Control of interference of molecular wavepackets and its dynamics by using delayed phaselocked ultrashort pulses

Anindita Bhattacharjee¹ and Krishna Rai Dastidar²
² Department of Spectroscopy, Indian Association for the Cultivation of Science, Kolkata 700032, India
E-mail: ¹ anny_b_2000@yahoo.com
E-mail: ² spkrd@mahendra.iacs.res.in

Abstract. We have shown by ab-initio calculation that quantum interference between two vibrational wavepackets on the bound \(A^1Σ^+\) state of NaH molecule can be controlled by controlling the delay time and relative phase between the ultrashort pulses which generate these wavepackets. Quantum interference between the wavepackets is probed by a third pulse which initiates photodissociation of the molecule via repulsive \(B^3Π\) state. Temporal evolution of the photodissociation cross section mimics the dynamics of interfering wavepackets on the bound state. We have shown that the evolution of photodissociation cross section with time can be utilized as time-dependent quantum gate whose nature is a function of the delay time and relative phase between the pulses.

1. Introduction
The use of coherent laser radiation to control chemical reactions [1-21] is a long cherished goal for chemical physicists. Major advances in laser technology which led to the generation of ultrashort pulses [22, 23] has contributed significantly to the development of the field of coherent control. Broadband ultrafast lasers generate wavepackets localized in space and time which can be engineered to control the outcomes of chemical processes. Coherent control of quantum systems has potential applications in various fields like quantum computation and information [7, 8, 18] and coherent cooling [4]. Wavepacket interferometry [9-21] is one of the schemes widely used in studies of quantum control. This technique basically comprises of generating wavepackets using phaselocked pulses, interference between the wavepackets depend on the delay and relative phase difference between the pulses. By careful choice of the time delay and precise phase between the pulses, population on the excited state can be enhanced or diminished. It was also shown [10, 15, 18] that a particular superposition of states can be selectively chosen over another superposition. Recently in different experiments, [14, 15] it has been shown that quantum interference can be used to extract both amplitude and phase information stored in the wavepackets. Quantum interference between wavepackets can be probed by fluorescence measurement [9, 13, 15], ionization [10, 12, 16] or photodissociation [19].

In the present study, we have theoretically studied quantum interference of wavepackets in NaH molecule which is probed by photodissociation of the molecule by excitation to a
repulsive state by a third pulse. Scheme for the present study is shown in Figure 1. Two phaselocked Gaussian pulses (pump and control) of duration (FWHM) 4 fs sequentially excite two wavepackets on the $A^1\Sigma^+$ state of NaH molecule. A third pulse (probe) delayed from the control pulse excites interfering wavepackets to the repulsive $B^1\Pi$ state initiating dissociation. In an earlier study [19], we have shown that quantum interference probed by photodissociation is dependent on the delay time between the first two pulses. It was also shown that temporal evolution of photodissociation cross section can be realized as time-dependent quantum gate. In this work, we have shown that oscillation in photodissociation cross section also depends on the relative phase between the phaselocked pulses. To calculate photodissociation cross section time dependent Fourier Grid Hamiltonian method [24, 25] has been used which is based on Heller’s model for photodissociation [26]. This method involves solving the one-dimensional time dependent Shrodinger equation for the nuclear motion to calculate time-dependent wavepackets at various times on the potential energy surfaces of the excited $A^1\Sigma^+$ and $B^1\Pi$ states. Photodissociation cross section at all energies can be obtained by Fourier transform of the autocorrelation function [24, 25].

2. Theory

Time dependent Fourier grid method [24, 25] is widely used to calculate total photodissociation cross section for one-photon excitation. We have extended this method to calculate two or three-photon dissociation cross section [19, 20]. The theory is as follows.

By the first pulse, the molecule is excited from ground vibronic state to the intermediate $A^1\Sigma^+$ state. Wavepacket amplitude on the excited surface (derived from time-dependent perturbation theory [27]) at time $t=T$ and at internuclear separation $R$ is,

$$ (ih)\chi_{e1}(R, T) = \int_0^T dt_1 e^{-i\epsilon(R-t_1)} D_{eg}(R, t_1) e^{-i\mu_{g1}} \chi_{gv}(R, 0) $$

Figure 1. Potential energy curves for the $X^1\Sigma^+$, $A^1\Sigma^+$, $B^1\Pi$ electronic states of NaH molecule. Pump-control-probe scheme to study quantum interference of molecular vibrational wavepackets (See text for details).
where $\chi_{gf}(R,0)$ is the eigenfunction of the vibrational level 'v' of the ground state $g$ at time $t=0$. $H_g$ and $H_e$ are the total Hamiltonian for the ground state 'g' and the excited state 'e' (bound $A^1\Sigma^+$ state) respectively. $D_{ge}$ is the electronic dipole transition moment for transition from the ground state 'g' to the state 'e', $T$ is the duration of the pump pulse. The ground vibrational wavefunction $\chi_{gf}(R,0)$ is obtained by using time-independent Fourier Grid Hamiltonian method described in [28] for which spatial 1-dimensional grid is set up on the internuclear axis. Following excitation, the wavepacket is allowed to propagate freely on the $A^1\Sigma^+$ state for a time interval $t'$ which is given by

$$t' = \tau_{\text{control}} + t_\phi$$  \hspace{1cm} (2)

$\tau_{\text{control}}$ is the delay between the pump and control pulses and $t_\phi = \frac{\phi}{\omega}$ is the delay corresponding to the relative phase difference $\phi$ between these two pulses. The control pulse excites another wavepacket $\chi_{e2}$ on the $A^1\Sigma^+$ state surface of the same form as in equation (1), with $T$ being replaced by $T'$ which is the duration of the second pulse. The resultant wavepacket on the $A^1\Sigma^+$ state surface at time $T + t' + T''$ is the sum of two wavepackets and is given by

$$\chi_e(R, T + t' + T'') = \chi_{e1}(R, T + t' + T') + \chi_{e2}(R, T + t' + T'')$$  \hspace{1cm} (3)

It is allowed to propagate for time $\tau$. A third pulse of duration $T''$ excites the propagating wavepacket $\chi_e$ to the second excited surface 'f' (repulsive $B^1\Pi$ state). Wavepacket amplitude on surface $f$ is

$$(i\hbar)\chi_f(R, T + t' + T'' + \tau + T''') = \int_{T+t'+T''+\tau}^{T+t'+T''+\tau+T'''} dt_2 e^{-\frac{iH_t(t''-t_2)}{\hbar}} [D_{fe}(R), \epsilon(t_2)] e^{-\frac{iH_t t_2}{\hbar}} \chi_e(R, T + t' + T' + \tau)$$  \hspace{1cm} (4)

where $D_{fe}$ is the electronic dipole transition moment for transition from 'e' to 'f' and $H_f$ is the total Hamiltonian of the state 'f'. Electric field at time $t_i$ given by

$$\epsilon(t_i) = g(t_i) \exp[i\omega t_i]$$  \hspace{1cm} (5)

g($t_i$) is the temporal profile of the pulse and $\omega$ is its carrier frequency. When the third pulse is considered a $\delta$-function ($g(t) = \delta(t)$), then for $T'' = t$ equation (4) reduces to

$$\chi_f(R, T + t' + T'' + \tau + t) = -\frac{i}{\hbar} \epsilon \exp[-\frac{iH_t t}{\hbar}] D_{fe}(R) \chi_e(R, T + t' + T'' + \tau)$$  \hspace{1cm} (6)

Equations (4) and (6) represent a wavepacket evolving on the $B^1\Pi$ state under the influence of Hamiltonian $H_f$. The initial wavepacket $|\chi_f(t=0)\rangle$ on $B^1\Pi$ state propagates on the repulsive potential energy surface to form time dependent wavepackets $|\chi_f(t)\rangle$. The entire time interval on the repulsive $B^1\Pi$ state is divided into small time steps and at each time step, time dependent wavepacket is calculated from which the autocorrelation function (overlap of initial wavepacket at $t=0$ with time dependent wavepacket), is obtained as

$$F(t) = \langle \chi_f(t=0)|\chi_f(t)\rangle$$  \hspace{1cm} (7)

Fourier transform of the autocorrelation function gives the required absorption spectrum (neglecting the effect of rotation).

$$\sigma(\nu) = g_f \frac{\pi \nu}{3 \epsilon_0 \epsilon \hbar} \int_{t=-\infty}^{\infty} e^{\frac{i\nu t}{\epsilon \hbar}} F(t) dt$$  \hspace{1cm} (8)
where, \( c \) is the velocity of light, \( \epsilon_0 \) is the permittivity of free space and \( E = E_i + h\nu \), \( E_i \) is the energy of the initial vibrational state. \( g_{i,f} \) is the degeneracy factor.

To calculate the spectrum for excitation from ground state to \( A^1\Sigma^+ \) state by pump and control pulses, equation (7) and (8) have been employed with \( \psi_f \) replaced by \( \psi_e \). The propagated wavepackets on the excited state surfaces ‘e’ and ‘f’ are calculated by using Chebyshev scheme [29].

3. Calculation

Potential energy curves for the ground \( X^1\Sigma^+ \) state, the excited \( A^1\Sigma^+ \) and \( B^1\Pi \) states (shown in Figure 1) and dipole transition moments for the \( X^1\Sigma^+ \leftarrow A^1\Sigma^+ \) and \( A^1\Sigma^+ \leftarrow B^1\Pi \) transitions have been obtained from the ab-initio calculations of Sachs et al. [30]. Both the pump and control pulses have carrier frequency of 25310 cm\(^{-1} \) (\( \approx 395 \text{nm} \)), width (FWHM) 4 fs and a Gaussian profile given by the normalised function

\[
g(t) = \frac{1}{\sqrt{2\pi}\sigma} e^{-\frac{t^2}{2\sigma^2}}
\]

where \( \sigma \) is a measure of the pulse duration.

We have considered a one-dimensional grid of length 19.8 a.u. and 1024 grid points. The time step for propagation is considered as 5 a.u. Two sets of excitation schemes have been considered for \( A^1\Sigma^+ \rightarrow B^1\Pi \) transition - 1) \( \delta \)-function excitation and 2) Excitation by a 4 fs (FWHM) Gaussian pulse of the form given by equation (8). The final propagation time on the repulsive \( B^1\Pi \) state has been so chosen that at the end of the propagation time, the ratio of final to initial autocorrelation function is within \( 10^{-5} \) and \( 10^{-6} \).

4. Results and discussion

First of all we have calculated the spectrum for excitation of NaH molecule from \( v=0 \) level of the ground state to the \( A^1\Sigma^+ \) state by the pump and control pulses. Wavepackets on the \( A^1\Sigma^+ \) state formed by the pump and control pulses interfere to modify population on this state depending upon the relative phase (\( \phi \)) as well as the delay (\( \tau_{\text{control}} \)) between these two pulses. Figure 2 shows interference of wavepackets on the \( A^1\Sigma^+ \) state for \( \tau_{\text{control}}=T_{\text{vib}} \) and \( \tau_{\text{control}}=1.5 \) \( T_{\text{vib}} \) in the lower and upper panels respectively. \( T_{\text{vib}} \) is the average classical vibrational period of the set of vibrational levels (\( v=6-14 \)) excited by the pulses.

When \( \tau_{\text{control}}=T_{\text{vib}} \), the first wavepacket excited by the pump pulse completes one oscillation within the potential well and returns to the inner turning point to completely interfere with the second wavepacket generated by the control pulse. When the relative phase between the pulses is \( \phi=0 \), wavepackets interfere constructively and hence the resultant wavepacket is enhanced in magnitude. When \( \phi = \pi \), destructive interference leads to damping of wavepacket magnitude. Constructive (or destructive) interference for phase difference \( \phi=0 \) (or \( \pi \)) results in enhanced (or diminished) cross section for excitation (Figure 3) to the \( A^1\Sigma^+ \) state for \( \tau_{\text{control}}=T_{\text{vib}} \). When \( \tau_{\text{control}} \approx 1.5 \) \( T_{\text{vib}} \), the first wavepacket is located at the outer turning point when it interferes with the second wavepacket so that they interfere partially. The resultant wavepackets for \( \phi=0 \) and \( \pi \) are comparable in magnitude but oscillate out of phase with \( \pi \) around \( R=6.0 \) a.u (see inset of Figure 2). This partial interference of wavepackets within the Franck-Condon region contributes to a modified distribution of population on the \( A^1\Sigma^+ \) state. Excitation spectrum for \( \tau_{\text{control}}=1.5 \) \( T_{\text{vib}} \) (Figure 4) shows that the excitation cross section of odd vibrational levels is enhanced in expense of that for even levels and vice versa. In particular, for \( \phi=\pi/2 \), population of the even vibrational levels is almost zero. With phase difference \( \phi=3\pi/2 \), this feature is reversed, i.e, even vibrational levels are populated while population of odd levels are damped. Hence, by carefully choosing the relative phase difference and delay between the pulses, one can
Figure 2. Interfering wavepackets on $A^1\Sigma^+$ state of NaH molecule produced by 4fs Gaussian pulses with delay time $\tau_{\text{control}} = T_{\text{vib}}$ (lower panel) and $\tau_{\text{control}} = 1.5 T_{\text{vib}}$ (upper panel) and phase difference 0 and $\pi$ between them.

Figure 3. Spectrum for excitation of NaH molecule from $v=0$ level of ground $X^1\Sigma^+$ state to $A^1\Sigma^+$ state by two 4fs (FWHM) Gaussian pulses with central frequency 25310 cm$^{-1}$ and time delay $\tau_{\text{control}}=T_{\text{vib}}$ and phase difference $\phi=0$ (lower panel) and $\phi=\pi$ (upper panel) between them.
control both the magnitude (Figure 3) and distribution (Figures 3 and 4) of population on the \( A^1\Sigma^+ \) state.

Interfering wavepackets generated by the pump and control pulses freely propagate on the bound potential energy surface of \( A^1\Sigma^+ \) state. The nature of wavepacket recurrence on the \( A^1\Sigma^+ \) state depends on the value of \( \tau_{\text{control}} \). For \( \tau_{\text{control}} = T_{\text{vib}} \), wavepackets are co-propagating and overlap at the same position on the internuclear axis. This resultant interfering wavepacket oscillates on the bound state potential and is localized at different positions on the internuclear axis at different values of time (Figure 5). The interference between these two wavepackets for \( \phi = 0 \) and \( \pi \) is in phase. For \( \tau_{\text{control}} = 1.5 \, T_{\text{vib}} \), wavepackets are counterpropagating (Figure 6) and initially these two are localized at different positions on the internuclear axis with a partial interference around the Franck-Condon region. With time these two wavepackets approach each other and overlap at the same position on the internuclear axis leading to complete interference at certain values of time. But the interference between these two wavepackets for \( \phi = 0 \) and \( \pi \) is completely out of phase. When these interfering wavepackets are excited to the repulsive \( B^1\Pi \) state by a third pulse after a delay \( \tau \), the molecule dissociates. The delay time \( \tau \) between the control and the probe pulse allows oscillation of the interfering wavepackets within the potential well of \( A^1\Sigma^+ \) state. Hence, the resulting dissociation cross section oscillates with \( \tau \). The nature of oscillation of photodissociation cross section carries the signature of wavepacket interference on the \( A^1\Sigma^+ \) state. We have considered two types of pulses for exciting the interfering wavepackets to the repulsive state, viz., \( \delta \)-function pulse (instantaneous excitation) and 4fs (FWHM) Gaussian pulse. Temporal evolution of photodissociation cross section for \( \delta \)-function excitation is shown in Figure 7 for \( \tau_{\text{control}} = T_{\text{vib}} \) and for relative phases \( \phi = 0 \) and
Figure 5. Interfering wavepackets propagating on the $A^1\Sigma^+$ state at different time $\tau$ as mentioned in respective panels. Delay between the pulses generating the interfering wavepackets is $\tau_{\text{control}} = T_{\text{vib}}$, and relative phase between them is $\phi = 0$ (solid line) and $\phi = \pi$ (dashed line).

Figure 6. Interfering wavepackets propagating on the $A^1\Sigma^+$ state for $\tau_{\text{control}} = 1.5 \ T_{\text{vib}}$. Other details are same as Figure 5.
Figure 7. Photodissociation cross section at frequency $\omega = 9201 \text{cm}^{-1}$ as a function of delay time $\tau$ for $\delta$-function excitation of interfering wavepackets on $A^1\Sigma^+$ state to repulsive $B^1\Pi$ state. Delay between the pulses generating the interfering wavepackets is $\tau_{\text{control}} = T_{\text{vib}}$.

Figure 8. Photodissociation cross section as a function of delay time $\tau$ for $\delta$-function excitation for $\tau_{\text{control}} = 1.5 T_{\text{vib}}$. Other details are same as Figure 7.

$\pi$ between the pulses. Magnitude of dissociation cross section is large in case of $\phi=0$ due to constructive interference. Dissociation cross sections corresponding to the relative phases $\phi = 0$ and $\pi$ oscillate in phase with each other owing to co-propagating wavepackets (Figure 5). Conversely, evolution curves for $\phi=0$ and $\pi$ in case of $\tau_{\text{control}} = 1.5 T_{\text{vib}}$ oscillate out of phase with each other (Figure 8). In Figure 9, wavepackets excited to the $B^1\Pi$ state at different values of probe delay $\tau$ are plotted. Due to instantaneous excitation, wavepackets on the repulsive $B^1\Pi$ state at different delays are of the same nature as propagating wavepackets (Figure 6) on the bound state. It can be noted that in Figure 6 wavepackets for phase $\phi=0$ and $\pi$ at delay $\tau = 500$ a.u. and 2250 a.u. oscillate out of phase with R around the Franck-Condon region. Cross section values for $\phi = 0$ and $\pi$ are minimum or maximum at these particular delays. Hence it can be inferred that out of phase oscillation in wavepackets with R leads to out of phase evolution of photodissociation cross section with probe delay.

The dependence of temporal evolution upon the relative phase of the pulses has two applications. Firstly, it can be utilized for retrieval of phase information of an unknown
wavepacket by interference with a reference wavepacket. Secondly, oscillation of dissociation cross section can be realized as time-dependent quantum gate as we have shown before [19, 20]. By comparing the nature of different evolution curves in Figures 7 and 8 we can say that time-dependent quantum gate is a function of the delay time and relative phase difference between the input (pump and control) pulses.

Probing the quantum interference with a Gaussian pulse of duration 4 fs produces results similar to that for δ-function excitation. Initial wavepackets for τ_{control} = T_{vib} and τ_{control} = 1.5T_{vib} on B^{1}Π states formed by a 4 fs pulse excitation are shown in Figure 10. Constructive and destructive interference of wavepackets on the A^{1}Σ^{+} state results in enhanced and damped magnitude of wavepacket for τ_{control}=T_{vib}, which modifies the magnitude of dissociation cross section accordingly. Temporal evolution of cross section is in phase for φ=0 and φ=π in case...
Figure 11. Photodissociation cross section at frequency $\omega = 8000\text{cm}^{-1}$ as a function of delay time $\tau$ for excitation by 4fs Gaussian pulse. Delay between pump and control pulses $\tau_{\text{control}} = T_{\text{vib}}$.

Figure 12. Photodissociation cross section at frequency $\omega = 8000\text{cm}^{-1}$ as a function of delay time $\tau$ for excitation by 4fs Gaussian pulse. Delay between pump and control pulses $\tau_{\text{control}} = 1.5 T_{\text{vib}}$.

of $\tau_{\text{control}} = T_{\text{vib}}$. (Figure 11) and out of phase in case of $\tau_{\text{control}} = 1.5 T_{\text{vib}}$. (Figure 12). The oscillation of photodissociation cross section in case of excitation by 4 fs pulses is much faster than that in case of $\delta$-function transition, since a pulse of longer duration generates delocalized wavepackets (Figure 10) as compared to $\delta$-function pulse. The finite width of 4 fs pulse also shifts the wavepacket on the repulsive state towards higher $R$ for $\tau_{\text{control}} = T_{\text{vib}}$ and the out of phase oscillation of the wavepackets for $\tau_{\text{control}} = 1.5 T_{\text{vib}}$ becomes more prominent and spreads over a large range of internuclear separation $R$. Due to the propagation of the wavepacket during the finite duration of the probe pulse, the complete out of phase oscillation of wavepackets (for $\phi = 0$ and $\pi$) on $A^1\Sigma^+$ state at $\tau = 500 a.u.$ and 2250$a.u.$ appears at larger time $\tau = 1500 a.u.$ and 3250$a.u.$ respectively on $B^1\Pi$ state for $\tau_{\text{control}} = 1.5 T_{\text{vib}}$. (Figure 13). This feature is completely different from that obtained for transition by $\delta$-function pulse (Figure 9). Therefore the nature
of oscillation also depends on the nature of the probe pulse used for the dissociative excitation.

5. Conclusions
In NaH molecule, we have found that interference of wavepackets and its evolution on the $A^1\Sigma^+$ state can be controlled by two delayed phase-locked ultrashort pulses. The set of even and odd vibrational levels of the excited state can be selectively populated by controlling the phase and delay between two ultrashort pulses. Also, the magnitude of dissociation upon excitation of the interfering wavepackets to a repulsive state can be enhanced or diminished. Oscillation of photodissociation cross section with delay of the probe pulse can be controlled by changing the delay and phase of two input pulses.

References
[1] Zewail A H 1988 Science 242 1645
  Warren W S, Rabitz H and Dahle M 1993 Science 259 1581 and references therein
  Tannor D J and Rice S A 1988 Adv. Chem. Phys. 70 441
  Brumer P and Shapiro M 1986 Chem. Phys. Lett. 126 541
[2] Baumert T, Grosser M, Thalweiser R and Gerber G 1991 Phys. Rev. Lett. 67 3753
[3] Lein M, Erdmann M and Engel V 2000 J. Chem. Phys. 113 3609
[4] Niikura H, Villeneuve D M and Corkum P B 2004 Phys. Rev. Lett. 92 133002
[5] Warmuth Ch et al. 2001 J. Chem. Phys. 114 9901
[6] Balint-Kurti G G et al. 2005 J. Chem. Phys. 122 084110
[7] Amitay Z, Kosloff R and Leone S R 2002 Chem. Phys. Lett. 361 530
  Vala J et al. 2002 Phys. Rev. A 66 062316
[8] Ahn J, Weinacht T C, and Bucksbaum P H 2000 Science 287 463
[9] Scherer N F et al. 1991 J. Chem. Phys. 95 1487
[10] Noel M W and Stroud C R, Jr. 1996 Phys. Rev. A 77 1913
[11] Chen X and Yeazell J A 1997 Phys. Rev. A 55 3264
[12] Blanchet V. Bouchene M A and Girard B 1998 J. Chem. Phys. 108 4862
[13] Ohmori K et al. 2003 Phys. Rev. Lett. 91, 243003
[14] Weinacht T C, Ahn J and Bucksbaum P H 1998 Phys. Rev. Lett. 80 5508
[15] Ohmori K et al. 2006 Phys. Rev. Lett. 96 093002
Katsuki H et al. 2006 Science 311, 1589
[16] Petersen C et al. 2004 Phys. Rev. A 70 033404
[17] Boleat E D and Fielding H H 2005 Mol. Phys. 103, 491
[18] Collins D, Kim K W, and Holton W C 1998 Phys. Rev. A 58 R1633
Lerch E W, Dai X, Gilb S, Torres E A, and Leone S R 2006 J. Chem. Phys. 124 044306
[19] Bhattacharjee A and Rai Dastidar K 2005 Phys. Rev. A 72 023419
[20] Bhattacharjee A and Rai Dastidar K 2003 J. Phys. B 36 4467
[21] Bhattacharjee A and Rai Dastidar K 2006 Mol. Phys. 104 2485
[22] Paul P M et al. 2001 Science 292 1689
Hentschel M et al. 2001 Nature 414 509
[23] Shirakawa A, Sakane I, Takasaka M and Kobayashi T 1999 Appl. Phys. Lett. 74 2268
Baltuska A and Kobayashi T 2002 Appl. Phys. B 75 427
[24] Balint-Kurti G G, Dixon R N and Marston C C 1992 Int. Rev. Phys. Chem. 11 317 and references therein
[25] Bhattacharjee A and Rai Dastidar K 2002 Phys. Rev. A 65 022701
Bhattacharjee A and Rai Dastidar K 2002 Pramana 58 569
[26] Heller E J 1978 J. Chem. Phys. 68 2066
[27] Lee S Y and Heller E J 1979 J. Chem. Phys. 71 4777
[28] Marston C C and Balint-Kurti G G 1989 J. Chem. Phys. 91 3571
[29] Kosloff R 1988 J. Phys. Chem. 92 2087
[30] Sachs E S, Hinze J and Sabelli N H 1975, J. Chem. Phys. 62, 3367; ibid. 62 3384