_p and of tunable frequency ω_p. The tunable probe pulse has the same duration and envelope as the fixed pump pulse. The probe amplitude $(F_p/F_0 \simeq 0.05)$ is such that it can only produce single photon transitions. For a HF molecule in its ground state, $G(\omega)$ is obtained by measuring the net energy absorbed as a function of ω_p and is shown in Fig. 5(a). It exhibits several clearly resolved peaks which play a dominant role in the dissociation enhancement under broadband light.

We have identified these peaks as originating from single or multiple photon processes for the level-structure of the HF molecule. For convenience, these processes can be classified as follows. All photoprocesses that involve the lowest two levels of the HF are termed A series, while the ones involving the next higher level (three levels) are termed B series, and so on. Figure 5(b) shows these excitation pathways for the given pump frequency $\omega = 0.007$ a.u. These basically involve n photons of the pump $(n = 0, \pm 1, \pm 2, \ldots)$ plus a single photon of the probe. Note that, in addition to the resonant single photon transitions, second- and third-order processes play an important role. Thus the diatomic molecule offers an interesting example where the role of higher order photoprocesses can be clearly isolated, which is nontrivial in the case of an analogous atomic system [13].

To highlight the contribution of the multiphoton transitions in the enhancement, we have eliminated the first four single-photon resonant frequencies from the noise spectrum. Such a filtered noise can be easily simulated by means of the chaotic light [13]. For a chosen hole width of 0.008 a.u. centered at the resonant frequencies of HF, a drop of more than one order of magnitude in the maximum η is observed, as shown in Fig. 5(c). Note that one is still left with a significant enhancement $(\eta \simeq 10^4)$, which can be clearly attributed to the higher order processes other than single photon resonant transitions. Although we have considered specifically HF, the approach used here can be applied to other diatomic molecules. We have found similar enhancement features for HCl and H_2 molecules within the framework of the Morse potential subjected to different MIR pulses. One can generate the broadband white noise $\xi(t)$, defined by Eqs. (7) and (8), using the modern pulse shaping techniques whereby it is possible to generate the chaotic light by randomizing the phases of the Fourier components of an ultrashort laser pulse. For the HF molecule, we have verified that realizable broadband noise of bandwidth 0.2 a.u. is sufficient to reproduce all features of the enhancement effect presented in this paper.

V. SUMMARY AND CONCLUSIONS

We have shown that it is possible to significantly enhance the dissociation probability of a diatomic molecule under a weak femtosecond MIR pulse by adding a small amount of noise to it. The net enhancement for a given laser pulse exhibits a single maximum as the noise level is varied. This maximum suggests an optimum noise amplitude to achieve the maximum dissociation, in analogy to the stochastic resonance phenomenon. The enhancement landscape, that is the enhancement as a function of laser amplitude and noise amplitude, exhibits a global maximum. Analyzing the frequency resolved gain profile of the molecule using a pump-probe setting we have identified the dominant frequencies and the corresponding physical processes activated by the noise. We conclude that, in addition to single-photon resonant transitions, multiphoton transitions play a significant role.

Similar effects are expected for other diatomic molecules if exposed to a combination of noise and laser pulse, where pulse duration and wavelength in the MIR regime may be chosen from a wide parameter range. Of particular interest in the future will be if the proposed nonlinear interplay can achieve selective bond breaking by enhancing dissociation of a particular bond in a polyatomic molecule.

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