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Effect of Environment on Photo-detachment Dynamics of Halide Ions: A Model Approach

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A two dimensional model approach for the photodetachment dynamics of closed shell anionic systems in presence of external light field have been proposed in the context of polar environmental media. The effects of strong coupling between the solvent polarization and the extra charge in the system were studied by a simple model. The electronic states of concerned halide ions are represented by a two dimensional model Hamiltonian with a potential $V(x, y) = -V_0 e^{-\sigma(x^2 + y^2)}$. The time dependent Fourier grid Hamiltonian method have been used to follow the detachment process with fairly high intensities of light. The environmental effects on the dynamics are sought to be modeled by two different ways. The first one was the presence of polar solvents which perturb the energy levels of anionic systems by changing the effective potential surface and the second one was allowing the fluctuation of the well depth randomly to mimic the system in a more realistic view point. The average detachment rate constant is calculated as a function of important parameters of the used light field to explain the effects of solvent field on the dynamical behavior of dipole bound anionic system at least in a qualitative way.

Key words: Photodetachment dynamics, Environmental effect, Time-dependent Fourier grid Hamiltonian, Stochastic deactivation

I. INTRODUCTION

The detachment of an extra electron from an atomic or molecular anion (A^-) in presence of external electromagnetic field is an interesting phenomenon. In this process the absorption of a photon ($h\nu$) is occurred by the anion followed by its destruction into the neutral parent atom (A) or molecule and an ejected electron (e^-). The study of photodetachment in the gas phase in presence of either monochromatic or bichromatic laser field has proved to be immensely important in sharpening our understanding in the field of spectroscopy of radicals, transition states, and intermediates of chemical reactions [1–14]. The ejected electron in a photodetachment experiment feels the potential of the neutral parent that it leaves behind. The coupling between these two are weak and comparatively short range so that different type of short range potentials which are qualitatively different from coulomb potential can be used to model this photodetachment phenomenon.

The phenomenon of gas phase photodetachment is

conceptually simple. By absorbing the energy of the photon the anion is excited into the ionization continuum and then ejects an electron. The departure of the electron can be viewed as sudden on the time scale of nuclear motion. For atomic anions the behavior of the detached electron is governed by Wigner's law [15]. The situation which is simple when the parent anion has no electronically excited bound state below the ionization threshold changes significantly if the anion is embedded in a medium with which it can interact. The effects of solvents become much more important when charged species are involved. Coulombic interactions between the solute and polar or polarizable solvents lead to changes of the potential energy surfaces by modification of the solute electronic structure. The detailed dynamics under the influence of strong solvent solute interaction has not been fully appreciated [16]. The interaction can stabilize the anionic ground state and produce quasi-bound excited anionic states embedded in the continuum just above threshold [12, 17]. The stabilization of the anion-ground state due to interaction with the medium or the surrounding (solvation) would have the effect that the detachment energy would increase (blue shift) and quasi-bound excited states would appear, leading to the emergence of an absorption spectrum, possibly a transient one prior to the onset of ion-

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ization [18]. The dynamics of ionization could be in consequence, modified. If the medium consists of dipolar solvent molecules, the ejected electron could ultimately be captured by a solvent dipole. If the dipole moment exceeds a critical value (μ_c), a molecular anion is produced, which then relaxes [19]. The process of ionization, capture and subsequent relaxation of the dipole-bound anion would occur in different time scales. It would be interesting therefore to model the photodetachment dynamics of an electron from atomic anions in the presence of strong dipole in the neighborhood. A full fledged simulation in condensed phase would be impractical unless approximations (*e.g.*, hybrid method of quantum classical mechanics) [20–22] are made. In the gas phase model, we may think of an anion interacting with one dipole in the rarefied atmosphere of a beam forming a 1:1 cluster. One can then study the phenomenon of photodetachment quantum mechanically by a suitable one-dimensional (1D) model [12, 23]. The solvent is assumed to interact with the anion by charge dipole and charge induced dipole interactions. The introduction of the solvent field is based on a simple one electron picture [22] which describe charge transfer processes in various system. Initially we assume that the wave function for the anionic ground state is sufficiently localized in space and the ejected electron has negligibly small probability of getting captured by the dipole within the short period of time over which the process of detachment takes place.

The purpose of the present work is to understand the photo detachment dynamics of halide ions (X^- , $X=\text{Cl}$, Br , I) by electromagnetic field in polar environmental situation by 2D model approach and compare the results with 1D model. The reason for the choice of such type of systems stems from the fact that, these ions are stable and can exist in contact with a medium. Several experimental [24, 25] and theoretical [26, 27] results are available on these systems. The key quantities of interest are the average detachment rate constant (k_{av}) and it depends on the systems parameters such as strength of dipole, intensity, and frequency of the used light field. The halide ion is expected to be in contact with an environment. There are several important methods for modeling environmental effects on the key dynamical quantities. In a classical contact, the environment can be modeled by introducing a phenomenological frictional force. In a quantum mechanical framework, the environment is often sought to be modeled by a collection of harmonic oscillators coupled to the system of interest. It maybe seek to mimic some aspects of the environmental perturbations in a rather simple manner by introducing a fluctuation in the potential (V) that has been used to model the states of the ion and then look for signature of environment in the photodetachment rate, detachment threshold, *etc.* A number of researchers have investigated the non-equilibrium statistical mechanical problem of escape of a Brownian particle over fluctuating barriers and the associated

phenomenon of “resonant activation” [28–32]. In the present case, the interest lies in the escape of a purely quantum mechanical particle out of a well of fluctuating (but finite) depth when driven by a regular external monochromatic field. It is conceivable, by analogy with the problem of escape over fluctuating barrier, that the solution of the present problem may reveal some interesting features arising from the interplay of regular and stochastic perturbations. For achieving this, we have to solve the quantum mechanical equation of motion of a particle in a finite well of fluctuating depth when perturbed by an external time varying field. We propose to do that in the Schrödinger picture by invoking the time-dependent Fourier grid Hamiltonian (TDFGH) method [33–39], the time independent variant of which was developed earlier by Marston and Balint-Kurti [40]. A complex scaled FGH method was suggested by Chu [41]. The environmental effects on the dynamics could also be grafted within the framework of redfield theory [42] or that of a mixed quantum-classical dynamical model [43, 44] in which the solvent coordinate are treated classically, while the system and its interaction, with the surrounding are handled quantum mechanically at an adiabatic, or a non-adiabatic level of approximation. However, they are much more difficult to apply in the context of the present problem as it involves bound to continuum transitions. We therefore investigate only the fluctuating well depth case.

The specific questions probed by us are as follows. (i) What kind of effects does the perturbing dipole have on the structure of the energy levels of the 2D model anionic system over the 1D model? (ii) How are the detachment rate constant (k_{av}) and threshold modified by the presence of the polar medium? In the following sections we have tried to answer these specific questions as fully as possible.

II. THEORETICAL MODEL OF THE SYSTEM

The model systems that we have concerned are halide ions (X^- , $X=\text{Cl}$, Br , I) in their respective ground states which are spherically symmetric ($l=0$) states. The model consists of one halide ions and two pairs of polar solvent molecules placed at a certain distance as illustrated schematically in Fig.1. The model potentials that have been used are $V(x)=V_0e^{-\sigma x^2}$ and $V(y)=V_0e^{-\sigma y^2}$ and the coupling between the two is $V(x,y)=V'_0e^{-\sigma(x^2+y^2)}$ (Fig.2(a)). The total hamiltonian for the system will be

$$\begin{aligned} H_0 &= \frac{P_x^2}{2m} + V_0e^{-\sigma x^2} + \frac{P_y^2}{2m} + \\ &\quad V_0e^{-\sigma y^2} + V'_0e^{-\sigma(x^2+y^2)} \\ &= H_x^0 + H_y^0 + V(x,y) \end{aligned} \quad (1)$$

where $-\infty \leq x \leq \infty$, $-\infty \leq y \leq \infty$. The two adjustable parameters of the model, V_0 and σ determine the depth

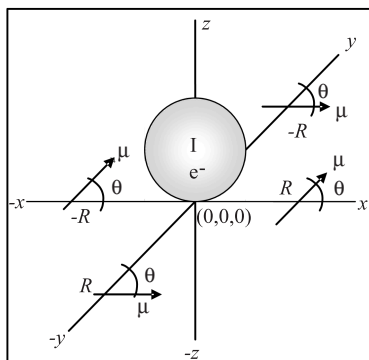


FIG. 1 Schematic representation of the model dipole bound anionic system.

TABLE I Characteristic parameters used in 2D model potential of halide ions. $V(x, y) = -V_0 e^{-\sigma(x^2 + y^2)}$. For three halide ions Cl^- , Br^- , and I^- , $\sigma = 0.1240 \text{ a}_0^{-2}$ and $n_b = 1$.

| Ion | $V_0/\text{a.u.}$ | $\text{IP}^{\text{a}}/\text{a.u.}$ | $-E_0^{\text{b}}/\text{a.u.}$ |
|---------------|-------------------|------------------------------------|-------------------------------|
| Cl^- | 0.13806 | 0.13266 | 0.13266 |
| Br^- | 0.13129 | 0.12351 | 0.12351 |
| I^- | 0.12289 | 0.11257 | 0.11257 |

^a Experiment [45].

^b Calculation.

and the width of the potential well respectively which can be fixed by requiring them to correctly reproduce the ground state ionization energy of the concerned halide ion. The adjustable potential parameters for different anionic systems which have been used for our calculations are listed in Table I.

The coupling with the environment is sought to be modeled by two ways. (i) The charge dipole interactions between the anion and the solvent molecule of dipole moment μ_s and polarizability $\bar{\alpha}$ is represented by the potential [46]

$$V_{\text{int}}(x) = -\frac{q\mu_s \cos\theta}{x^2} - \frac{\bar{\alpha}q^2}{2x^4} \quad (2)$$

$$V_{\text{int}}(y) = -\frac{q\mu_s \cos\theta}{y^2} - \frac{\bar{\alpha}q^2}{2y^4} \quad (3)$$

where q is the net charge of the anion, and θ is the angle made by the dipole μ_s with the line joining the anion and the center of the dipole (Fig.1).

If L is the distance between the anion and the dipole in each direction, the interactions feel by the electron for each separate direction at the point x and y can be written as

$$V_{\text{int}}(x) = -\frac{q\mu_s \cos\theta}{(x-L)^2} - \frac{\bar{\alpha}q^2}{2(x-L)^4} \quad (4)$$

$$V_{\text{int}}(y) = -\frac{q\mu_s \cos\theta}{(y-L)^2} - \frac{\bar{\alpha}q^2}{2(y-L)^4} \quad (5)$$

The modified coupling potential of the dipole bound

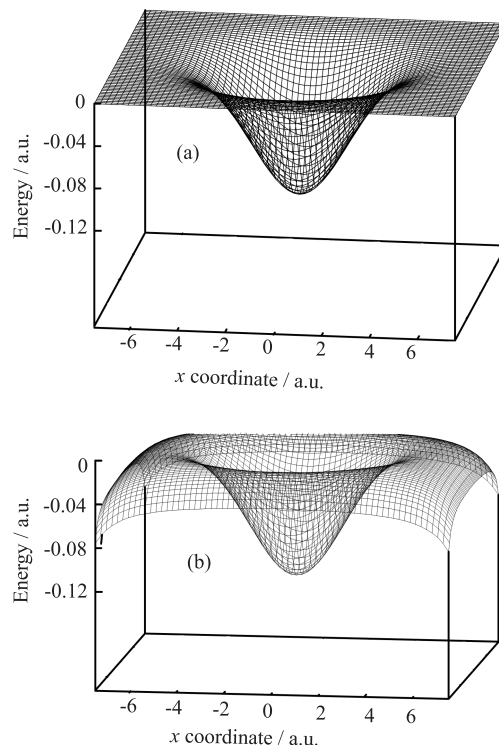


FIG. 2 (a) Two dimensional bare anion model potential. (b) Shape of the same potential in presence of dipole molecules.

iodide anion that have been used is the following form and shown in Fig.2(b).

$$V'(x, y) = V(x, y) + V_{\text{int}}(x) + V_{\text{int}}(y) \quad (6)$$

Here it is obvious that $V_{\text{int}}(x)$ and $V_{\text{int}}(y)$ have a singularity at $x=L$ and $y=L$, but as long as $|x-L|$ and $|y-L| \gg 0$, *i.e.*, the motion of the electron is confined within the perimeter of the well $V(x)$ and $V(y)$, $V_{\text{int}}(x)$ and $V_{\text{int}}(y)$ can be treated as a perturbation and FGH [40] calculation can be carried out without any difficulty with $V_{\text{int}}(x)$ and $V_{\text{int}}(y)$ as given in Eqs.(2) and (3). However, when the electron is excited into continuum, it is delocalised over wide region and the constraint $|x-L|$ and $|y-L| \gg 0$ can no longer be ensured. In these cases one can map $V_{\text{int}}(x)$ and $V_{\text{int}}(y)$ into the form

$$V_{\text{int}}(x) \approx A_0 e^{-\lambda(x-\sigma_0)^2} \quad (7)$$

$$V_{\text{int}}(y) \approx A_0 e^{-\lambda(y-\sigma_0)^2} \quad (8)$$

by any suitable fitting procedure and use it for the entire range of x and y ($-L \leq x \leq L$, $-L \leq y \leq L$) used in our numerical calculation. By choosing A_0 , λ , and σ_0 carefully, a very good fit could be produced that permits us to use the TDFGH [33] recipe even when the electronic motion extends into the region where the dipole is located, and beyond, enabling us to take into account the possibility of electron capture by the dipole and look

for its signature in the ionization dynamics. The parameters A_0 , λ , and σ_0 will, however, vary with the orientational angle (θ) of the dipole.

(ii) Allowing V'_0 to fluctuate randomly with time by taking $V'(x, y, t) = -V'_0(t)V'(x, y)$, where $V'_0(t) = V'_0[1 + R(t)\Delta V]$, $R(t)$ assuming +1 or -1 randomly, ΔV being the strength of the fluctuation of the well depth such that $\langle R(t) \rangle = 0$.

The interaction of the anion X^- with the incident electric field radiation is modeled by including an interaction term $V'_{\text{int}}(x, t)$ in the Hamiltonian where

$$V'_{\text{int}}(x, t) = \epsilon^0 S(t) x e \sin(\omega t) \quad (9)$$

The electric field is along the x direction and $S(t)$ is the appropriate pulse shape function, a function slowly varying in time compared with the optical oscillations.

III. THEORETICAL FRAMEWORK FOR NUMERICAL CALCULATION

Let us describe the total Hamiltonian of the system in two-dimensional model including the charge dipole interaction between the anion and dipole as

$$\begin{aligned} H_0 &= \frac{P_x^2}{2m} + V_0(x) + \frac{P_y^2}{2m} + V_0(y) + V(x, y) + \\ &\quad V_{\text{int}}(x, \mu_s, \bar{\alpha}, \theta) + V_{\text{int}}(y, \mu_s, \bar{\alpha}, \theta) \\ &= H_x^0 + H_y^0 + V'(x, y) \end{aligned} \quad (10)$$

where μ_s and $\bar{\alpha}$ are the dipole moment and the average ground state polarizability of the solvent molecule respectively and θ is the orientational angle defined by the dipolar direction (μ_s) of the solvent molecule and the anion (Fig.1). We suppose that $V_0(x) = V_0 e^{-\sigma x^2}$ and $V_0(y) = V_0 e^{-\sigma y^2}$ are the potential in each individual direction and $V(x, y) = V'_0 e^{-\sigma(x^2 + y^2)}$ describes coupling between the coordinates (modes). Let $\epsilon^0 S(t) x e \sin(\omega t)$ be the external field linearly coupled to the one mode (along x axis). To study the problem we have used the time dependent mean field approach [35–37] within the basic framework of the FGH method [40]. The mean field description starts by approximating $|\psi(x, y, t)\rangle$ by a product of a pair of one dimensional wave functions $|\phi(x, t)\rangle$ and $|\chi(y, t)\rangle$ and introducing the time dependent variational principle that leads to a pair of coupled one dimensional Schrödinger equations that are to be solved. These equations are

$$H_x^{\text{eff}} |\phi(x, t)\rangle = i\hbar \dot{|\phi(x, t)\rangle} \quad (11)$$

$$H_y^{\text{eff}} |\chi(y, t)\rangle = i\hbar \dot{|\chi(y, t)\rangle} \quad (12)$$

where

$$H_x^{\text{eff}} = H_x^0 + \tilde{\epsilon}_y + V'(x, \bar{y}) \quad (13)$$

$$H_y^{\text{eff}} = H_y^0 + \tilde{\epsilon}_x + V'(\bar{x}, y) \quad (14)$$

$$\tilde{\epsilon}_x = \langle \phi(x, t) | H_x^0 | \phi(x, t) \rangle \quad (15)$$

$$\tilde{\epsilon}_y = \langle \chi(y, t) | H_y^0 | \chi(y, t) \rangle \quad (16)$$

$$V'(\bar{x}, y) = \langle \phi(x, t) | V'(x, y) | \phi(x, t) \rangle \quad (17)$$

$$V'(x, \bar{y}) = \langle \chi(y, t) | V'(x, y) | \chi(y, t) \rangle \quad (18)$$

We assume that the system interacts with the time varying electric field of light in x polarization then Eq.(11) becomes

$$\begin{aligned} H(x, t) |\phi(x, t)\rangle &= [H_x^{\text{eff}} + \epsilon^0 S(t) x e \sin(\omega t)] |\phi(x, t)\rangle \\ &= i\hbar \dot{|\phi(x, t)\rangle} \end{aligned} \quad (19)$$

We now invoke the time dependent Fourier Grid Hamiltonian (TDFGH) method in one dimension to integrate Eqs.(11) and (12). Since the one dimensional potential in each direction is the same type, the effective Hamiltonian in each direction will be the same and we have the same results whether the systems interact with either x polarised or y polarised electromagnetic field. If we expand $|\phi(x, t)\rangle$ in appropriate coordinate grids, the eigen states of time independent Hamiltonian by the FGH [40] recipe may be represented as

$$|\phi_i(x)\rangle = \sum_{p=1}^{n_x} w_{pi}^x |x_p\rangle \Delta x \quad (20)$$

where $|x_p\rangle$ is the coordinate vector at the p th grid point, Δx is the spacing of the uniform coordinate grid, and w_{pi}^x is the p th grid point amplitude of the i th eigen state. It follows then that

$$|\phi_i(x, t)\rangle = \sum_{p=1}^{n_x} w_{pi}^x(t) |x_p\rangle \Delta x \quad (21)$$

The expanded form in the other direction $|\chi(y, t)\rangle$ will be the same as above. The full form of the time dependent Hamiltonian that we have used for modeling the dynamics of photodetachment of an electron from an anion in presence of light field is $H(x, t) = H_x^{\text{eff}} + \epsilon^0 S(t) x e \sin(\omega t)$, where $S(t)$ is the appropriate pulse shape function, we have used the continuous pulse and have assumed the linear coupling between the electron and the electric field of light, and the coupling with the environment has not been considered in the model. However, such a coupling as mentioned already can be introduced in the proposed model by making fluctuation in the potential well in time. In that case, $H(x, t)$ have the new form

$$\begin{aligned} H(x, t) &= H_x^0 + H_y^0 + V'_0[1 + R(t)\Delta V]V'(x, y) + \\ &\quad \epsilon_x^0 s(t) x e \sin(\omega t) \end{aligned} \quad (22)$$

For $t > 0$, $R(t)$ is assumed to be (± 1) randomly while $R(0)$ is taken to be zero. The time dependent Schrödinger equation (TDSE), describing the model X^- interacting with light of appropriate frequency and intensity in presence of dipolar solvent, is then solved by

TABLE II Ground and first excited state energy of the dipole bound anionic system with variation of the dipole moment of the solvent molecule.

| Solvent molecule | $\mu_s/\text{a.u.}$ | $E_1^{\text{a}}/\text{a.u.}$ | $E_2^{\text{b}}/\text{a.u.}$ | $\Delta E_{1 \rightarrow 2}^{\text{c}}/\text{a.u.}$ |
|--------------------|---------------------|------------------------------|------------------------------|---|
| No solvent | 0.0000 | -0.11257 | 0.02698 | 0.13955 |
| Methylene chloride | 0.6299 | -0.11898 | 0.01885 | 0.13783 |
| Methanol | 0.6693 | -0.11936 | 0.01837 | 0.13773 |
| Water | 0.7283 | -0.11993 | 0.01765 | 0.13758 |
| Acetone | 1.1024 | -0.12355 | 0.00971 | 0.13327 |

^a Ground state energy.^b Excited state energy.^c Transition energy.

invoking the time dependent Fourier Grid Hamiltonian method [33, 34]. The relevant TDSE is ($\hbar=1$, $e=1$, $m=1$)

$$i \frac{\partial}{\partial t} \phi_i(x, t) = [H_x^{\text{eff}} + \epsilon^0 S(t) \epsilon x \sin(\omega t)] \phi_i(x, t) \quad (23)$$

Then we arrive at the corresponding time evolution equations for the p th grid point amplitudes $\dot{w}_p^x(t)$ ($p=1, \dots, n_x$) of i th state by appealing to the Dirac-Frenkel variational principle. The equation will be

$$\dot{w}_p^x = \frac{1}{i} \left\{ \sum_{q=1}^{n_x} \Delta x [\langle x_p | H_x^{\text{eff}} + \epsilon^0 S(t) \epsilon x \sin(\omega t) | x_q \rangle] w_q(t) \right\} \quad (24)$$

$p = 1, \dots, n_x$

These equations have been integrated numerically by using the fourth order Runge-Kutta method. At $t = 0$, $V'(x, t)$ is zero so that the system can be described by an appropriate eigenstate of h_x^0 . This is found by solving the corresponding energy eigenvalues by the FGH method [40].

Let us suppose that n_b is the number of bound states $\phi(x, t=0)$ supported by h_x^0 . The time dependent detachment probability is then computed by using the generalized time dependent overlap amplitudes $s_i(t)$ obtained by projecting the evolving wave function $\phi(x, t)$ on the eigenstates $\phi(x, t=0)$ of h_x^0 , so that

$$s_i(t) = \langle \phi(x, t) = 0 | \phi(x, t) \rangle \quad (25)$$

The detachment probability $P_d(t)$ can be considered as the probability of the system being in the unbound part of the spectrum which is given by

$$P_d(t) = 1 - \sum_{i=1}^{n_b} |s_i(t)|^2 \quad (26)$$

By plotting $-\ln P_d(t)$ against t and computing the slopes at different intervals one can calculate the time dependent average detachment rate constant (k_{av}) as a function of the parameters of the used light field.

IV. RESULTS AND DISCUSSION

A. Energy levels of the perturbed anions

The energy levels of the dipole bound anions will be significantly different from that of the bare anions (considering the system in the gas phase where there is no solvent field) due to charge dipole interaction. We have computed the energy levels of the perturbed anions in the field produced by the solvent, such as water, acetone, methyl iodide, etc in 2D model systems and have shown in the Table II. The presence of the dipole is seen to affect the energy levels of the anions strongly in the 2D model even when the dipole is at a fairly large distance (9.0 a.u.) from the center of the anion compared to 1D model [14]. The ground state of a particular anionic system in presence of polar solvents is more stabilized in 2D model compared to the 1D results [14] and it is also found the more stabilization in case of strong polar solvents (Table II).

Another very interesting point is that the polar solvents also stabilize the excited states of the dipole bound complex and it is more stabilized compared to the ground state and the effect is comparatively higher in 2D cases. So the transition energy from ground to first excited state is comparatively less for strongly polar solvent in 2D model.

B. Comparison of detachment dynamics of 1D and 2D model system both for bare and dipole bound anion

When the electric field of light is turned on in each cases, the bare and the dipole bound anionic system experiences excitations from the ground state and the populations in the higher continuum levels are seen to grow and decay systematically and sequentially. The net growth of population in the unbound part of the spectrum represents the detachment probability $P_d(t)$ which is the net probability of finding the system in a state that is not in the bound part of the spectrum of anion at t . For each cases the nature of detachment probability *vs* time that is $P_d(t)$ - t curve totally controlled by the interaction term $V'(x, t)$ which is a product function

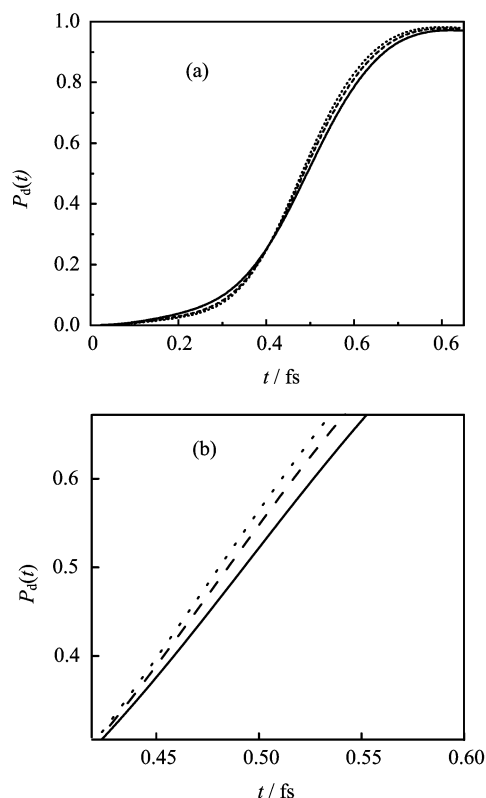


FIG. 3 Variation of detachment probability for I^- with time for bare and dipole bound cases for fixed external field of light. The solid lines refer to bare anion, the dashed lines refer to anion in polar solvent, and the dotted lines refer to anion in a strongly polar solvent. $\hbar\omega=0.06$ a.u., $\epsilon^0=0.03$ a.u..

of $S(t)$, x and $\sin(\omega t)$. Since this is a sinusoidal function the effective interaction varies with time sequentially. This may be the reason that the detachment probability systematically and sequentially grows and decays. We have taken here the pulse shape $S(t)$ as a continuous function. The detachment probability of I^- interacting with external light in presence and absence of polar environment (H_2O , $\mu=0.7283$ a.u.) for a particular frequencies and intensities of the used light field ($\hbar\omega_1=0.06$ a.u., $\epsilon^0=0.03$ a.u.) have been shown in Fig 3. From Fig.3 we may say that the detachment probability for dipole bound anion is a little bit more than that for the case of bare anion. This may be due to the fact that, in case of dipole bound anion the ground state is more stabilized over the bare anion but the transition energy is less in case of dipole bound anionic system (Table II). In Fig.3 we have also shown the variation of detachment probability with variation of polarity of the solvent. For the higher the solvent polarity the excited state of the coupled system (dipole bound anion) is much more stabilized, the transition energy is reduced and the detachment probability is enhanced. But there is a saturation in the stabilization of the energy level of excited state for further increase in solvent polarity which is also reflected in this figure. The other two an-

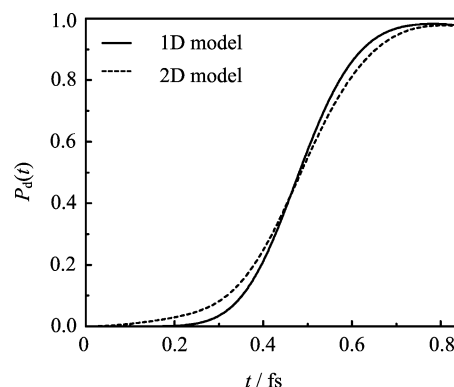


FIG. 4 Variation of detachment probability for I^- ion with time for dipole bound anion for fixed external field of light. $\hbar\omega=0.06$ a.u., $\epsilon^0=0.03$ a.u. in 1D and 2D model.

ions namely Cl^- and Br^- have the same type of $P_d(t)$ - t profile.

Now if we compare the detachment dynamics for the particular anion I^- in 1D and 2D model, the 2D model shows the earlier initiation of detachment and the detachment rate constant is also little bit higher. One possible reason is that in 1D model [14] the transition energy is more than that of 2D model. Since in the later case we have taken one more pair of dipole in another direction, the effective ion dipole interactions are more in 2D case compared with 1D case. In Fig.4 the comparison of detachment probability between 1D and 2D model is shown for the case of I^- taking water as a polar solvent which has polarizable volume 1.48×10^{-30} m³. The other solvents of different polarities show the similar behavior.

C. Average detachment rate constant with intensity variation of field

It is interesting to investigate the dependence of the intensity of the used light sources on detachment processes. In Fig.5(a) the detachment probability profiles of dipole bound anions (I^-) have been shown for three different field intensity ($\epsilon^0=0.03, 0.04$, and 0.05 a.u.) and one for bare anion ($\epsilon^0=0.05$ a.u.) by keeping all the others parameters of the light being constant ($\hbar\omega_1=0.06$ a.u.). From this figure it is observed that with increase in field intensity, the detachment probability increases but there is a clear saturation that is after certain intensity of light there is no more field intensity effect on detachment processes. From this figure it is also noted that the detachment rate in case of dipole bound anion is more compare to anion for the fixed field.

The $P_d(t)$ - t profiles of I^- can be used to compute the photo-detachment rate constant $k_0(t)$ at a particular

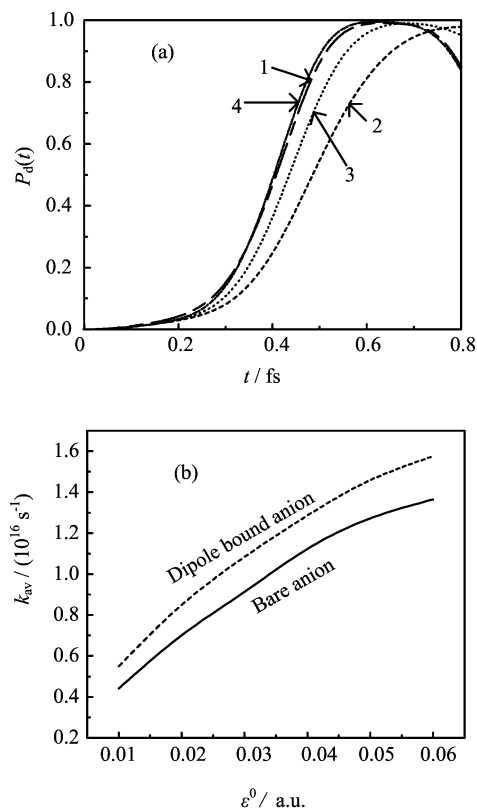


FIG. 5 (a) Variation of detachment probability for I^- ion with time in different field-intensity. The arrows 1, 2, 3, and 4 refer to $\epsilon^0=0.05$ a.u. for bare anion, $\epsilon^0=0.03$ a.u. for dipole bound anion, $\epsilon^0=0.04$ a.u. for dipole bound anion, and $\epsilon^0=0.05$ a.u. for dipole bound anion, respectively. (b) Intensity dependence on average detachment rate constant (k_{av}) for I^- ion for bare anion and dipole bound anion.

time by making use of the relation

$$\frac{d}{dt}[-\ln P_d(t)] = k_0(t) \quad (27)$$

for a given field strength of the light, and then the mean or average detachment rate constant k_{av} can be generated. For the calculation of k_{av} , 25 a.u. of time interval have been used in each cases.

In Fig.5(b), we have shown how the computed k_{av} for I^- varies with the intensity of the light field for both the bare and the dipole bound anion at particular frequency. From the figure it may be seen that in the case of dipole bound anionic system the detachment rate constant is slightly higher than that of bare anionic case at a particular intensity of light which supports the results shown in Fig.3 in which we have tried to show the detachment probability for bare and solvated anions. Since the model for Cl^- and Br^- behave similarly the corresponding figures are not shown.

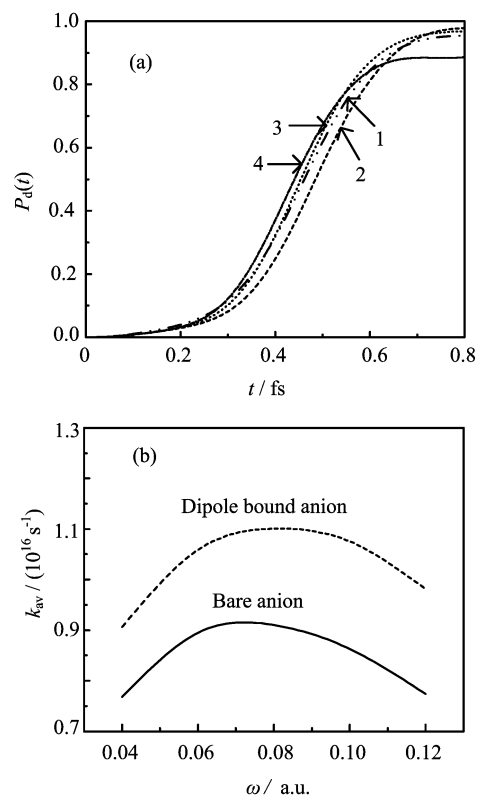


FIG. 6 (a) Variation of detachment probability for I^- with time in different frequency. The arrows 1, 2, 3, and 4 refer to $\omega=0.08$ a.u. for bare anion, $\omega=0.06$ a.u. for dipole bound anion, $\omega=0.08$ a.u. for dipole bound anion, and $\omega=0.10$ a.u. for dipole bound anion, respectively. (b) Frequency dependence on the average detachment rate constant (k_{av}) of a model I^- . Note it passes through the maxima at resonance frequency.

D. Detachment rate constant with frequency variation of light field

We have explored the detachment rate constant against the frequency of the used light when all the other parameters of the field remain constant. In Fig.6(a) the detachment probability profile *vs.* time ($P_d(t)$ - t) for the dipole bound anion I^- for three different frequency ($\omega=0.06$, 0.08, and 0.10 a.u.) of the used light field have been shown by keeping the intensity fixed. It is obvious from the figure that with increasing the frequency, detachment probability increases up to a certain values of frequency and then decreases. In Fig.6(b), we have shown the corresponding frequency *vs.* average detachment rate constant based on the Eq.(27). From the figure it may be infer that, as the frequency of the used light increases the detachment rate constant increases and passes through a flat maximum. The corresponding frequency in which the detachment rate constant is greater, is more or less close to the resonance frequency of the 1 \rightarrow 2 transition which we have found numerically (Table II). So we may conclude that if we

fix the driving field frequency matching with the corresponding $1 \rightarrow 2$ transition frequency the detachment rate constant will be maximum and this is due to resonance activation. Since the frequency of the electric field changes the polarity of the solvent we have used the solvent which has relatively smaller polarizable volume so that the effect is minimum. If we further increase the frequency, the detachment rate constant decreases probably due to some short of energy dissipation to the bulk.

E. Influence of anion well depth fluctuation on detachment rate constant

If the binding energy (*i.e.*, the well depth of the model anion potential) is made to fluctuate, by keeping the orientation of the dipole and its distance from the anion being fixed, the computed average detachment rate constant for a given peak field intensities (ϵ_0) and frequencies (ω) of the light is seen to depend on the frequency of the fluctuation (Ω). A critical value Ω_c for both the cases in presence and absence of dipolar medium are seen to exist for which the average detachment rate constant attains the lowest value (Fig.7). For both cases, Ω_c values are almost equal and the value is equal to 2.5×10^{16} cycle/s. The only difference is that in presence of dipolar medium the detachment rate constants are little bit larger. The appearance of the minimum suggests that there are two competing factors guiding the detachment dynamics when the well depth fluctuates. The stochastic perturbation $[R(t)\Delta V]$ sets up population oscillation at frequencies controlled by Ω while the regular perturbation does the same thing at ω . For $\Omega \gg \omega$, the electric field of the light probes all possible values of the randomly changing well depth $[V_0 + R(t)\Delta V]$ where $\Delta V = 0.006$ a.u. of energy and the response is determined by the average depth. Since $\langle R(t) \rangle = 0$, the external field virtually sees the static well depth (V_0) at high fluctuation frequencies. For $\Omega \ll \omega$, the situation would be effectively the same. When $\Omega \approx \omega$, stochastic resonance can take place which apparently deactivates the ionization process sharply at $\Omega = \Omega_c$. It appears that the stochastic perturbation deexcites the higher levels populated due to excitations produced by the regular perturbation more effectively at least for a range of Ω . The behavior observed here is not different from what was observed previously in the free one dimensional anion cases [44].

V. CONCLUSION

We have proposed a two dimensional model approach on the photo detachment dynamics of halide ions in presence of polar environmental medium. A simple model was provided for better understanding the effects of coupling between the solvent polarization and the ex-

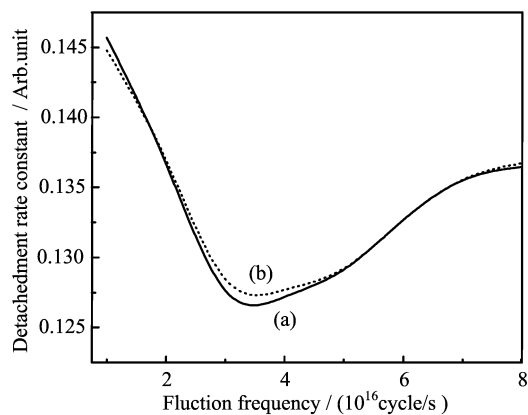


FIG. 7 Dependence of the rate constant for field induced detachment on the fluctuation frequency of the well depth. (a) Bare anion and (b) dipole bound anion.

tra charge in the system. Such knowledge is needed to explain how the environment can influence the dynamics of molecular or atomic anions compared with their dynamics in non polar situation. In order to concentrate on the effect of solvent polarization and for simplicity we have not included the possibility for the usual cage effect by the solvent. In that regard the 2D character of the model should be reasonable for our purposes. Our model is for a generic halide anions for which we focus on the behavior of the extra charge of the anions under the influence of solvent polarization.

The introduction of solvent field to describe the polarization effect may be considered quite different from more conventional treatment of polarizable solvents [16]. The asymmetric solvent configuration is represented by a uniform electric field as has been done in the other studies [24] and it has been assumed that the solvent molecules are fixed at certain position with respect to the anion. Despite of the limitations discussed above, the present model is expected to enhance our understanding of the physical picture for the dynamics of the atomic ion. One of the advantages in using a simplified model system is that we can avoid complications due to the complex dynamics of real systems.

The main shortcomings of the present model are that it can not describe the real system fully. However we have tried to model the photodetachment dynamics of anionic system based on the model potential without well-depth fluctuation indicates that the average detachment rate constant has non linearly dependent on the intensity of the used light and saturated at higher intensities. The detachment process is not instantaneous but is characterized by an intensity dependent time threshold, however short. To make the model realistic, the environmental effects has been introduced through ion dipole interaction and also the fluctuation of the potential well.

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