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Dissociation and ionization of small molecules steered by external noise

Anatole Kenfack\textsuperscript{1,3}, Jan M Rost\textsuperscript{1} and Frank Großmann\textsuperscript{2}

\textsuperscript{1} Max Planck Institute for the Physics of Complex Systems, Nöthnitzer Strasse 38, 01187 Dresden, Germany
\textsuperscript{2} Institute for Theoretical Physics, Technical University of Dresden, 01062 Dresden, Germany
E-mail: kenfack@pks.mpg.de

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Abstract. We show that ionization and dissociation can be influenced separately in a molecule with appropriate external noise. Specifically, we investigate the hydrogen molecular ion under a stochastic force quantum mechanically beyond the Born–Oppenheimer approximation. We find that up to 30\% of dissociation without ionization can be achieved by suitably tuning the forcing parameters.

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\textsuperscript{3} Author to whom any correspondence should be addressed.
1. Introduction

The anharmonicity of molecular vibrations makes the dissociation of a molecule by irradiation of laser light a relatively difficult task \cite{1}. Consequently, high intensity is required for dissociation, for instance, \( I > 10^{14} \text{ W cm}^{-2} \) for HF in monochromatic fields \cite{2}. In half cycle pulse fields the situation is improved due to the broad frequency content of this radiation. Even in that case, however, intensities \( I > 10^{13} \text{ W cm}^{-2} \) are required to achieve on the order of 15\% dissociation probability \cite{3}. At such high intensities, the ionization process dominates and masks vibrational excitation and dissociation. Chelkowski et al \cite{4} suggested that the dissociation threshold of a diatomic molecule can be lowered by two orders of magnitude using a down-chirped laser, tracing the decrease in spacing of the excited energies levels, and hence dissociation without ionization should be possible. In a similar spirit, circularly chirped pulses have been used by Kim et al \cite{5} for the dissociation of diatomic molecules. They found that the threshold laser intensity is substantially reduced, which may allow dissociation without ionization to be achieved.

Recently, dissociation of diatomic molecules under a stochastic force was investigated representing the diatom as a Morse oscillator \cite{6}. A phenomenon, akin to stochastic resonance has also been identified in the interaction of an atom with a strong laser field and additional noise \cite{7}.

In the present study, the external force is a sequence of pulses (kicks) at random times, each kick carrying an independent weight \cite{6,8}. Both the weights \( \Gamma_i \) and the intervals between kicks \( \Delta t_i \), follow a Poisson distribution with averages \( \gamma \) and \( \langle \Delta t \rangle \), respectively. This type of force, similar to white shot noise, has also been used to model the passage of ions through carbon foils \cite{9}. Through its inherent time-structure characterized by \( \langle \Delta t \rangle \), it can couple selectively to bound degrees of freedom with comparable timescales of the noise. Given the difficult dissociation without ionization as described above, it is natural to ask if stochastic forcing may allow one to separate effectively ionization from dissociation.

In order to answer this question we have to include both nuclear as well as electronic degrees of freedom in our description. The simplest molecule displaying ionization and dissociation is the hydrogen molecular ion \( \text{H}_2^+ \) in an external field. Using a two-level approximation for the electron \cite{10} or a soft-core potential for the Coulomb interaction \cite{11,12}, this system has been investigated previously under strong laser fields. A recent review of experimental as well as theoretical work is given in \cite{13}.

As in \cite{14}, we refrain from these approximations and investigate this molecule under the influence of a stochastic field with the only restriction that the random force is directed along the molecular axis. This leads to cylindrical symmetry of the problem and therefore three degrees of freedom (two for the electron and one for the nuclei) have to be taken into account explicitly. On the same level, the interaction of \( \text{H}_2^+ \) with laser light has been investigated recently and a sensitive dependence of the dissociation on the carrier envelope phase has been found \cite{15}. Yet, the maximal dissociation probability reported is around 20\%.

We begin the main text of this paper in section 2, with a description of the noise source and a brief explanation of how quantum evolution under a stochastic force is solved for in time. In section 3, we discuss the influence of the same stochastic force on an atom (electronic degrees of freedom) and a molecule (vibrational degrees of freedom) separately, since the effect of coupling strong noise to quantum systems is not widely known. Then in section 4, we describe how we handle \( \text{H}_2^+ \) numerically, in particular how we extract ionization and dissociation from...
the numerically obtained time-dependent wavefunction. In section 5, results for the dissociation and the ionization probability of H$_2^+$ will be presented and discussed, while section 6 concludes the paper.

2. Description of the noise

The stochastic force $F(t)$ we consider here is given by [8, 16]

$$F(t) = \sum_{i=1}^{N_t} \gamma_i \delta(t - t_i),$$

and stands for a series of random impulses of strength $\gamma_i$ at times $t_i$, i.e. $F(t)$ is a kind of white shot noise [17] responsible for multiple $\delta$-kicks undergone by the molecule, where $N_t$ is the number of kicks up to time $t$ controlled by the Poisson counting process $N_t$. It is characterized by the average kicking interval $\langle \Delta t \rangle \equiv \lambda^{-1}$ about which the actual intervals $\Delta t_i = t_i - t_{i-1}$ are exponentially distributed, and similarly for the actual kicking strengths $\gamma_i$ about their mean $\gamma$.

$$P(\Delta t_i) = \lambda \exp(-\lambda \Delta t_i), \quad P(\gamma_i) = \gamma^{-1} \exp(-\gamma_i / \gamma).$$

In analogy to periodically applied half cycle pulses [18], we restrict our analysis to positive $\gamma_i$ and assume that $\gamma_i$ and $t_i$ are mutually uncorrelated random variables generated by the distribution functions of equation (2). The restriction to $\gamma_i > 0$ does not change the results qualitatively, but leads to a faster transfer of energy to the system which reduces the computational effort. The determination of $F(t)$ reduces to the construction of a stochastic sequence $(\gamma_i, t_i)$ which can be done assuming that the random times $t_i$ form a Poisson sequence of points leading to a delta correlated process [8]. It is easy to show [16] that the stochastic force constructed has the properties

$$\langle F(t) \rangle = \gamma \lambda, \quad \langle F(t)F(s) \rangle = 2\gamma^2 \lambda \delta(t - s) + \gamma^2 \lambda^2,$$

where $\langle \rangle$ is understood as an average over a sufficiently large number of deterministic realizations $j = 1, \ldots, N$ of $F(t)$ in terms of specified stochastic sequences $(\gamma_i^{(j)}, t_i^{(j)})$. The corresponding power spectrum, i.e. the Fourier transform of $\langle F(t)F(s) \rangle$, is given by

$$S(\omega) = 4 \frac{\gamma^2 \lambda}{\sqrt{2\pi}} + \gamma^2 \lambda^2 \sqrt{2\pi} \delta(\omega).$$

These properties reveal the difference between the present stochastic force (white shot noise) and pure white noise which is delta-correlated with zero mean. Note that $\langle \Delta t \rangle$ and $\gamma$ are the two relevant parameters characterizing the present noise source. This type of noise could in principle be generated with strong field pulse shaping techniques [19, 20] by suitably randomizing the frequency components.

The determination of the time evolution of a system with a deterministic Hamiltonian $H_0$ and an additional stochastic driving $H = H_0 + x F(t)$ is straight forward by solving first the conventional deterministic time-dependent Schrödinger equation for each realization $F^{(j)}$ of the stochastic force, forming from it the desired observable $O^{(j)}$ and finally averaging over the realizations, $O = N^{-1} \sum_{j=1}^{N} O^{(j)}$.  

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Figure 1. The population of the (electronic) ground state of the hydrogen H atom versus the population of the vibronic ground state of a Morse oscillator, describing the HF molecule as function of time for the same amount of noise. For the HF model, \( \mu_0 = 3.54076 \text{ au}, \alpha = 1.1741 \text{ au} \) and \( D = 0.225 \text{ au} \) [22].

3. Ionization and dissociation under stochastic forces

To demonstrate that coupling white shot noise to a bound quantum system is sensitive to the timescale of bound motion, we briefly describe how an atom and a diatomic molecule respond to noise. To this end, we show in figure 1 how the electronic ground state of a one-dimensional soft-core model of the H-atom and the vibrational ground state of a Morse oscillator describing a HF molecule are depopulated under stochastic forcing. The potential in the atom case is given in atomic units by

\[
V(x, t) = V_C + x F_a(t) = -\frac{1}{\sqrt{x^2 + a}} + x F_a(t),
\]

with \( a = 2 \) such that the ground state energy corresponds to that of the 3d hydrogen atom. In the molecular case it is given by

\[
V(x) = V_M + \mu_0 x F_m(t) = D(1 - \exp\{-\alpha x\})^2 + \mu_0 x F_m(t),
\]

with the dissociation energy \( D \), the length scale \( \alpha \), and the dipole gradient \( \mu_0 \). Note that the eigenstates and the eigenenergies of this Morse potential model are analytically known [21]. We expose both systems to the same stochastic external perturbation, as described above, by adjusting the molecular force such that \( \mu_0 F_m(t) = F_a(t) \). The average time between kicks is chosen to equal the electronic period in the hydrogen atom, which in atomic units is given by \( T_e = 2\pi \).

Numerically, we find a very promising indication that the electron in the atom case does react much less to the force than the binding of the molecule. This is shown in figure 1, where the auto-correlation function of the ground state electron wavefunction for the atomic, as well as of the vibrational ground state in the molecular case is shown. While the atom is still dominantly
in its ground state, the ground state of the molecule has already been depopulated by more than 50%.

In general, we expect for a system S with a characteristic period $T_S^c$ of bound motion that noise will couple energy into the system if its kick spacing is smaller than the bond period, $(\Delta t) < T_S^c$. In the opposite case, $(\Delta t) \gg T_S^c$, the bound motion will be insensitive to the noise. Since the molecular vibrational period is much larger than the electronic period in an atom, $T_{vib}^c \gg T_e^c$, there is a window in $(\Delta t)$, where dissociation without substantial ionization should be possible (see the sketch, figure 2).

We double check this conjecture in the following with the hydrogen molecular ion $H_2^+$ in an external field which is the simplest molecule displaying both ionization and dissociation. However, given that $H_2^+$ does not have a permanent dipole moment it is a priori not clear if selective dissociation by dipole-coupled noise works. Since this problem is sensitive to different timescales, we avoid the Born–Oppenheimer approximation which could be an (artificial) source of physical effects to be predicted.

4. Molecular ionization and dissociation dynamics in $H_2^+$ under external driving

We solve the time-dependent Schrödinger equation for the hydrogen molecular ion in a linearly polarized laser field neglecting the center of mass and the rotational motion [14]. Adding a dipole coupled stochastic force $F(t)$ the time-dependent stochastic Schrödinger equation is given by (in atomic units)

$$i \frac{\partial}{\partial t} \Psi(z, \rho, R, t) = [K_{vib} + K_e + V + z \kappa F(t)] \Psi(z, \rho, R, t),$$

with the kinetic energy $K_{vib} = -M_p^{-1} \frac{\partial^2}{\partial R^2}$ of the protons, the electronic kinetic energy

$$K_e = -\frac{\beta}{2} \frac{\partial^2}{\partial z^2} - \frac{1}{2} \frac{\partial^2}{\partial \rho^2} - \frac{1}{2} \frac{\partial}{\partial \rho}$$

Figure 2. Schematic ionization and dissociation (including fragmentation) probabilities as function of the kick spacing $(\Delta t)/T_e$ at a given finite time and for a given kicking strength $\gamma$. 

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and the potential energy

\[ V(\rho, z, R) = -[\rho^2 + (z - R/2)^2]^{-1/2} - [\rho^2 + (z + R/2)^2]^{-1/2} + 1/R, \tag{9} \]

where \( \beta = 1/2 + 1/(4M_p) \), \( \kappa = 1 + 1/(2M_p + 1) \), \( M_p \) is the proton mass in units of the electron mass, \( R \) is the internuclear distance and \( z \) and \( \rho \) are cylindrical coordinates of the electron.

Due to the cylindrical symmetry of the stochastically driven system an expansion of the wavefunction in a Bessel–Fourier series in \( \rho \) is performed. The singularities of the Coulomb potential is retained, without any softening of the potential. The time-dependent stochastic Schrödinger equation (7) can then be solved by the standard split operator FFT technique [23]. We start from the ground state as initial state \( \Psi(\rho, z, R, t = 0) \), represented very accurately by the product of the vibrational ground state \( \phi_0(R) \) and the 1s\( \sigma_g \) electronic wavefunction of \( \text{H}_2^+ \).

The observables we are interested in are the ionization probability

\[ P_I(t) = 1 - \int_0^{R_{\text{max}}} f_1(R, t) \, dR \tag{10} \]

and the dissociation probability which is defined without ionization according to

\[ P_D(t) = \int_{R_0}^{R_{\text{max}}} f_1(R, t) \, dR. \tag{11} \]

Here, \( f_1 \) is obtained by integrating \( |\Psi(\rho, z, R, t)|^2 \) over electronic coordinates inside a cylinder of radius \( \rho_0 = 8 \) au and height \( 2 \times z_1 + R \) as sketched in figure 3. The integration area would split into two cylinders if \( R > 2z_1 \). The splitting, however, is never reached in the present calculation due to the smallness of our \( R \)-grid. For \( z > z_1 + R/2 \), the system is considered to be ionized since the electron is sufficiently distant to each of the nuclei. The nuclear separation defining the onset of dissociation into the \( \text{H}+\text{H}^+ \) channel is taken as \( R_0 = 9.5 \) au and [14]. In this configuration, \( f_1 \) is explicitly given by

\[ f_1(R, t) = 2\pi \int_{-(z_1+R/2)}^{(z_1+R/2)} \, dz \int_0^{\rho_0} \, d\rho \rho |\psi(R, z, \rho, t)|^2 \]
Figure 4. Ionization and dissociation probabilities as a function of time for different average kick spacings, with $\langle \Delta t \rangle / T_e$ as indicated in panels and for a constant kicking strength $\gamma = 0.9$ au.

In our calculations, the electronic grid for $z$ contains 1024 points and extends from $-50 \text{ au}$ to $50 \text{ au}$. The time step was equal to $0.01 \text{ au} = 2.4 \times 10^{-4} \text{ fs}$. A quadratic imaginary potential has been used to avoid unphysical reflections at the grid boundaries. The onset of ionization was defined to be at $z_I = 32 \text{ au}$. The nuclear grid consists of 256 points, extending from $R_{\text{min}} = 0.38 \text{ au}$ to $R_{\text{max}} = 24 \text{ au}$ and 16 basis functions were used in the Bessel–Fourier expansion for $\rho$.

5. Numerical results

Dissociation and ionization probabilities of $\text{H}_2^+$ as described in the previous section have been obtained for different parameters of the stochastic forcing. Averaging over around 20 realizations of the noise was enough to converge the results for all the cases presented below.
Figure 5. Ionization (black) and dissociation (red) probabilities as a function of time for different noise strength and for fixed spacing $\langle \Delta t \rangle / T_e = 0.2$: ionization (a) and dissociation (a'): $\gamma = 0.9$ au ionization (b) and dissociation (b'): $\gamma = 0.75$ au ionization (c) and dissociation (c'): $\gamma = 0.5$ au.

The maximum propagation times for the wavefunction were always well below 500 fs around which rotational motion of the molecule (not included in the present approach) would come into play.

In figure 4, we present results for a fixed strength $\gamma = 0.9$ au of the noise. The average spacing of the kicks was varied to cover the switching of the dynamics from pure ionization ($\langle \Delta t \rangle / T_e \ll 1$, figure 4(a)) to pure dissociation ($\langle \Delta t \rangle / T_e \approx 1$, figure 4(c)). While the ionization probability reaches unity the dissociation probability has a maximum of 25% as can be seen in figure 4(c).

In figure 5, the spacing between the kicks is fixed at the intermediate value of $\langle \Delta t \rangle / T_e = 0.2$, where both dissociation and ionization coexist for a certain amount of time. From (a) to (c), we reduce the strength of the external forcing. Reducing $\gamma$ reduces the ionization rate and correspondingly shifts the peak in the dissociation without ionization to later times.

What are close to optimal parameters for dissociation without ionization for the stochastically driven hydrogen molecular ion? This question is answered in figure 6. Here, at fixed final time of 100 fs, the probabilities as a function of the average kick intervals are displayed. Beyond $\langle \Delta t \rangle / T_e \approx 1$ the ionization quickly goes to zero. However, also the dissociation approaches zero, as the system does not respond to rare kicks. An intermediate value of $\langle \Delta t \rangle / T_e \approx 0.5$ turns out to maximize dissociation without fragmentation of the whole system. The maximal probability is close to 30% and therefore higher than any comparable value we have found in the literature. We did many additional calculations for different final times, as well as for different field strengths and found results qualitatively similar to those presented in figure 6.

These results confirm the possibility of selective dissociation by dipole-coupled noise. However, for the real molecule, the onset of ionization limits the maximum dissociation which can be achieved. The actual value of the maximum, of course, can only be calculated as we have done (see figure 6).
Figure 6. Ionization and dissociation probabilities as a function of kick spacings at a given finite time for a kicking strength of $\gamma = 0.5$ au.

6. Discussion and conclusions

Achieving efficient dissociation in small molecular systems without ionization has been a longstanding goal. Here, we have explored an alternative to the standard tools, such as chirped laser pulses: the application of stochastic driving in the form of white shot noise with a characteristic internal timescale.

For the hydrogen molecular ion we have shown that dissociation and ionization can be well separated by a suitable choice of the noise parameters. Thereby, the internal timescale of the noise, that is the average interval between kicks, plays a major role. Increasing the kicking intervals beyond the electronic ground state period of the hydrogen atom the driven system switches from ionization to dissociation even for moderate field strengths below one atomic unit.

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References

[1] Blömberger N and Zewail A H 1984 J. Phys. Chem. 88 5459
[2] Chelkowski S and Brandrauk A D 1990 Phys. Rev. A 41 6480
[3] Lin J T, Lin S H and Jiang T F 2000 Phys. Rev. A 61 033407
[4] Chelkowski S, Brandrauk A D and Corkum P B 1990 Phys. Rev. Lett. 65 2355
[5] Kim J H, Liu W K, McCourt F R W and Yuan J M 2000 J. Chem. Phys. 112 1757
[6] Kenfack A and Rost J-M 2005 J. Chem. Phys. 123 204322

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[7] Singh K P and Rost J-M 2007 Phys. Rev. Lett. 98 160201
Singh K P and Rost J-M 2007 Phys. Rev. A 76 063403

[8] Masoliver J 1987 Phys. Rev. A 35 3918
Moss F and McClintock P V E (ed) 1989 Noise in Nonlinear Dynamical Systems vol 1 (Cambridge: Cambridge University Press) p 146

[9] Arbó D G, Reinhold C O, Kürpick P, Yoshida S and Burgdörfer J 1999 Phys. Rev. A 60 1091
Arbó D G, Reinhold C O, Yoshida S and Burgdörfer J 2000 Nucl. Instrum. Methods Phys. Res. B 164–5 495

[10] Lin J T and Jiang T F 2000 Phys. Rev. A 63 013408

[11] Volkova E A, Popov A M and Tikhonova O V 1998 JETP 86 71

[12] Feuerstein B and Thumm U 2003 Phys. Rev. A 67 043405

[13] Posthumus J H 2004 Rep. Prog. Phys. 67 623

[14] Chelkowski S, Zuo T, Atabek O and Bandrauk A D 1995 Phys. Rev. A 52 2977

[15] Roudnev V, Esry B D and Ben-Itzhak I 2004 Phys. Rev. Lett. 93 163601

[16] Luczka J, Bartussek R and Hänggi P 1995 Europhys. Lett. 31 431
Honda T and Sawada Y 1996 Europhys. Lett. 35 313
Hänggi P, Bartussek R, Talkner P and Luczka J 1996 Europhys. Lett. 35 315
Hänggi P 1980 Z. Physik B 36 271

[17] Van Den Broeck C 1983 J. Stat. Phys. 31 467

[18] Frey M T, Dunning F B, Reinhold C O, Yoshida S and Burgdörfer J 1999 Phys. Rev. A 59 1434

[19] Wollenhaupt M et al 2006 Phys. Rev. A 73 063409

[20] Weiner A M 2000 Rev. Sci. Instrum. 71 1929

[21] Ter Haar D 1946 Phys. Rev. 70 222

[22] Goggin M E and Milonni P W 1988 Phys. Rev. A 37 796
Goggin M E and Milonni P W 1988 Phys. Rev. A 38 5174
Martin D L and Wyatt R E 1982 Chem. Phys. 64 203

[23] Fleck J A Jr, Morris J R and Feit M D 1976 Appl. Phys. 10 129