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Nonlinear dynamics of multiphoton dissociation of molecules induced by laser pulses

Research Team

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Introduction

The dynamics of atoms and molecules driven simultaneously by two color fields of commensurate frequencies, ω and $n\omega$, n = 2, 3,.., is a subject with considerable interest, mainly because quantum mechanics predicts that the superposition of two fields, each with its own controlled parameters, gives rise to phenomena that single laser excitation cannot produce. The most conspicuous such phenomenon is the dependence of the processes of dissociation or ionization on the relative phase, φ, of the two laser fields, e.g [1-3]. The effect of φ on the ionization /dissociation yield has been demonstrated by two-color experiments that have been conducted using either 1ω-2ω or 1ω-3ω fields, e.g. [4-6], as well as by corresponding theoretical works and numerical applications, e.g. [7-10]. These developments have been interpreted in the context of quantum interference since the second frequency adds alternative pathways towards fragmentation, thereby adding transition amplitudes causing interference effects that are sensitive to relative phase variations.

As is well-known, there is also interest in the application of nonlinear classical mechanics to quantum systems, one of the aims being to determine areas of correspondence between classical and quantum mechanics and to discover possibilities of applications where classical mechanics produces meaningful and physically relevant results.

As regards the general theory of classical dynamics, a thorough investigation of the relative phase effects on the escape dynamics, (ionization or dissociation), and of its dependence on the system and field parameters has, heretofore, been absent. The work reported here aims at rectifying this situation, via an application in the area of molecular dissociation dynamics. In order to be general, the study has utilized the Morse potential for the description of vibrational motion, a potential that has been used before in classical and in quantum mechanical investigations of dissociation dynamics induced by a laser field, e.g., [11-13]. Along with the ionization of H atoms, its laser-induced dissociation behavior constitutes a paradigm for the phenomenology of the quantum mechanical manifestations of regular and chaotic behavior in classical phase space, this being the core of the quantum chaos problem.

Apart from the dissociation of Morse molecules by single frequency laser, effects of the simultaneous driving with two laser fields has also been investigated, both classically and quantum mechanically, [13-15]. The main concern in those studies was to find the field parameters for which the addition of the second laser enhances the

dissociation process, thereby lowering the required field intensity for the occurrence of dissociation. However, no work has been reported yet on the effects of φ, and of its combination with variations of intensity, on the dissociation process.

Description of the system and methodology

We consider the pure vibrational motion of a diatomic molecule for a fixed electronic configuration, under the assumption that rotational motion is not involved in the dissociation process. The molecular potential is modeled by a Morse potential:

$$V_M(r) = D(1 - e^{-\alpha(r-r_e)})^2 \qquad (1)$$

where D is the dissociation energy, r_e is the equilibrium bond distance, and α^{-1} is the range of the potential. HF, HCL, H_2 and NO are some examples of diatomic molecules that have been modeled by the Morse potential.

The shape of the laser pulses is chosen to be trapezoidal. The case of ac-fields with constant amplitudes during the whole interaction has also been considered. The interaction between the molecule and the lasers is chosen to be a linear dipole function. Selected calculations with other functions did not show significant modifications of the results. Thus, the Hamiltonian of the system is written as:

$$H(r,t) = H_o(r) + (r - r_e)\varepsilon(t)(A_1 \sin(f_1 t) + A_2 \sin(f_2 t + \varphi)) \qquad (2)$$

where $H_o(r) = p^2/2m + V_M(r)$ is the unperturbed Hamiltonian, A_1, A_2 are the maximum amplitudes of the electric fields of two lasers, $\varepsilon(t)$ is the envelope of the laser pulses (the same for both lasers), f_1, f_2 are the corresponding laser frequencies and φ is the relative phase of the two lasers. The computational methodology involves the solution of the equations of the classical dynamics of the time-dependent nonlinear Hamiltonian (2), in conjunction with an appropriate choice of the ensemble of initial conditions.

In order to imitate more closely the quantum photodissociation process, the initial classical state is chosen as an ensemble of initial conditions with specific energy E and angle variables θ uniformly distributed between $-\pi$ and π.

All calculations reported below were done keeping the frequencies $\omega_{1,2}$ of two lasers and the initial vibration energy constant. The fast laser frequency is red-shifted from the Morse harmonic frequency Ω_M and its normalized value is taken as $\omega_2 = 0.84$, so that single laser driving leads to maximal dissociation yield for all laser amplitudes [11-13]. The frequency of the slow laser is chosen to be one third of the fast laser: $\omega_1 = \omega_2/3 = 0.28$. Also, the molecule is considered to vibrate initially in its ground state. For the molecular constants of HF, the frequency of the fast laser is $f_2 = 3476$ cm^{-1} while the normalized ground state energy is $E_o = 0.045$. A normalized field amplitude F_1 or $F_2 = 1$ corresponds to a laser intensity of 320 TW/cm^2. The remaining parameters are varied so as to examine their effect on the properties of the dissociation process. The main interest will be in mapping the dissociation behavior on the plane of the normalized field amplitudes (F_1, F_2) and examine the regions of maximum relative phase or stabilization effects on dissociation.

Relative phase effects on dissociation dynamics

Based on the well-known dissociation criterion for classical trajectories[11-13], we calculate the sensitivity SP_D of P_D to φ, on a grid in the $F_2 - F_1$ plane. At each grid point, (F_2, F_1), SP_D is defined as

$$SP_D(F_2,F_1)= P_D^{max}(F_2,F_1) - P_D^{min}(F_2,F_1) \qquad (7)$$

where $P_D^{max}(F_2, F_1) = max(P_D(F_2, F_1 ; \varphi), 0 < \varphi \leq 2\pi)$ and $P_D^{min}(F_2, F_1) = min(P_D(F_2, F_1; \varphi), 0 < \varphi \leq 2\pi)$.

Taking into account that $P_D(\varphi) = P_D(2\pi - \varphi,)$ [16], we implement the above estimation by calculating P_D for $\varphi = 0, 30, 60, 90, 120, 150, 180^o$. Figure 1 shows a contour plot of $SP_D(F_2, F_1)$ for initial energy equal to E_o. We observe that the region where SP_D comes close to its maximum value, $(SP_D > 0.87)$, is clearly located above the diagonal $F_1 = F_2$, i.e. the effect of the relative phase on P_D is maximized for slow laser intensities larger than those of the fast laser $(F_1 > F_2)$.
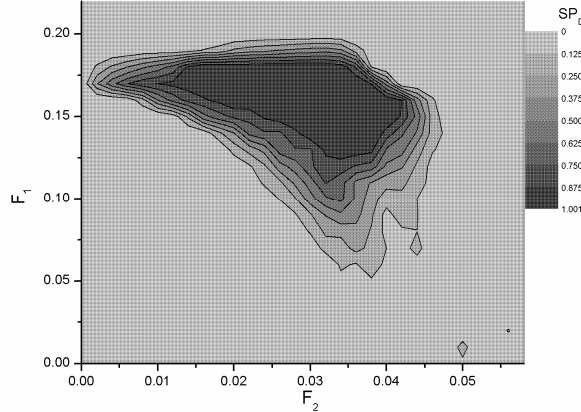

Figure 1. Contour plot on the plane F_2 - F_2 of the sensitivity, SP_D, defined as the maximum recorded difference of P_D as φ varies (see text for details). The darker the region is, the greater is the sensitivity of P_D to changes of φ.

How does this φ-dependence emerge? Which relative phases lead to maximum P_D and which to minimum P_D? Figure 2 shows the representative P_D maps for $\varphi = 0, 30, 90, 180^o$ and reveals that the φ-dependence effect is associated with a stabilization phenomenon, (reduction of the P_D), that is prominently present at $\varphi = 0^o$ and is disappearing as φ increases. The stabilization, (or chemical bond hardening), occurs in two cases. First, for slow laser amplitudes just above the single slow laser dissociation threshold $(F_1^{thres} \approx 0.13)$, when the second fast laser is added, ('*fast laser stabilization*'). Second, for fast laser amplitudes about the single fast laser threshold $(F_2^{thres} \approx 0.042)$ when the slow laser is added, ('*slow laser stabilization*').

Phase Space Origins Of Stabilization And Of Relative Phase Effects .

A typical stroboscopic plot of the phase space of the driven molecule is shown in Fig. 3a, which records the trajectories of the initial state at integral multiples of the period T_1 of the slow laser. As we can see, there are two regular regions (I and II) inside a chaotic sea of dissociating trajectories. The regular region I consists of KAM tori of the unperturbed Morse potential that have survived in the strongly perturbed system of Fig. 3a. They surround the stable periodic orbit emanating from the lowest energy fixed point of the Morse potential. On the other hand, the regular region II is in fact the island of stability corresponding to the lowest energy common resonance mentioned above, (E = 0.29). The red line shown also in Fig. 3a represents the ensemble of the initial conditions with energy $E = E_o = 0.045$ and equidistributed angles θ, as defined in Section II. The classical dissociation probability of the ground state is proportional to the part of the red line lying in the chaotic sea. Thus, the phase space origins of the
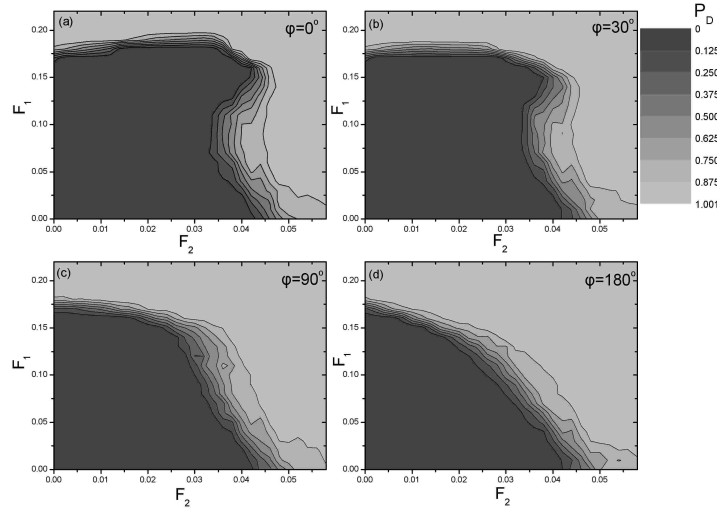
Figure 2. Contour plots of dissociation probability, P_D, in the plane F_2 - F_1, for various relative phases: $\varphi = 0^o$ (a), $\varphi = 30^o$ (b), $\varphi = 90^o$ (c), $\varphi = 180^o$ (d). Notice the reduction of P_D, (stabilization), as F_2 (F_1) increases with F_1 (F_2) just above (below) the single laser dissociation threshold, as well as its association with the maximum sensitivity region of Figure 1.
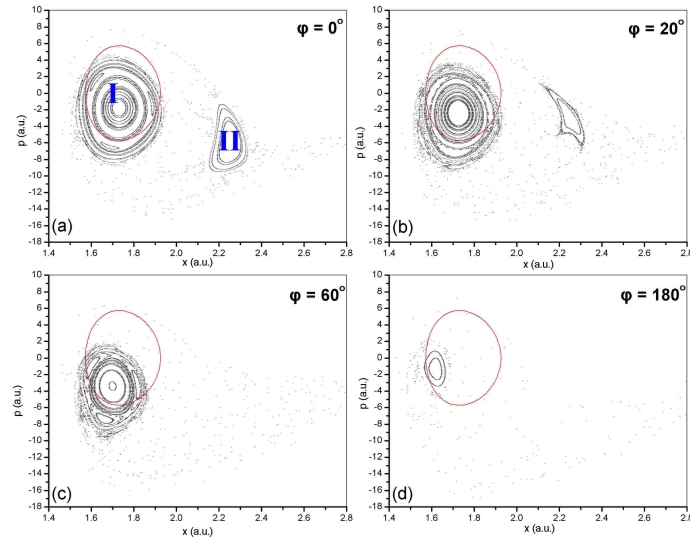

Figure 3. Stroboscopic plots of phase space for $F_1 = 0.18$, $F_2 = 0.02$ and $\varphi = 0^o$ (a), $\varphi = 20^o$ (b), $\varphi = 60^o$ (c), $\varphi = 0^o$ (d).

stabilization and relative phase effects detected in the previous Section probably have to do with the behavior of these regular regions, I and II, as φ and F_2 vary.

Indeed we observe that the increase in φ modifies both regular regions (Fig. 3b,c,d). More pronounced is the effect that it has on the region of the common resonance since it induces the disappearance of the resonance island for $\varphi > 25^o$. More detailed recording of the phase space structure as φ increases indicates that this disappearance occurs gradually through a bifurcation process of the stable periodic orbit of the specific common resonance. We can say that, in some sense, the regular region II "is diluted" into the surrounding chaotic sea as φ increases.

The disappearance of the resonance does not seem to affect significantly the dissociation probability, since there is no overlap of the island with the initial state. On

the contrary, it is expected to influence the dissociation rate as it takes place in the dissociation paths of the escaping trajectories.

Less impressive but more influential on the dissociation dynamics is the effect of the variation of φ on the KAM regular region I. As one can see in Figure 3, increasing φ causes the shrinking of that region and at the same time the movement of its position in phase space. The combination of these effects has drastic results concerning the overlapping of the KAM region with the line of the initial state and, in fact, constitutes the phase space origin of the relative phase effect on the dissociation probability in maximum sensitivity regions of the plane F_1- F_2. No such modifications of the KAM region I have been observed for F_1 and F_2 outside maximum sensitivity regions.

In the previous paragraph, we demonstrated numerically the possibility of both slow- and fast-laser stabilization of the dissociation dynamics when appropriate choices for the other laser field are made. Further, these stabilization effects are φ-sensitive; they are present for $\varphi = 0^o$ but diminish as φ increases. In Fig. 4,5 we show that, in phase space terms, this stabilization behavior is generated by the response of the KAM region I to laser intensity variations, in a similar way to the relative phase effects discussed above.
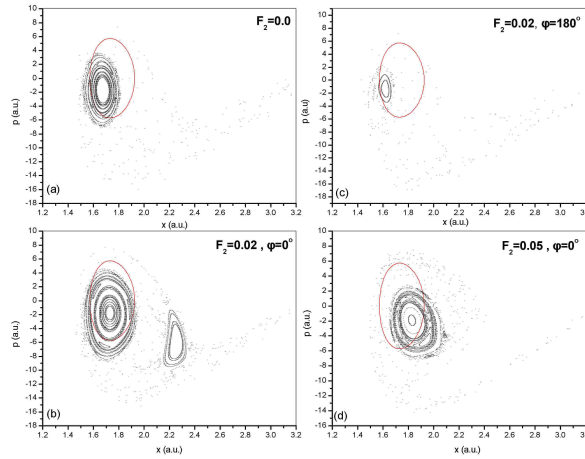

Figure 4. Stroboscopic plots revealing the phase space origins of fast-laser stabilization effect. For all plots, $F_1 = 0.18$, i.e. just above the single laser dissociation threshold, while the values of the second laser intensity and the relative phase are shown on the plots.

Conclusions

In this project, the dissociation dynamics of a dichromatically laser-driven diatomic Morse molecule vibrating in the ground state has been investigated, by applying tools of the nonlinear theory of Hamiltonian systems. Emphasis has been placed on the role of the relative phase of the two fields, φ. Firstly, it has been found that, just like in quantum mechanics, there is dependence of the dissociation probability on φ. Then, it has been demonstrated that addition of the second laser leads to suppression of probability ('stabilization'), when the intensity of the first laser is kept constant just above or below the single laser dissociation threshold. This 'chemical bond hardening' diminishes as φ increases. These effects have been investigated and interpreted in terms
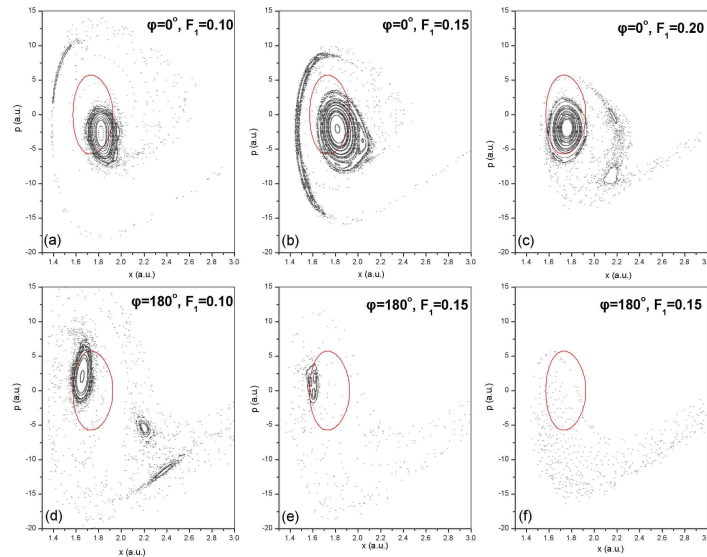
Figure 5. Stroboscopic plots revealing the phase space origins of slow laser stabilization effect. For all plots, $F_2 = 0.04$, i.e. just below the single laser dissociation threshold. The values of the other laser intensity and the relative phase are shown on the plots.

of modifications in phase space topology. Variations of φ as well as of the intensity of the second laser may cause i) appearance/ disappearance of the stability island corresponding to the common resonance with the lowest energy and ii) deformation and movement of the region of Kolmogorov Arnold Moser (KAM) tori that survive from the undriven system. The latter has been demonstrated to be the main origin in phase space of stabilization and φ-dependence effects[17].

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