

Field optimized initial state based control of photodissociation

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Abstract. A new scheme for controlling photodissociation through preparation of a variationally optimized linear superposition of field free vibrational eigenstates is applied for selective control of IBr and HI dissociation. The dependence of photodissociation on various field parameters and initial conditions is examined to investigate the mechanistic basis of selective control. The parametric equations of motion approach for determining vibrational dynamics as a function of field parameters without having to solve the time dependent Schrödinger equation explicitly for each field parameter separately is outlined and its use to identify field characteristics which will provide the requisite population mix represented by the optimal linear superposition of vibrational states is advocated.

Keywords. Photodynamics; selective control; optimal initial state; time dependent Schrödinger equation.

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1. Introduction

The easy availability of ultrafast high intensity lasers has fueled the dream of their use as molecular scissors to cleave selected bonds [1, 2]. Theoretical approaches to laser assisted selective control of chemical reactions have kept pace and demonstrated remarkable success [3, 4] and some experimental results [5, 6] buttress these theoretical claims. The different established theoretical approaches to control have been reviewed recently [7]. Some of these approaches, based on field induced control have been perturbative [8] and hence of somewhat limited utility or have provided fields with undesirable attributes like very high intensity and require computationally demanding procedures for their specification [4]. While the focus of these theoretical approaches has been on field design, the photodissociation yield has also been found to be extremely dependent on the choice of initial vibrational state from which photolysis is induced and results for HI [9, 10], HCl [5] and HOD [6] reveal a crucial role for the initial condition of the system in product selectivity and enhancement.

This critical dependence on initial vibrational state indicates that a suitably optimized linear superposition of the initial vibrational levels may be another route to selective control of photodissociation. In any case, since in the field design based control, high intensity is undesirable, phase dependence has been found to be weak [11] and considerable success has been demonstrated using a single carrier frequency, it seems desirable

to choose a well motivated field to induce photolysis and focus on achieving selectivity and control through optimization of the linear superposition of vibrational states for the enhanced photodissociation out of the desired channel.

Recently we have proposed a simple Rayleigh–Ritz variational optimization procedure [9, 12] for obtaining the optimal linear superposition of the field free vibrational eigenstates that would lead to flux maximization out of the desired channel for a given photodissociation pulse. This approach to control shifts the focus from control via field design to the design of an optimal initial state for the chosen field and is computationally simple to implement. The initial demonstrative application to the IBr and HI photodissociation has shown a marked enhancement in selectivity and product yield using these field optimized initial states [9, 12]. However, our method requires an identification of field parameters which will help achieve the requisite optimal superposition. The parametric equations of motion (PEM) approach [13–15] provides an economic means for charting the photodynamics as a function of different field parameters and we have found it to be quite economic in determining the field parameters which will produce the desired population mix in hydrogen fluoride molecule [14, 15].

It is our purpose here to present a brief summary of some of the main results from our application of the field optimized initial state based approach to selective control of photodissociation. The formal and computational considerations of this method have been detailed elsewhere [9, 12] and only a skeletal outline is provided in the following section. Some demonstrative results from its application to IBr photodissociation are discussed in § 3. Section 4 contains some representative results from our application of the PEM approach to the bi-chromatic control of vibrational dynamics of HF and an assessment of the strengths and weaknesses of the methods introduced here concludes this paper.

2. Method

For molecules possessing a dipole moment $\vec{\mu}$, the effect of the radiation field $\vec{\epsilon}(t)$ may be obtained by solving the time dependent Schrödinger equation (TDSE),

$$i\hbar \frac{\partial}{\partial t} \psi = \hat{H}(t)\psi, \quad (1)$$

where

$$\hat{H}(t) = \hat{H}_0 + \vec{\mu} \cdot \vec{\epsilon}(t)$$

with H_0 being the field free Hamiltonian. The solution ψ at some time T can be expressed as

$$\psi(T) = \hat{U}(T, 0)\psi(0), \quad (2)$$

where $\hat{U}(T, 0)$ is the (not necessarily unitary) propagator and $\psi(0)$ is the wavefunction for the initial state of the molecule to which the photodissociation pulse $\epsilon(t)$ is applied. Defining the time integrated flux operator \hat{F} as

$$\hat{F} = \int_0^T dt \hat{U}^\dagger(t, 0) \hat{j} \hat{U}(t, 0), \quad (3)$$

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where

$$\hat{j} = \frac{1}{2m} [\hat{p}\delta(r - r_d) + \delta(r - r_d)\hat{p}] \quad (4)$$

with m as the reduced mass, \hat{p} the momentum operator along the reaction coordinate and r_d the grid point in the asymptotic region where the flux is evaluated. Note that in the case of more than one possible dissociation channel, operator \hat{j} is channel specific and in a discrete representation of the electronic curves on a spatial grid, r_d denotes the grid point appropriate to the desired channel. The time integrated flux, which is directly related to the product yield, is

$$\int_0^T dt \langle \hat{j} \rangle_t = \int_0^T dt \langle \psi(t) | \hat{j} | \psi(t) \rangle = \int_0^T dt \langle \psi(0) | \hat{U}^\dagger(t, 0) \hat{j} \hat{U}(t, 0) | \psi(0) \rangle, \quad (5)$$

$$\int_0^T dt \langle \hat{j} \rangle_t = \langle \psi(0) | \hat{F} | \psi(0) \rangle, \quad (6)$$

and it is clear from equation (6) that the product yield may be controlled by both altering the field dependent part \hat{F} or the field free initial state $\psi(0)$. Earlier control schemes [8,16,17] have attempted control over photodissociation entirely through field manipulation for a fixed $\psi(0)$. Recently we have proposed a scheme where control over product yields is sought through preparation of the initial wavefunction $\psi(0)$ as a coherent superposition of vibrational eigenstates of the ground electronic potential for the chosen photolysis pulse [9] (for the short femtosecond pulses to be considered here, rotational motion is ignored). Of course, the field itself may also be altered which will change the nature of the optimal $\psi(0)$. By expanding $\psi(0)$ in a basis of $(M + 1)$ field free vibrational eigenfunctions,

$$\psi(0) = \sum_{m=0}^M c_m \phi_m, \quad (7)$$

flux maximization is reduced to the familiar Rayleigh–Ritz variational optimization of $\{c_m\}$ through diagonalization of an $(M + 1 \times M + 1)$ matrix \mathbf{F} whose elements

$$F_{kl} = \langle \phi_k | \hat{F} | \phi_l \rangle \approx \Delta t \sum_{n=0}^{N_t} \langle \psi_k(n\Delta t) | \hat{j} | \psi_l(n\Delta t) \rangle, \quad (8)$$

with ΔT as the step size for the numerical time propagation and $N_t \Delta t = T$. The largest eigenvalue f_{\max} of \mathbf{F} is the maximum product yield (flux) and the corresponding eigenvector $\{C_m^{\max}\}$ is the set of coefficients which defines the optimal initial wavefunction

$$\psi^{\max}(0) = \sum_{m=0}^M c_m^{\max} \phi_m \quad (9)$$

constituting the superposition that will provide the maximum achievable product yield f_{\max} out of the particular channel specified by \hat{F} for the chosen field $\vec{\epsilon}(t)$. As in other similar calculations, the larger the basis set size ‘better’ the results. However, due to difficulties in simultaneous overtone excitation of many vibrational levels, the basis set expansion in eq. (7) is restricted only to first few vibrational eigenstates (only the first

two excited vibrational levels in our case) and so the size of the F matrix is small and therefore computationally trivial to diagonalize.

The solution proceeds by propagating the TDSE $M + 1$ times from $t = 0$ to $t = T$ for each initial condition $\psi(0) = \chi_m$, $m = 0, 1, \dots, M$ in the basis set expansion (eq. (7)). During the propagation, the matrix elements F_{kl} are accumulated according to eq. (8) as has been described in detail elsewhere [9]. The field free vibrational eigenstates χ_m are obtained using the Fourier grid Hamiltonian method [18] and an analysis of the $\psi_{\max}(0)$ for different $\vec{\epsilon}(t)$ helps in investigating the mechanistic underpinning of photodynamic control of product selectivity and yield [19].

For a periodic field of period τ , Floquet theory [20–22] permits the computation of full dynamics for pulses of arbitrary length $n\tau$ at any field intensity by solving the TDSE over only one optical cycle. The governing equation in the Floquet approach is given by

$$\mathcal{H}\phi_m(t) = \epsilon_m(t)\phi_m(t), \quad (10)$$

where

$$\mathcal{H}(r, t) = H(r, t) - i\hbar \frac{\partial}{\partial t} \quad (11)$$

with

$$H(r, t) = H_0(r) + V(r, t) \quad (12)$$

and ϵ_m is the quasienergy and ϕ_m are the Floquet eigenvectors. H_0 is the field free molecular Hamiltonian and $V(r, t)$ represents the molecule-radiation interaction. For a periodic field with period τ , the unitary propagator $U(n\tau, 0)$ of eq. (2) can be expanded in the Floquet eigenbasis ϕ for any arbitrarily large n (longer the pulse length larger the savings)

$$U(n\tau, 0) = \phi(0) \exp(-i\epsilon n\tau) \phi^\dagger(0) \quad (13)$$

and dependence of photodynamics on any field parameter λ may be investigated by solving equations of motion in λ for ϕ and ϵ to construct $U_\lambda(T, 0)$ such that

$$C_\lambda(T) = U_\lambda(T, 0)C_\lambda(0).$$

The variation of $C_\lambda(T)$, $T = n\tau$, with respect to various field parameters – amplitude, frequency and phase can be studied using the PEM equations. For example, when the perturbation parameter λ corresponds to the intensity of the laser field, the PEM equations are given by [15]:

$$\frac{d\epsilon_n}{d\lambda} = H'_{nn} = V_{nn}, \quad (14)$$

$$\frac{dH'_{nn}}{d\lambda} = 2 \sum_{m \neq n} \frac{|H'_{mn}|^2}{\epsilon_n - \epsilon_m}, \quad (15)$$

$$\frac{dH'_{mn}}{d\lambda} = \sum_{l \neq m, n} H'_{ml} H'_{ln} \left[\frac{1}{\epsilon_n - \epsilon_l} + \frac{1}{\epsilon_n - \epsilon_l} \right] + \frac{H'_{mn} H'_{mm}}{\epsilon_n - \epsilon_m} + \frac{H'_{mn} H'_{nn}}{\epsilon_m - \epsilon_n}, \quad (16)$$

$$\frac{d\phi_n}{d\lambda} = \sum_{m \neq n} \frac{H'_{mn}}{\epsilon_n - \epsilon_m} \phi_m. \quad (17)$$

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The parametric equations of motion for frequency and phase as a function of the perturbation parameters are detailed elsewhere [14,15] and the investigation of photodynamics as a function of field parameters is achieved by solving the coupled ordinary differential equations (14–17) and their equivalent for $\lambda = \omega$ and δ instead of repeated solution of TDSE for each new value of λ . This method has been found to be more economic than the brute force solution of the TDSE by as much as a factor of 100 in some cases [15]. For multicolor cw fields the dependence of these c_m on different field parameters may be efficiently investigated by solving the parametric equations of motion and this approach can therefore be used for bichromatic ($\omega_{10} + \omega_{21}$) control of population mix in $v = 0$, $v = 1$ and $v = 2$ levels required by eq. (9). In the following sections we offer some selected results.

3. Selective control of IBr photodissociation

For the ultrashort photolysis pulse considered here, IBr has been modelled as a rotationless oscillator, the three potential energy curves are given in figure 1 and the transition dipole moments used here are same as those employed earlier [4]. The energies of the vibrational eigenstates of the ground potential energy curve were evaluated using the Fourier grid Hamiltonian (FGH) method [18] and the TDSE was numerically solved using the split operator fast Fourier transform (SOFFT) method [23, 24] incorporating propagation via Pauli matrices [17]. The total spatial grid of 10 a.u. starting from 2.0 a.u. was divided into 1024 equally spaced points. The flux was monitored at 10.0 a.u. beyond which ‘ramp’ type optical barrier of height 0.01 a.u. was set up till the end of the grid to prevent any unphysical reflection of the wave packet. The flux out of the channel 1 labelled J_1 corresponds to the products $I + \text{Br}({}^2P_{3/2})$ (electronic states 1 and 2) and J_2 denotes flux out of the second excited $I + \text{Br}^*({}^2P_{1/2})$ (the Π_0^+ state labelled 3 in figure 1) product channel. The analysis to be presented here is for a multicolor cw field of the form

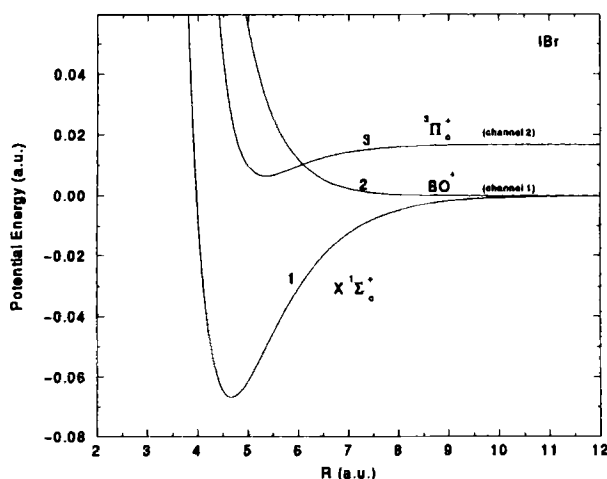


Figure 1. Potential energy curves of IBr.

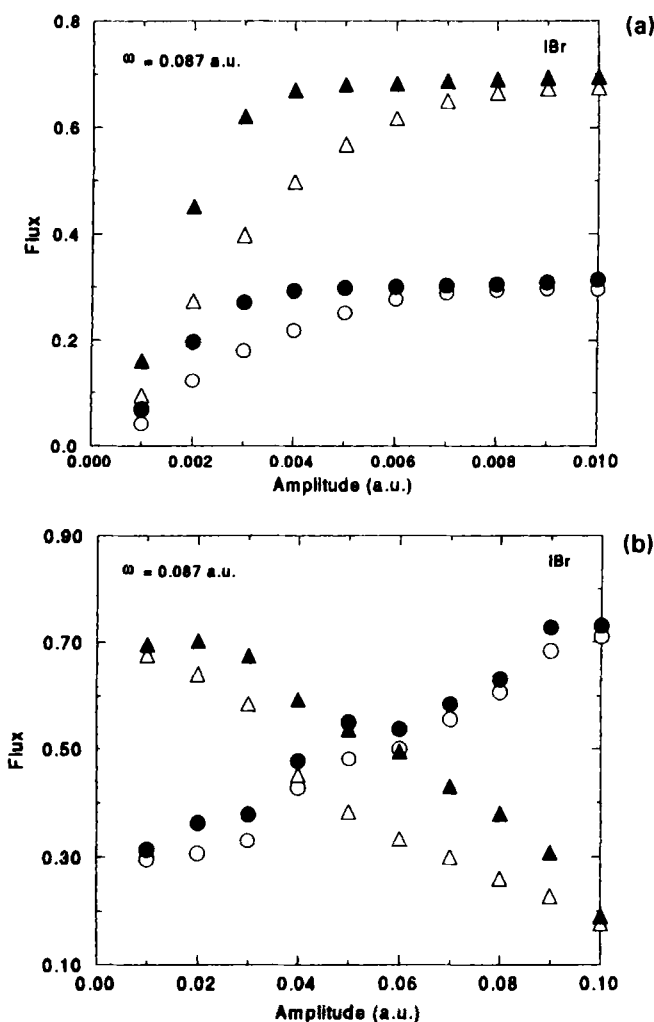


Figure 2. (a) Variation of maximum flux out of channel 1 [$I + Br(^2P_{3/2})$] (circles) and channel 2 [$I + Br^*(^2P_{3/2})$] (triangles) as a function of field amplitude A . The open symbols denote maximum flux from any of the three $v = 0, v = 1$ and $v = 2$ vibrational eigenstates and the filled symbols represent those utilizing the channel specific optimized superposition of these states $\psi_1^{\max}/\psi_2^{\max}$. The results are for the three colour cw field $\epsilon(t) = A \sum_{p=0}^2 \cos(\omega - \omega_{p,0})t$ with $\omega = 0.087$ a.u. (b) Same as figure 2a but for a higher amplitude range.

$E(t) = A \sum_{p=0}^2 \cos(\omega - \omega_{p,0})t$ where A is the amplitude, ω the photodissociation frequency and $\omega_{(p,0)} = (E_p - E_0)/\hbar$ the Bohr frequency for transition between the p th and the ground vibrational energy levels. Propagation is done for $T = 20,000$ a.u. (485 fs) with this field on and allowed to propagate further for another 16,000 a.u. (390 fs).

The variation of maximized flux out of channels 1 and 2 as a function of field amplitude at a laser frequency $\omega = 0.087$ a.u. (19094 cm^{-1}) using the optimal combinations ψ_1^{\max}

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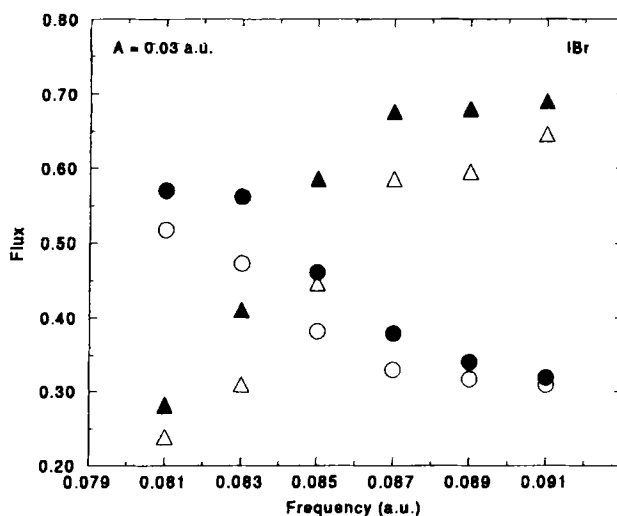


Figure 3. Variation of maximum flux with change in laser frequency at amplitude $A = 0.03$ a.u. Conventions of figure 2 apply.

and ψ_2^{\max} of the ground, first and second vibrational levels (filled symbols) is compared with maximum from any one of the $v = 0$, $v = 1$ and $v = 2$ vibrational eigenstates (open symbols) in figures 2a and 2b. The circles represent J_1 and J_2 is represented by triangles. We infer from figure 2a that considerable total dissociation is seen for field amplitude $0.003 \text{ a.u.} \leq A \leq 0.01 \text{ a.u.}$ ($19\text{--}65 \text{ TW/cm}^2$) but in this range there is an uniform increase in the dissociation out of both the channels and thus amplitude alone does not seem to be a suitable agent for enhanced selectivity. Also, for field amplitudes $A \leq 0.002 \text{ a.u.}$ (13 TW/cm^2) the total dissociation is small and for $A \geq 0.006 \text{ a.u.}$ the dissociation is more or less complete whereby for $A \leq 0.002 \text{ a.u.}$ and $A \geq 0.006 \text{ a.u.}$ the extent of enhancement offered by the optimized linear combinations (filled symbols) is almost negligible as compared to the maximum flux that can be obtained with $v = 0$, $v = 1$ or $v = 2$ eigenstate as the initial condition (open symbol). As we approach larger field amplitudes (figure 2b), the uniform increase of dissociation out of both the channels gives way to increased dissociation out of the $\text{I} + \text{Br}$ channel and decrease in the yield of $\text{I} + \text{Br}^*$, till, at the larger amplitudes the yield is predominantly out of the lower $\text{I} + \text{Br}$ channel. All these results for amplitude dependence are for $\omega = 0.087 \text{ a.u.}$ chosen so that both the channels are asymptotically open. It is experimentally advantageous to maintain as low an amplitude as possible and we explore the possibility of selective product enhancement at a comparatively low field amplitude of $A = 0.03 \text{ a.u.}$ (195 TW/cm^2) by varying the field frequency. The results for the frequency band $0.081\text{--}0.091 \text{ a.u.}$ [$17780\text{--}19971 \text{ cm}^{-1}$] are presented in figure 3 where it can be seen that even at this low amplitude, considerable selectivity and enhancement may be achieved by varying the field frequency.

This complementary role of amplitude and frequency variation can be understood by examining the change in the dressed electronic curves as a function of field variations. The field free potential curves are plotted in figure 4a and the dressed adiabatic electron

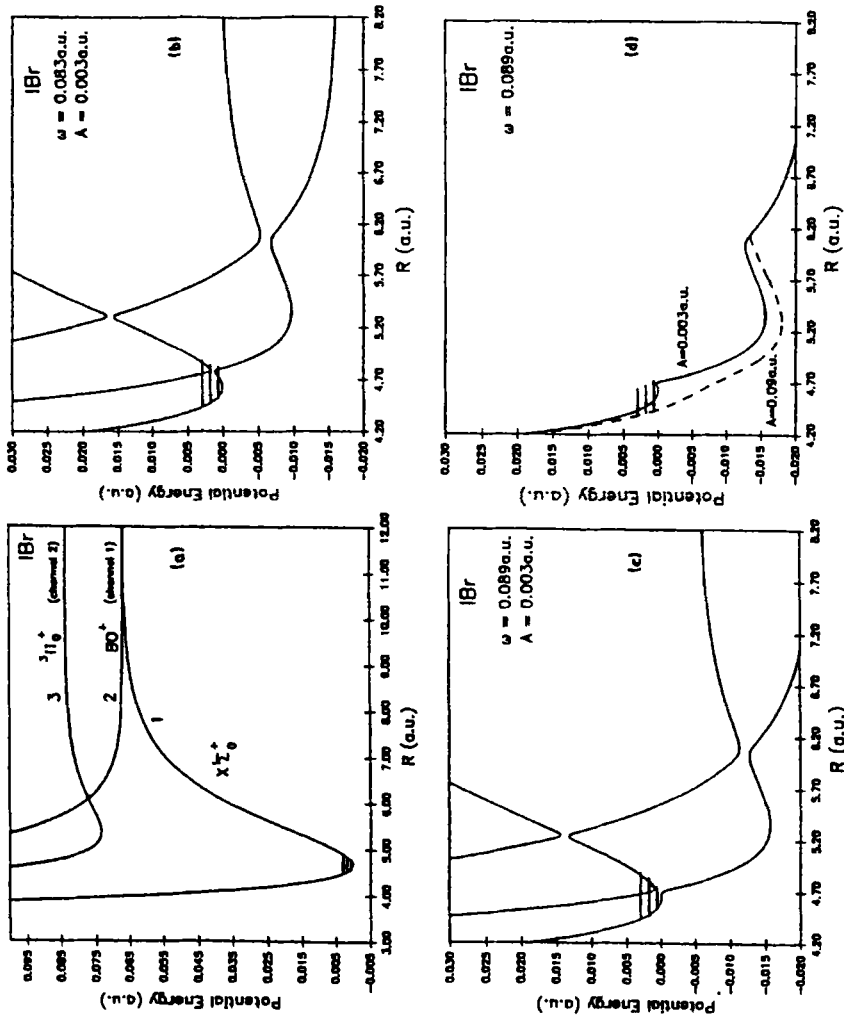


Figure 4. The field free potential curves and the vibrational levels $v = 0, v = 1$ and $v = 2$ of IBr (a) and the dressed potential energy curves at $\omega = 0.083$ a.u., $A = 0.003$ a.u. (b), $\omega = 0.089$ a.u., $A = 0.003$ a.u. (c), and the dressed BO^+ state at $\omega = 0.089$ a.u. and $A = 0.003$ a.u. (solid line) and for same ω but $A = 0.09$ a.u. (dashed line) (d).

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field curves [25] for different field parameters are presented in figure 4b–d, where we see that in the presence of the field, even at low amplitude, the $v = 0$ level becomes unbound (figure 4b) and the speed with which the molecule will approach the outermost crossing controlling dissociation depends on field frequency (figure 4c) with higher frequencies providing a higher velocity diabatic approach to the ${}^3\Pi_0^+ - \text{BO}^+$ crossing, favouring exit out of the $\text{I} + \text{Br}^*$ channel. As the amplitude is increased (figure 4d), the depth of the well to be traversed before approaching the crossing point increases leading to the slower approach to the ${}^3\Pi_0^+ - \text{BO}^+$ crossing whereby exit out of the lower channel is favoured as seen earlier in figure 2b.

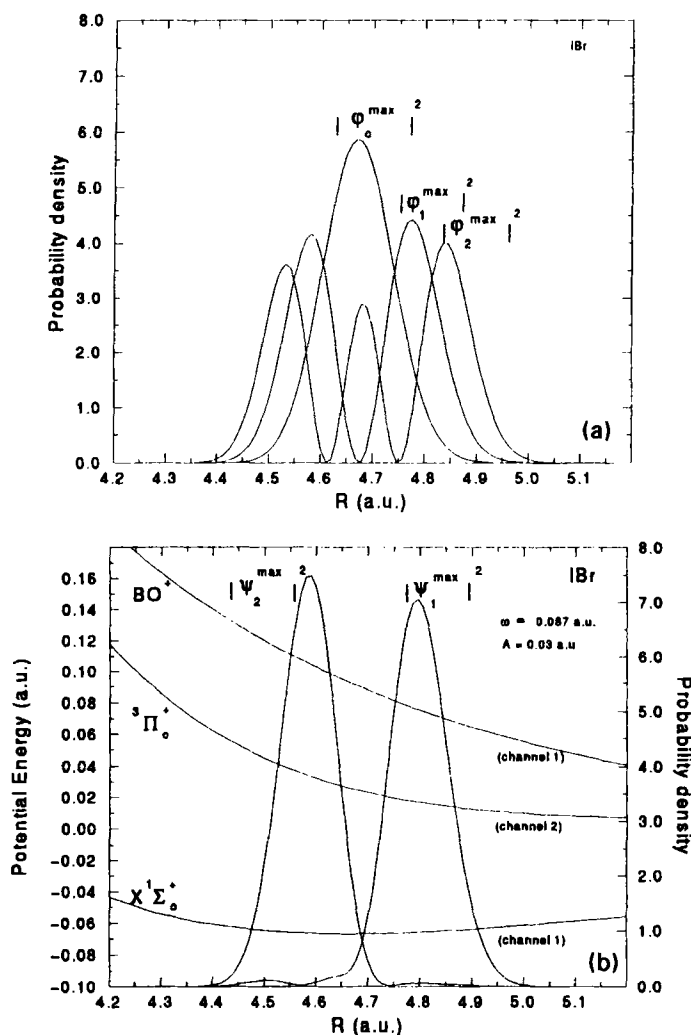


Figure 5. (a) Probability density plots for $v = 0, 1, 2$ vibrational eigenstates of IBr. (b) Same as figure 5a except for ψ_1^{\max} and ψ_2^{\max} with $A = 0.03$ a.u. and $\omega = 0.087$ a.u.

The structural features responsible for the enhanced selectivity and increased yield through the use of these optimal combinations as the initial state can be understood from the probability density plots of the variationally optimized superpositions of the first few vibrational eigenstates. In case of both IBr and HI we have shown elsewhere [19] that the optimization alters the spatial profiles such that ψ_2^{\max} is always peaked to the left of ψ_1^{\max} whereby for any given frequency, Franck Condon transitions occur to the energetically higher or steeper, more repulsive region of the ${}^3\Pi_0^+$ potential energy curve and the excited molecule described by the ψ_2^{\max} traverses the ${}^3\Pi_0^+-\text{BO}^+$ crossing with greater velocity compared to where the molecule is represented by ψ_1^{\max} which posits it in a relatively smoother region of the ${}^3\Pi_0^+$ potential energy curve and thereby facilitates a slow adiabatic exit out of the lower channel. This feature is, more or less, independent of actual field parameters and for a representative set of laser amplitude and frequency we present this spatial separation of ψ_1^{\max} and ψ_2^{\max} in figure 5.

4. Efficient investigation of vibrational population dynamics as a function of field parameters using the PEM approach

The parametric equations of motion (PEM) approach provides a route to arrive at the field parameters required to obtain the desired population mix specified by the Rayleigh–Ritz variational procedure. Due to its large dipole moment, hydrogen fluoride has been a prototypical molecule for testing different methods for solving the TDSE and we also considered vibrational excitation of rotationless hydrogen fluoride in its ground electronic state for initial demonstrative applications [14, 15]. Potential and dipole functions are from ref. [27]. Bound state energies and wavefunctions used to compute the dipole matrix elements were computed using the FGH [18]. Numerically, both the TDSE equation (1) and the PEM equations (eqs (14–17)) were integrated with a fifth order Runge-Kutta integrator. The molecule is initially assumed to be in the ground vibrational state and all the results are for time averaged populations in accordance with actual laboratory conditions. In other words, at each value of $\lambda = \delta$ where the population dynamics is to be evaluated, we compute (see ref. [15] and [22]) the time-averaged population P_n of the n th vibrational state using

$$P_n = \sum_{m=1}^m |\phi_{nm}(0)|^2 |\phi_{lm}(0)|^2, \quad (18)$$

where m is the total number of states included in the calculation (here 14 states were found to be sufficient).

The dependence of HF vibrational population dynamics as a function of field amplitude and frequency for the bichromatic field $\epsilon(t) = A_1 \cos(\omega_1 t) + A_2 \cos(\omega_2 t + \delta)$ have been discussed in detail elsewhere [14, 15]. Here we present the population dynamics as a function of two variables (A and δ/ω and δ) simultaneously. The effect of phase and frequency variation on the population in the first excited level is presented in figure 6. In this case, we set $\omega_1 = 0.01814$ a.u. and $\omega_2 = \omega_1/2$. The frequency ω_1 chosen to be nearly resonant with the first fundamental ($\nu = 0 \rightarrow 1$) transition. Note that there is very little population transfer for frequency values which do not satisfy the resonance condition and the same feature is observed for population transfer to other levels as well. This 3-D plot

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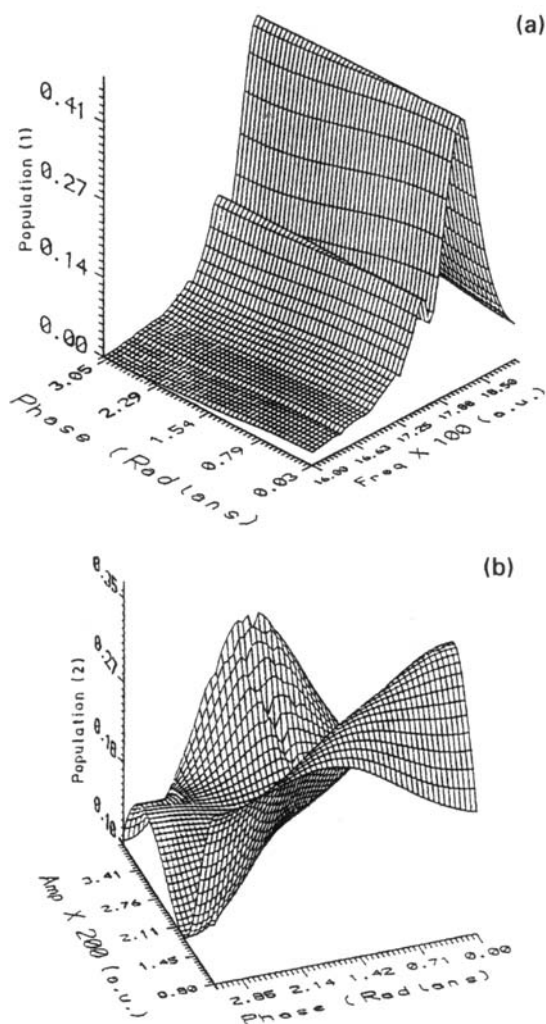


Figure 6. (a) Population transferred to the first excited vibrational level by the bichromatic field $E(t) = A_1 \cos(\omega t) + A_2 \cos(\frac{1}{2}\omega t + \delta)$. The critical role of resonance is manifested through the peak at $\omega = 0.01814$ a.u. for all values of the phase difference δ . (b) Population transferred to the second excited vibrational level as a function of A and δ for the bichromatic field $E(t) = A[\cos(\omega t) + \cos(\frac{1}{2}\omega t + \delta)]$, $\omega_1 = 0.01820$ a.u., $\omega_2 = 0.95\omega_1$.

therefore establishes the critical role of the resonance condition in photoexcitation. Similar results were observed in our earlier study [14] where an increase in intensity only leads to some power broadening of the excitation spectrum. Otherwise the maximum population transfer is indeed seen only for the resonant frequency.

We next examine the case where $\omega_1 = 0.01820$ and $\omega_2 = 0.95 * \omega_1$. Here, the ω_1 field component is nearly resonant with ($\nu = 0 \rightarrow 1$) and ω_2 is nearly resonant with $\nu = 1 \rightarrow 2$ transition. Note that in this case there will be greater transition probability to states above

$\nu = 1$. Computationally, we note that the period τ in this case is $20 * 2\pi/\omega_1$; in this way an integral number of optical cycles of both the ω_1 and ω_2 components fall within the Floquet period τ . Although multiple cycles of both field components are incorporated into τ , the Floquet formalism is still valid since we define τ as the Floquet period; a similar situation occurred in ref. [7] where population dynamics with Gaussian pulse train were studied.

From both figures 6a and 6b it is clear that even for low amplitudes, a suitable choice of phase can induce substantial population transfer which would otherwise have required much more intense fields. Such results would be difficult without the 3-D plots presented here, which in turn would be too demanding to generate without recourse to the PEM-based approach to the solution of TDSE summarized here.

5. Concluding remarks

In this paper we have offered some results from our investigations of selective maximization of IBr photodissociation products using Rayleigh–Ritz variational optimization procedure for the flux operator. Optimization increases the product yield out of both the channels and our results demonstrate that a careful choice of frequency and amplitude achieves selective control without requiring highly intense fields with attributes not reproducible in the laboratory. The optimal control approach applied to this problem [4] also achieved large flux and almost total selectivity but required three order of magnitude more intense fields and a functional form which cannot be reproduced in the laboratory. The approach advocated here therefore offers the possibility of obtaining controlled selective dissociation using moderate intensity lasers. The selective maximization procedure outlined here is equally effective with the cw or Gaussian pulses [12], offering additional experimental convenience and flexibility.

Results for selective control of IBr photodissociation through maximization of flux out of the desired channel using the optimal superpositions selected by the Rayleigh–Ritz variational procedure [9, 12] reveals that the selective maximization is effected through localization of the probability density in different parts of the Franck–Condon region of the appropriate state. Localization of the probability density on the more steep, repulsive part of the excited curves favours high radial velocity diabatic exit at the crossing point. Localization away from the repulsive wall favours slow adiabatic exit out of the same state. The Rayleigh–Ritz variational maximization of flux generating an optimal spatial profile for the initial wavefunction therefore does offer a viable alternative to selective control through field variation. It appears that the variational alteration of the initial wavepacket profile is equivalent to that of varying field frequency for the chosen amplitude, both of which allow sampling of different portions of the Franck–Condon region.

The preparation of the optimal initial linear combination however requires overtone excitation using a two colour ($\omega_{10} + \omega_{21}$) IR laser. Parametric equations of motion provide an efficient investigation of quantum dynamics in the presence of bichromatic lasers. The resulting equations offer computational savings of up to a factor of 100 over the brute force approach to the solution of the TDSE for each new value of the phase difference. These PEM based savings have made possible 3-D plots of population in various levels as

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a simultaneous function of phase and frequency or phase and amplitude permitting a global insight which could be tapped advantageously for selecting optimal field parameter for a given photodynamical task.

We conclude by mentioning that the results presented here demonstrate sufficient promise to this new Field Optimized Initial State (FOIST) based alternative approach to selective control. The field required to achieve the requisite $\{c_m^{\max}\}_{m=0}^2$ values may be obtained analytically for the three vibrational levels [9] or the more general optimal control theory [16] may also be applied to this task. At this stage of development, however, what would serve the purpose better is an experimental test of the ideas presented here and hopefully the detailed demonstration of its promise will stimulate some experimental investigations.

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