Control of photodissociation branching using the complete reflection phenomenon: Application to HI molecule

Hiroshi Fujisaki\textsuperscript{a}, Yoshiaki Teranishi\textsuperscript{b}, and Hiroki Nakamura\textsuperscript{a,c}

\textsuperscript{a}Department of Theoretical Studies, Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan
\textsuperscript{b}Advanced Photon Research Center, Japan Atomic Energy Research Institute, Kizu-cho, Kyoto 619-0215, Japan
\textsuperscript{c}Department of Functional Molecular Science, The Graduate University for Advanced Studies, Myodaiji, Okazaki 444-8585, Japan

March 31, 2022

Abstract

The laser control of photodissociation branching in a diatomic molecule is demonstrated to be effectively achieved with use of the complete reflection phenomenon. The phenomenon and the control condition can be nicely formulated by the semiclassical (Zhu-Nakamura) theory. The method is applied to the branching between I(2\textsuperscript{3}P\textsubscript{3}/2) (HI → H + I) and I*(2\textsuperscript{3}P\textsubscript{1}/2) (HI → H + I*) formation, and nearly complete control is shown to be possible by appropriately choosing an initial vibrational state and laser frequency in spite of the fact that there are three electronically excited states involved. Numerical calculations of the corresponding wavepacket dynamics confirm the results.

1 Introduction

Controlling chemical dynamics\textsuperscript{[1]} is one of the hot topics recently in chemical physics. Since the works of Bruner and Shapiro (coherent control) and Tannor and Rice (pump-dump method), a lot of studies have been made on the subject both theoretically and experimentally. The essence of control consists in transferring a certain prepared (initial) quantum state into a desired (target) quantum state, in which the coherent interaction between a molecule and a laser field plays a crucial role. Each one of the ideas proposed so far has its own advantages and disadvantages. For instance, the optimal control theory initiated by Rabitz, Kosloff, Rice and others can, \textit{in principle}, deal with any kind of target, but its numerical cost becomes formidable for more than 3D systems, and the optimal field generated is often a bit too complicated to be realized in experiment. Our basic idea, on the other hand, is to regard the molecular processes in a laser field as a sequence of nonadiabatic transitions and to control them. This concept can be justified by the Floquet theory for periodically perturbed systems, and introducing the Floquet (or dressed) states\textsuperscript{[2, 3, 4, 5, 6, 7]}. Namely, we try to control nonadiabatic transitions among dressed states.

Previously we have proposed such methods of control with the help of the semiclassical theories of nonadiabatic transitions including the Zhu-Nakamura theory as a complete solution of the Landau-Zener-Stückelberg (LZS) type curve crossing problems\textsuperscript{[7, 8]}. They are categorized as the method using (a) the time-dependent and (b) the time-independent theory of nonadiabatic transitions. In the former case\textsuperscript{[2, 4, 5, 6, 7]}, periodical sweeping of laser parameters or a sequence of linearly chirped pulses are employed to control various processes. In the latter case\textsuperscript{[8]}, the complete reflection phenomenon in the time-independent nonadiabatic tunneling type transition\textsuperscript{[4, 8]} has been employed to discuss the possibility of controlling photodissociation by
using the *model* 1D and 2D molecules, i.e., models of HOD and CH$_3$SH. However, up to now, there has been no application of the theory to a real molecule. In this paper, following the same strategy as in [3], we try to control photodissociation branching of a real HI molecule with use of the complete reflection phenomenon and ab initio data of the potential curves. The complete reflection phenomenon, the existence of which was quantum mechanically exactly proved by Zhu and Nakamura [9], can be accurately formulated by the Zhu-Nakamura semiclassical theory [7, 8] (see also [10, 11, 12]) and has been utilized to propose a new molecular switching [13, 14, 15].

This paper is organized as follows: In Sec. 2, we briefly summarize the semiclassical theory and the phenomenon of complete reflection. In Sec. 3, we describe an HI molecule in a laser field where the ab initio data for HI calculated by Alekseyev et al. [16] are also shown. With use of the Zhu-Nakamura theory, we find effective conditions for controlling photodissociation branching: HI $\rightarrow$ H + I/HI $\rightarrow$ H + I$^*$. In Sec. 4, we report the results of full numerical solutions of wave packet dynamics. The semiclassical prediction is confirmed to be accurate, and the present control scheme is proved to be effective. Section 5 is devoted to concluding remarks and discussions.

2 Complete reflection in a diatomic molecule — Semiclassical theory of nonadiabatic transition

Here we briefly summarize the relevant portion of the Zhu-Nakamura theory to describe the complete reflection phenomenon [3, 7, 8]. The overall transmission probability $P$ at energy $E$ in the nonadiabatic tunneling type curve crossing [see Fig. 1 (a)] is given by

$$P = \frac{4 \cos^2 \Psi(E)}{4 \cos^2 \Psi(E) + \rho^2/(1 - p)}$$

(1)

with

$$p = \exp\left\{- \frac{\pi}{4\sqrt{\alpha \beta}} \sqrt{\frac{2}{1 + \sqrt{1 - \beta^{-2} f}}} \right\} \quad \text{and} \quad \Psi(E) = \sigma - \phi_s - g,$$

(2)

where $p$ represents the nonadiabatic transition probability for one passage of the crossing region, and

$$\phi_s = \frac{\delta}{\pi} \ln \left( \frac{\delta}{\pi} \right) - \frac{\delta}{\pi} - \arg \Gamma \left( \frac{i \delta}{\pi} \right) - \frac{\pi}{4},$$

(3)

$$\sigma = \int_{t_1}^{t_2} \sqrt{\frac{2m[E - E_2(x)]}{\hbar}} dx,$$

(4)

$$g = \frac{0.23 \alpha^{1/4}}{\alpha^{1/4} + 0.75} 40^{-\sigma},$$

(5)

$$f = 0.72 - 0.62 \alpha^{0.715},$$

(6)

$$\delta = \frac{\pi}{16\sqrt{\alpha \beta}} \sqrt{6 + 10\sqrt{1 - \beta^{-2}}},$$

(7)

$$\alpha = \frac{(1 - \gamma^2) \hbar^2}{m(x_b - x_t)^2(E_b - E_t)},$$

(8)

$$\beta = \frac{E - (E_b + E_t)/2}{(E_b - E_t)/2},$$

(9)

and

$$\gamma = \frac{E_b - E_t}{E_2 \left( \frac{x_b + x_t}{2} \right) - E_1 \left( \frac{x_b + x_t}{2} \right)}.$$

(10)
Here $E_1(x)[E_2(x)]$ is the lower [upper] adiabatic potential, $x_t(x_b)$ and $E_t(E_b)$ represent the position of the top (bottom) of the lower (upper) adiabatic potential and the corresponding energy at $x_t(x_b)$, $t_1$ and $t_2$ are the turning points on $E_2(x)$ at energy $E$, and $m$ is the reduced mass of the system. It is easily seen that the transmission does not occur at all when

$$\Psi(E) = (n + 1/2)\pi \quad (n = 0, 1, 2, \cdots)$$

is satisfied. This is the condition for the complete reflection in the potential system schematically shown in Fig. 1 (a). This phenomenon is due to the quantum mechanical interference effect between the wave trapped on the upper adiabatic potential and the wave transmitting along the lower adiabatic potential without any transition to the upper state, and occurs irrespective of the potential shape and coupling strength.

In the case of a diatomic molecule as shown in Fig. 1 (b), predissociation cannot occur if the condition (11) is satisfied in the region designated in the figure. A big advantage of the present scheme is that this condition can always be satisfied by appropriately choosing the CW laser frequency $\omega$, since molecular potential curves can be shifted up and down by $\hbar \omega$ in the case of one-photon process. If there are more than one dissociative states, we may control the dissociation branching as we wish. Thus, the key factors of this scheme are (1) initial preparation of an appropriate vibrationally excited eigenstate with energy $E_v$, and (2) appropriate choice of the stationary laser frequency $\omega$. The laser intensity coupled with the transition dipole moment determines the diabatic coupling between the two states and mainly controls the shape of the complete reflection dip. Experimentally, (2) may be easy, but (1) might be difficult especially in the case of homonuclear nonpolar molecules. Hereafter we call $\Psi_v(\omega) = \Psi(E_v + \hbar \omega)$ a complete reflection manifold.

Figure 1: (a): Schematic picture representing the nonadiabatic tunneling type transition. (b): Schematic picture representing the complete reflection condition in a diatomic molecule.

### 3 HI molecule in a laser field

The present control scheme is applied to the photodissociation of an HI molecule in the energy range $\hbar \omega = 3 \sim 6$ eV, where three electronically excited states, $^1\Pi_1$, $^3\Pi_{0+}$, and $^3\Pi_1$, are involved \[16\]. The electronically ground state is $^1\Sigma$ and is coupled to these three excited states through the transition dipole moment (see Eq. (13) below). The couplings among the latter due to the laser field can be neglected, because the corresponding transitions are off-resonant. The coupling between $^1\Pi_1$ and $^3\Pi_{0+}$ induced by the spin-rotation interaction is also neglected as in \[17\], since it is very weak.
Thus, we have the following $4 \times 4$ Schrödinger equations:

$$i\hbar \frac{\partial}{\partial t} \phi(R, t) = \mathcal{H}(t)\phi(R, t) = \left( -\frac{\hbar^2}{2m} \frac{d^2}{dR^2} + V(t) \right) \phi(R, t),$$  \hspace{1cm} (12)

where

$$V(t) = \begin{pmatrix}
V_1(R) & -\mu_{12}(R)F(t) & -\mu_{13}(R)F(t) & -\mu_{14}(R)F(t) \\
-\mu_{12}(R)F(t) & V_2(R) & 0 & 0 \\
-\mu_{13}(R)F(t) & 0 & V_3(R) & 0 \\
-\mu_{14}(R)F(t) & 0 & 0 & V_4(R)
\end{pmatrix},$$  \hspace{1cm} (13)

Here $i = 1, 2, 3, 4$ corresponds to the $^1\Sigma$, $^1\Pi_1$, $^3\Pi_0$, $^3\Pi_1$ electronic states, respectively. $V_i(R)$ are the potential energy curves (PEC), $\mu_{ij}(R)$ the transition dipole coupling between PEC $i$ and $j$, and $m = 126.9/127.9 \simeq 0.99$ amu is the reduced mass of HI.

Ab initio data for $V_i(R)$ and $\mu_{ij}(R)$ are shown in Fig. 2. These data \cite{18} are based on the ab initio calculations by Alekseyev et al. \cite{16}. In Refs. \cite{19, 20}, the authors used a Morse potential for the ground state and exponential functions for the excited states, but this approximation has turned out to be poor. It should be noted that the dipole moments between the electronically ground and excited states significantly depend on the inter-nuclear distance [see Fig. 2 (b)]; and the Condon approximation must be very poor. Note also that the two electronic states $^1\Pi_1$ and $^3\Pi_1$ are asymptotically connected to the same channel: HI $\rightarrow$ H+I. This makes the control of branching rather complicated, because both states should be stopped simultaneously. In the following numerical calculations, we use a laser field

$$F(t) = F_0 \cos(\omega t)\Theta(t),$$  \hspace{1cm} (14)

where $\Theta(t)$ represents an envelope function which should be wide and smooth enough. This is used simply to avoid any unnecessary transitions due to the sudden switching of the field. In the present calculation, we have used $F_0 = 2.8 \times 10^9$ V/m which corresponds to $I_0 = \varepsilon_0 c F_0^2/2 \simeq 1$ TW/cm$^2$. This is a moderate intensity which does not cause any strong multiphoton transitions.

![Figure 2](image)

**Figure 2:** (a): Ab initio PECs for HI. Unit for the vertical axis is cm$^{-1}$. (b): Ab initio transition dipole moments between the electronically ground and excited states. Taken from \cite{18}. Unit for the vertical axis is au.

We have used the 1D spline fitting to the PECs and dipole moments as done by Balakrishnan et al. \cite{17}. From the theory described in the previous section, we construct the complete
reflection manifolds: $\Psi_v^{(i)}(\omega)$ for each electronically excited state $i$. Since the dipole moment is not very strong, i.e., less than 0.2 a.u. in the crossing region, $\phi_n \simeq \pi/4$ and $\delta \ll 1$ for the laser intensity less than $\sim 10$ TW/cm$^2$, which is close to the diabatic limit.

The complete reflection phenomenon itself can be analyzed with use of the time independent picture in the Floquet (or dressed state) representation. The relevant time-independent Schrödinger equation is

$$
\left( -\frac{\hbar^2}{2m} \frac{d^2}{dt^2} + W(R) \right) \phi(R) = E\phi(R),
$$

where

$$
W(R) = \begin{pmatrix}
V_1(R) + \hbar \omega & -\mu_{12}(R)F_0/2 & -\mu_{13}(R)F_0/2 & -\mu_{14}(R)F_0/2 \\
-\mu_{12}(R)F_0/2 & V_2(R) & 0 & 0 \\
-\mu_{13}(R)F_0/2 & 0 & V_3(R) & 0 \\
-\mu_{14}(R)F_0/2 & 0 & 0 & V_4(R)
\end{pmatrix}.
$$

The adiabatic potential $E_1(x)$ [$E_2(x)$] in section 2 corresponds to the ground adiabatic state [one of the excited adiabatic state] obtained by diagonalizing $W(R)$.

Figures 3 show some manifolds for various $v$ ($v = 3, 4, 5, 6$). Since the vertical axis represents $\Psi_v^{(i)}(\omega)/\pi$, the crossing points with the horizontal lines $(n+1/2)$ ($n = 0, 1, 2, \cdots$) represent the laser frequencies where the complete reflection occurs. The transmission probabilities $P$ given by Eq. (11) are also shown in Fig. 3 for the case of $^3\Pi_1$ state ($i = 2$). To make the control efficient, we should be able to stop the dissociation along the two states $^1\Pi_1$ and $^3\Pi_1$ simultaneously, as mentioned above. As seen from Fig. 3 (a), $\hbar \omega \simeq 4.1$ eV for $v = 3$ nicely satisfies this condition. However, this cannot be a good candidate, unfortunately, because the energy $\simeq 4.1$ eV is a bit too high and the flux from the $v = 0$ component degrades the control efficiency significantly, as will be explained later. To circumvent such a situation, we need to search for such cases that require photon energies less than 4 eV. Actually such cases can be found for $v = 4$ and $v = 5$ in the energy range $\hbar \omega \simeq 3.5 \sim 3.7$ eV [see Fig. 3 (b) and (c)]. In these cases, the photodissociation branching is dominated by $\text{HI} \rightarrow \text{H} + \text{I}$. On the other hand, we can easily find such a laser frequency that completely blocks the dissociation along the $^3\Pi_{0+}$ state. In the next section, we carry out the full quantum wave packet dynamics and confirm the above prediction by the semiclassical theory.

## 4 Wavepacket dynamics calculations

In order to prepare a vibrationally excited state in the electronically ground state, we have employed the screening method [21]. The actual calculation of wavepacket dynamics is carried out by utilizing the sixth-order symplectic integrator method [22] with use of the orthogonal transformation $U$ which diagonalizes $V(t)$, i.e.,

$$
\phi(t + \Delta t) = e^{-ic_k\Delta t} e^{-id_jV(t)\Delta t} e^{-ic_l\Delta t} e^{-id_kV(t)\Delta t} \times \cdots e^{-id_1V(t)\Delta t} e^{-ic_1\Delta t} \phi(t) + \mathcal{O}(\Delta t^7)
$$

$$
= e^{-ic_k\Delta t} U(U^t e^{-id_2V(t)\Delta t} U) U^t e^{-ic_2\Delta t} U(U^t e^{-id_1V(t)\Delta t} U) U^t \times \cdots U(U^t e^{-id_1V(t)\Delta t} U) U^t e^{-ic_1\Delta t} \phi(t) + \mathcal{O}(\Delta t^7)
$$

where $K = -\frac{\hbar^2}{2m} \frac{d^2}{dt^2}$ is the kinetic energy operator, and $c_i$ and $d_j$ are the coefficients in the symplectic method [22]. We have used the following parameters: $\Delta R = 7.8 \times 10^{-3}$ a.u. and $\Delta t = 0.043$ fs. This method is faster than the usually employed split-operator method.

To avoid artificial reflection at the rightend of the PECs, we put an imaginary absorbing potential in the asymptotic region $R = 9 \sim 10$ a.u. of each electronically excited state [23, 24].
Figure 3: The complete reflection manifolds and the transmission probabilities $P$ in the case of the $^1\Pi_1$ state ($i=2$) for (a) $v = 3$, (b) $v = 4$, (c) $v = 5$, and (d) $v = 6$. 
We calculate the time-integrated fluxes $J_i(t)$ on PEC $i$ according to

$$J_i(t) = \int_0^t dt' \frac{\hbar}{m} \text{Im} \left\{ \frac{d}{dR} \phi_i(R, t') \phi_i^*(R, t') \right\} \bigg|_{R=R_c},$$

where $\phi_i(R, t)$ is the wavefunction on the surface $i$, and $R_c$ is an asymptotic position taken here to be 6 a.u.. Actual calculations of the fluxes are carried out by using the five-point numerical differentiation [23]. The total duration time to calculate the time-integrated fluxes is $T = 3.5$ ps.

Figures [4] show the time-integrated fluxes at the final time $T = 3.5$ ps as a function of the laser energy $\hbar \omega$. The time-integrated fluxes $J_i(t)$ represents the probability of the state $i$ at $t = T$, and is equal to the overall dissociation probability at $t = \infty$. The initial excited vibrational state is prepared at $t = 0$. The final time $T = 3.5$ ps is chosen rather arbitrarily in order to save the CPU time (see Fig. [5]).

Figure [4] (a) is the result when the initial state is $v = 0$. From this figure we can easily see (1) $v = 0$ is not suitable for the control of photodissociation branching of HI, and (2) the $v = 0$ component degrades the control efficiency, if $\hbar \omega$ is higher than $\approx 4$ eV. Figure [4] (b) shows the result for $v = 3$, in which, as predicted in Fig. [3] (a), the time-integrated fluxes on the two states $^1\Pi_1$ and $^3\Pi_1$ vanish at $\hbar \omega \approx 4.1$ eV. As mentioned above, however, the flux from $v = 0$ at this energy ($\approx 4.1$ eV) is not negligible and the control efficiency may be very much deteriorated, since the $v = 0$ component is considered to be dominant in the actual experimental condition unless the scheme of complete excitation is employed to prepare the initial $v = 3$ state [3, 4]. In order to avoid this circumstance, we can choose $v = 4$ at $\hbar \omega \approx 3.58$ eV [see Fig. [4] (c)] or $v = 5$ at $\hbar \omega \approx 3.68$ eV [see Fig. [4] (d)]. To confirm this, in Figs. [5], we show the time variation of the time-integrated fluxes at $\hbar \omega = 3.58$ eV for $v = 4$ [Fig. [5] (a)] and $v = 0$ [Fig. [5] (b)]. The undesirable fluxes along the states $^1\Pi_1$ and $^3\Pi_1$ from $v = 4$ and from $v = 0$ component of the ground electronic state are negligibly small. The inverse case that HI $\rightarrow$ H+I is dominant can be easily achieved by choosing the laser frequency at $\hbar \omega \approx 3.47$ eV with $v = 4$, for instance [see Fig. [4] (c)]. Even the initial vibrational state lower than $v = 4$ can be used, if we want to stop only one channel correlated to $I^*$.  

5 Concluding remarks

Controlling photodissociation branching between HI $\rightarrow$ H + I and HI $\rightarrow$ H + $I^*$ was discussed from the viewpoint of the complete reflection phenomenon and analyzed by the semiclassical Zhu-Nakamura theory of nonadiabatic transition. The nearly complete control was shown to be achieved despite the fact that the three electronically excited states are involved, if the initial vibrational state and the CW laser frequency are appropriately selected. This was also confirmed by carrying out much more time consuming quantum wavepacket calculations. The enhancement of the branching ratio by using vibrationally excited states has been reported by Alekseyev et al. [14] and by Kalyanaraman and Sathyamurthy [20]. Using their own accurate ab initio potential curves, the same ones as those used here, the former authors suggested to use $v = 1$ and $v = 2$ at relatively high laser frequencies. The latter authors employed the inaccurate potential curves of Levy and Shapiro [13] and reported the best branching of $I^*$ formation with $v = 4$ again at relatively high energies. In both of these works the population of the initial vibrationally excited state was assumed to be hundred percents, and the possibly large contribution from $v = 0$ was neglected. Besides, any clear and precise picture such as that based on the complete reflection phenomenon as done in this work has not been provided.

In the present treatment, the rotational degree of freedom has been disregarded as in Refs. [16, 17, 20]. In order to compare with any real experiment, it is required to take into account the effects of initial rotational state distribution, depending on the experimental condition. The completeness would be deteriorated by the distribution to some extent, but the control may
Figure 4: The time-integrated fluxes at $T = 3.5$ ps as a function of $\hbar \omega$ for (a) $v = 0$, (b) $v = 3$, (c) $v = 4$, and (d) $v = 5$. 
be achieved to good extent. This will be discussed elsewhere in near future. The present idea can be applied to other diatomic molecules, and even to triatomic molecules, if appropriate conditions are satisfied. Applications to Cl$_2$[28], HOD, and N$_2$O are planned.

We thank Dr. N. Balakrishnan for providing us ab initio data of HI, and Dr. K. Nagaya for pointing us the importance of the initial state preparation. Acknowledgements are also due to C. Zhu, H. Kamisaka, T. Yasuike, S. Nanbu, H. Katayanagi, and K. Hoki. This work was partially supported by the research grant No. 10440179 from the Ministry of Education, Culture, Sports, Science, and Technology of Japan.

References

[1] S. A. Rice and M. Zhao, *Optical Control of Molecular Dynamics*, John-Wiley & Sons (2000).

[2] Y. Teranishi and H. Nakamura, J. Chem. Phys. **111**, 1415 (1999).

[3] K. Nagaya, Y. Teranishi, and H. Nakamura, J. Chem. Phys. **113**, 6197 (2000).

[4] Y. Teranishi, K. Nagaya, and H. Nakamura, in “Advances in Muti-Photon Processes and Spectroscopy”, Vol. 14, edited by R. J. Gordon and Y. Fujimura (World Scientific, Singapore, 2001).

[5] K. Nagaya, Y. Teranishi, and H. Nakamura, in “Laser Control and Manipulation of Molecules”, edited by A. D. Bandrauk, R. J. Gordon, and Y. Fujimura (Amer. Chem. Soc. 2002).

[6] K. Nagaya, Y. Teranishi, and H. Nakamura, J. Chem. Phys. (to be published, 2002).

[7] C. Zhu, Y. Teranishi, and H. Nakamura, Adv. Chem. Phys. **117**, 127 (2001).

[8] H. Nakamura, *Nonadiabatic transition: Concepts, Basic Theories and Applications*, World Scientific, Singapore (2002).

[9] C. Zhu and H. Nakamura, J. Chem. Phys. **97**, 1892 (1992).
[10] H. Nakamura, J. Chem. Phys. 87, 4031 (1987).
[11] M. Ya. Ovchinnikova, Dokl. Phys. Chem. 161, 259 (1965).
[12] M. Baer and M. S. Child, Mol. Phys. 36, 1449 (1978).
[13] H. Nakamura, J. Chem. Phys. 97, 256 (1992).
[14] S. Nanbu, H. Nakamura, and F. O. Goodman, J. Chem. Phys. 107, 5445 (1997).
[15] H. Nakamura, J. Chem. Phys. 110, 10253 (1999).
[16] A. B. Alekseyev, H-P. Liebermann, D. B. Kokh, and R. J. Buenker, J. Chem. Phys. 113, 6174 (2000).
[17] N. Balakrishnan, A. B. Alekseyev, and R. J. Buenker, Chem. Phys. Lett. 341, 594 (2001).
[18] N. Balakrishnan, private communication.
[19] I. Levy and M. Shapiro, J. Chem. Phys. 89, 2900 (1988).
[20] C. Kalyanaraman and N. Sathyamurthy, Chem. Phys. Lett. 209, 52 (1993).
[21] K. Takatsuka and N. Hashimoto, J. Chem. Phys. 103, 6057 (1995).
[22] K. Takahashi and K. Ikeda, J. Chem. Phys. 99, 8680 (1993).
[23] D. Neuhauser and M. Baer, J. Chem. Phys. 90, 4351 (1989).
[24] J. Z. H. Zhang, Theory and Application of Quantum Molecular Dynamics, World Scientific, Singapore (1999).
[25] S. E. Koonin and D. C. Meredith, Computational Physics, Fortran Version, Addison-Wesley, Singapore (1990).
[26] A. Sugita, K. Suto, M. Kawasaki, and Y. Matsumi, Chem. Phys. Lett. 340, 83 (2001).