

Observation of the phase lags among the molecules in the coherent phase control of multiphoton ionization

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Abstract

The phase lags among the molecules have been observed in the coherent phase control of multiphoton ionization. Coherent phase control using three- and one-photon excitation scheme has been applied to the multiphoton ionization of the $(\text{CH}_3)_3\text{N}$, $(\text{CH}_3)_2\text{S}$, $\text{C}_2\text{H}_5\text{SH}$, CH_3I , and CD_3I molecules. The phase lags of methyl iodide (CH_3I and CD_3I) relative to other molecules showed considerable dependence on the excitation wavelength, especially in the vicinity of the absorption peak of CD_3I . The energy dependence of the phase lag indicates that the molecular phase for the ionization of methyl iodide is not zero.

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1. Introduction

Phase lag is the key factor in the coherent phase control [1] of the product branching ratio of a photoreaction. The most common method of the coherent control is to use the interference between the three-photon and one-photon excitation connecting the same initial and final states [2]. In that scheme, the transition probability is

$$P = P_1 + P_3 + 2P_{13} \cos(\Delta\phi + \delta) \quad (1)$$

where P_1 and P_3 are the one- and three-photon transition probability, respectively, P_{13} the amplitude of the interference term, $\Delta\phi$ the phase difference between the two laser fields, and δ is the molecular phase. When the excited molecule undergo two reaction channels A and B with each own molecular phase, the phase lag is defined as

$$\Delta\delta = \delta(A) - \delta(B) \quad (2)$$

If the phase lag is not zero, one can manipulate the photoreaction by changing the relative phase of the two lasers. The control efficiency of the product branching ratio critically depends on phase lag. Gordon and co-workers observed phase lags between the ionization and dissociation of the HI [3] and DI [4] molecules.

Recently, we have applied the coherent control to the photodissociation of the dimethylsulfide [5] and found a phase lag between the two dissociation products corresponding to C–S and C–H bond breaking.

As it is shown in Eq. (2), the observed phase lag is the relative value of the molecular phase. However, the absolute value of a molecular phase cannot be determined experimentally because of the difficulty to measure the absolute value of the phase difference between the two lasers.

A simple aspect of a molecular phase is that if the excited molecule has no reaction channel or only one product channel, the molecular phase is expected to be zero. Coherent phase control of photoexcitation of various molecules were reported [6]. In spite of the neat molecular beam condition, phase modulations of the ion signals were observed. This result suggested that the molecular phase had no value and no dependence on internal state distribution. In our previous work on the coherent control of the photoexcitation in methyl iodide and its clusters [7], no phase lag was observed between the ionizations of CH_3I and $\text{CH}_3\text{I}(\text{CH}_3)$. Although the result shows that both monomer and cluster molecules have the same molecular phase, it is not clear whether the molecular phase of methyl iodide is zero or not.

In the present work, we have measured the relative value of the molecular phase in the coherent control of photoexcitation. Molecules compared are trimethylamine $\{(\text{CH}_3)_3\text{N}\}$, dimethylsulfide $\{(\text{CH}_3)_2\text{S}\}$, ethanethiol ($\text{C}_2\text{H}_5\text{SH}$), methyl io-

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dide (CH_3I), and d_3 -methyl iodide (CD_3I). The excitation energy dependence of the molecular phase was discussed on relation to the structure of the absorption spectra.

2. Experimental

The experimental procedure for the coherent phase control is described in detail in our previous paper [7]. Briefly, output of a dye laser pumped by Nd:YAG laser was frequency tripled by the third harmonic generation using CH_3I vapor [8] in the tripling cell. Both fundamental (600–603 nm) and tripled (200–201 nm) outputs were introduced into the phase tuning cell filled with Ar gas. The relative phase were varied by changing the pressure of Ar in the phase tuning cell. The two laser beams were achromatically focused with the two spherical mirrors in the tuning cell to a pulsed molecular beam in a vacuum chamber, and product ions were detected with a time of flight (TOF) mass spectrometer. The source of the molecular beam was a mixture of the sample molecules 2% in He buffer with total pressure of 760 Torr. $(\text{CH}_3)_3\text{N}$ (Nakarai, 98%), $(\text{CH}_3)_2\text{S}$ (Nakarai, 97%), $\text{C}_2\text{H}_5\text{SH}$ (Nakarai, 98%), CH_3I (Nakarai, 99.5%) and CD_3I (Aldrich, 99.5 at.%) were used without further purification.

3. Results and discussion

3.1. Phase modulation of the ion signals

In the TOF mass spectra, the signals of parent ions were dominant except for $(\text{CH}_3)_2\text{S}$ and $\text{C}_2\text{H}_5\text{SH}$. Signals of CH_3S^+ and $\text{CH}_3\text{SCH}_2^+$ fragment ions were dominant in the spectrum of $(\text{CH}_3)_2\text{S}$, and in that of the $\text{C}_2\text{H}_5\text{SH}$, fragment ions of C_2H_5^+ and $\text{C}_2\text{H}_5\text{S}^+$ were dominant. The multiphoton ionization process with the fundamental (visible) laser is three-photon resonant and two-photon ionization (3+2 REMPI), except for $(\text{CH}_3)_3\text{N}$ that has rather lower ionization energy so that one-photon energy is enough for ionization from the resonant state (3+1 REMPI). The three-photon excited states of the $(\text{CH}_3)_2\text{S}$ and $\text{C}_2\text{H}_5\text{SH}$ molecules are directly dissociative [9,10] so that most of the molecules dissociate into the fragments. The observation of the fragment ions in the mass spectra is due to this direct dissociation followed by the further multiphoton ionization of the fragments [5].

The ion signal of $(\text{CH}_3)_3\text{N}$ was the strongest in all wavelength range of the excitation laser, because it requires less photon for ionization [11]. Therefore, we used this molecule as a benchmark to compare the molecular phases of other molecules. In the measurement of $(\text{CH}_3)_2\text{S}$ and $\text{C}_2\text{H}_5\text{SH}$ molecules which gave poor signal intensity of the parent ions, ion signals of CH_3S^+ and C_2H_5^+ fragment ions were used, respectively.

Phase modulations of the ion signals were observed with variation of the Ar pressure that is proportional to the relative phase of the two laser fields. Typical phase modulations of the $(\text{CH}_3)_3\text{N}^+$ and CH_3I^+ ion signals are shown in Fig. 1. The two modulation curves were recorded simultaneously, with the sample mixture of $(\text{CH}_3)_3\text{N}$ and CH_3I . The excitation wavelength of the fundamental laser is 602.5 nm. The smooth curves in the

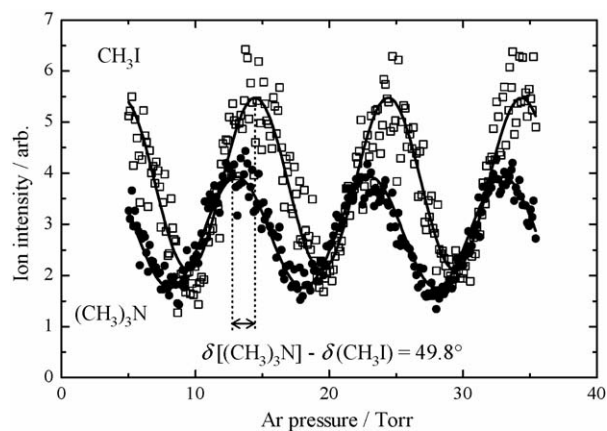


Fig. 1. Modulation of the ion signals of CH_3I (full circle) and $(\text{CH}_3)_3\text{N}$ (open square) as a function of Ar pressure in the phase tuning cell. The solid curves are least square fits of a cosine function. A phase lag of 49.8° is observed between the two curves.

figure show the result of fitting by using

$$I_i = a_i + b_i \cos(cP_{\text{Ar}} + d_i) \quad (3)$$

where I_i denotes the signal intensity of ions, and P_{Ar} is the pressure of Ar. The subscript i indicates the two molecules. The phase lag defined in Eq. (2) is obtained by a least-square fitting of the a_i , b_i , c , and d_i parameters. Then the lag is defined as the difference between the d parameters of the two molecules, $\Delta\delta = d_{\text{N}(\text{CH}_3)_3} - d_{\text{CH}_3\text{I}}$. In Fig. 1, a phase lag of 49.8° is observed. Phase modulations of the ion signals were observed at 600–603 nm wavelength range of the fundamental laser, where the third harmonic generation by CH_3I is efficient [8].

3.2. Observation of the phase lag

We have measured the phase lag of each modulation of the ion signal relative to that of the $(\text{CH}_3)_3\text{N}$ ion signal. The results are shown in Fig. 2. The phase lags of CH_3I (circle), $(\text{CH}_3)_2\text{S}$ (triangle), and $\text{C}_2\text{H}_5\text{SH}$ (square) are plotted against the excitation wavelength of the fundamental laser. The REMPI excitation spectra of the four molecules are also shown below the plot in Fig. 2.

The phase lag of CH_3I is sensitive to the excitation wavelength. It increases up to 50° along the laser wavelength, while those of other molecules, $(\text{CH}_3)_2\text{S}$ and $\text{C}_2\text{H}_5\text{SH}$, are almost constant. The observed lag of a molecule (M) corresponds to the relative difference of its molecular phase from that of the $(\text{CH}_3)_3\text{N}$ molecule, $\Delta\delta = \delta\{(\text{CH}_3)_3\text{N}\} - \delta(\text{M})$. It is expected that the molecular phases of $(\text{CH}_3)_3\text{N}$, $(\text{CH}_3)_2\text{S}$ and $\text{C}_2\text{H}_5\text{SH}$ take almost constant value in the excitation energy range. On the other hand, the molecular phase of CH_3I shows a significant change with the excitation energy. It means that the molecular phase of CH_3I is not zero although the absolute value is not known.

One can see the relation of the phase lags to the REMPI excitation spectra shown in the lower panel of Fig. 2. The REMPI excitation spectrum of each molecule is corresponding to the

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