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

Hidekazu Nagai *, Hideki Ohmura, Taisuke Nakanaga, Masanori Tachiya

National Institute of Advanced Industrial Science and Technology (AIST), Research Institute of Instrumentation Frontier, Tsukuba Central 5, Tsukuba, Ibaraki 305-8565, Japan

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 $(CH_3)_3N$, $(CH_3)_2S$, C_2H_5SH, CH_3I, and CD_3I molecules. The phase lags of methyliodide (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 methyliodide 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

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

where P_1 and P_3 are the one- and three-photon transition provability, 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

$$\Delta\delta = \delta(A) - \delta(B) \tag{2}$$

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 methyliodide and its clusters [7], no phase lag was observed between the ionizations of CH_3I and $CH_3I(CH_3)$. Although the result shows that both monomer and cluster molecules have the same molecular phase, it is not clear whether the molecular phase of methyliodide 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 $\{(CH_3)_3N\}$, dimethylsulfide $\{(CH_3)_2S\}$, ethanethiol (C_2H_5SH), methylio-

* Corresponding author. Tel.: +81 298619297; fax: 81 298615301.
E-mail address: nagai-hidekazu@aist.go.jp (H. Nagai).

dide (CH_3I), and d_3-methyliodide (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. $(CH_3)_3N$ (Nakarai, 98%), $(CH_3)_2S$ (Nakarai, 97%), C_2H_5SH (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 $(CH_3)_2S$ and C_2H_5SH. Signals of CH_3S^+ and $CH_3SCH_2^+$ fragment ions were dominant in the spectrum of $(CH_3)_2S$, and in that of the C_2H_5SH, fragment ions of $C_2H_5^+$ and $C_2H_5S^+$ were dominant. The multiphoton ionization process with the fundamental (visible) laser is three-photon resonant and two-photon ionization (3 + 2 REMPI), except for $(CH_3)_3N$ 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 $(CH_3)_2S$ and C_2H_5SH 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 $(CH_3)_3N$ 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 $(CH_3)_2S$ and C_2H_5SH 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 $(CH_3)_3N^+$ and CH_3I^+ ion signals are shown in Fig. 1. The two modulation curves were recorded simultaneously, with the sample mixture of $(CH_3)_3N$ and CH_3I. The excitation wavelength of the fundamental laser is 602.5 nm. The smooth curves in the

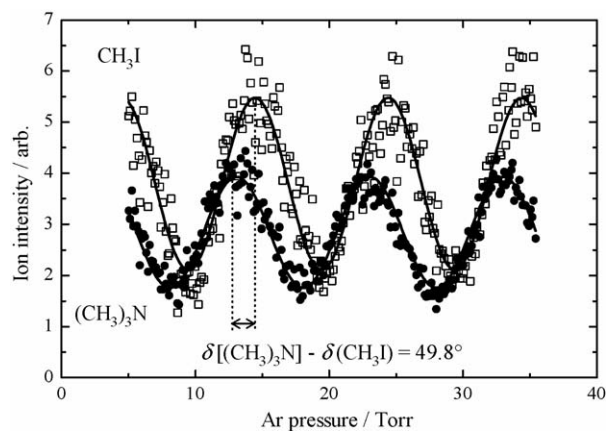
Fig. 1. Modulation of the ion signals of CH_3I (full circle) and $(CH_3)_3N$ (open square) as a function of Ar pressure in the phase tuning cell. The solid curves are least square fits of a cosine function. A phase lag of 49.8° is observed between the two curves.

figure show the result of fitting by using

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

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, $\Delta\delta = d_{N(CH_3)_3} - d_{CH_3I}$. 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 $(CH_3)_3N$ ion signal. The results are shown in Fig. 2. The phase lags of CH_3I (circle), $(CH_3)_2S$ (triangle), and C_2H_5SH (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, $(CH_3)_2S$ and C_2H_5SH, are almost constant. The observed lag of a molecule (M) corresponds to the relative difference of its molecular phase from that of the $(CH_3)_3N$ molecule, $\Delta\delta = \delta\{(CH_3)_3N\} - \delta(M)$. It is expected that the molecular phases of $(CH_3)_3N$, $(CH_3)_2S$ and C_2H_5SH 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
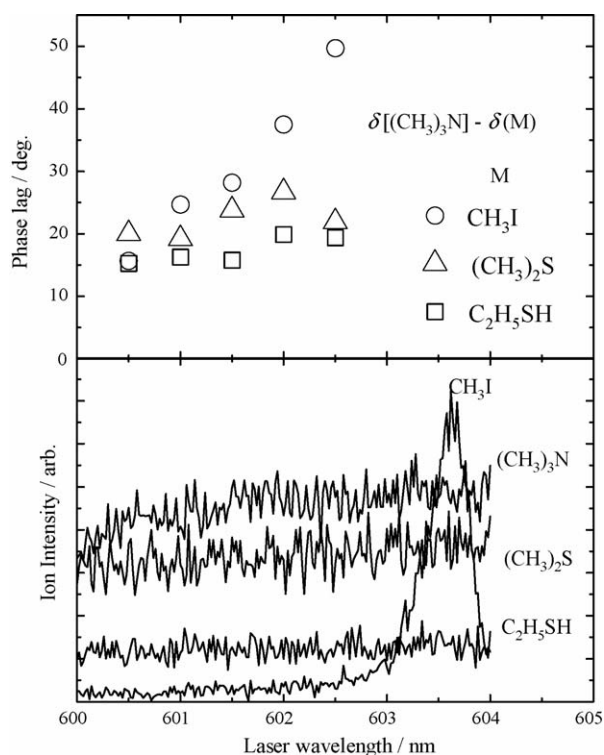
Fig. 2. Phase lag plotted against the excitation wavelength of the fundamental laser. The relative phases of CH_3I (circle), $(CH_3)_2S$ (triangle), and C_2H_5SH (square) were obtained by using $(CH_3)_3N$ as a bench mark. The REMPI excitation spectra measured with fundamental laser only are shown in the lower panel.

three-photon absorption spectrum. Except CH_3I, the spectra of the other molecules are broad and have no structure. The sharp peak at 603.6 nm in the spectrum of CH_3I corresponds to the band origin of the $\tilde{B} - \tilde{X}$ band. The rotational structure of this band is obscured [12–15] by the line broadening due to the pre-dissociation lifetime [16–19]. Therefore, even in the rotationally cooled condition of the molecular beam, we could not resolve the rotational lines. The asymmetric structure of the peak is expected to be the rotational envelope.

As the excitation wavelength approaches to the peak, the phase lag of CH_3I increases. Since the phase lag is defined as the relative difference between the molecular phases of CH_3I and $(CH_3)_3N$, the change of the phase lag is ascribed to a decrease of the molecular phase of CH_3I. It is valid to consider that the molecular phases of $(CH_3)_3N$, $(CH_3)_2S$ and C_2H_5SH are almost constant in this region of the excitation energy, because the lags among them show no change. Therefore, it is evident that the molecular phase of CH_3I is not zero. In our previous work on the CH_3I cluster, we did not observe any phase lag between the CH_3I monomer and $(CH_3I)CH_3$ cluster [7]. It can be concluded that the molecular phase is not affected by a cluster formation.

3.3. Phase lag in the vicinity of the absorption peak of CD₃I

It would be interesting to observe the behaviour of the phase lag of CH_3I at around the wavelength of the band peak. Unfortunately, the peak wavelength is out of the tuning range of the

THG source. Therefore, we observed the phase lag of CD_3I of which the band peak is shifted to 601.8 nm. The result is shown in Fig. 3. Similar to Fig. 2, the phase lag relative to $(CH_3)_3N$ is plotted as a function of the wavelength of the fundamental laser (upper panel) with the REMPI excitation spectrum (lower panel). The phase lag takes a maximum at around 600.6 nm and starts decreasing to take a minimum at around the peak wavelength of the REMPI excitation spectrum.

The energy dependence of the phase lag is similar to the results observed in the ionization and dissociation of HI [3] and DI [4] molecules. The phase lag takes minimum at the excitation energy resonant to the autoionization state. Theoretical works [20–24] on the phase lag made qualitative explanation for the energy dependence with the relation of electronic state structure. In the case of HI and DI, the excited state is an autoionization state interacting with the ionization and dissociation continua underlying in the same energy. It was shown that the molecular phase of the ionization channel would vanish at the resonance with the autoionization state and take maximum in the vicinity of the resonance.

The situation is similar to the present case of CH_3I, where the $\tilde{B}$ state interacting with dissociation continua. The $\tilde{B}$ state is predissociative [16] due to interaction with other states that have anti-bonding potentials. Although the predissociation dynamics of the $\tilde{B}$ state is not clear, at least two dissociation channels are available to produce CH_3 and $I\ (^2P_{3/2})$ or $I^*\ (^2P_{1/2})$. The recent measurement by the femtosecond photoionization spectroscopy [18,19] reported the $\tilde{B}$ state lifetimes of CH_3I and CD_3I to be 1.38 and 1.84 ps, respectively. It is possible to rationalize the
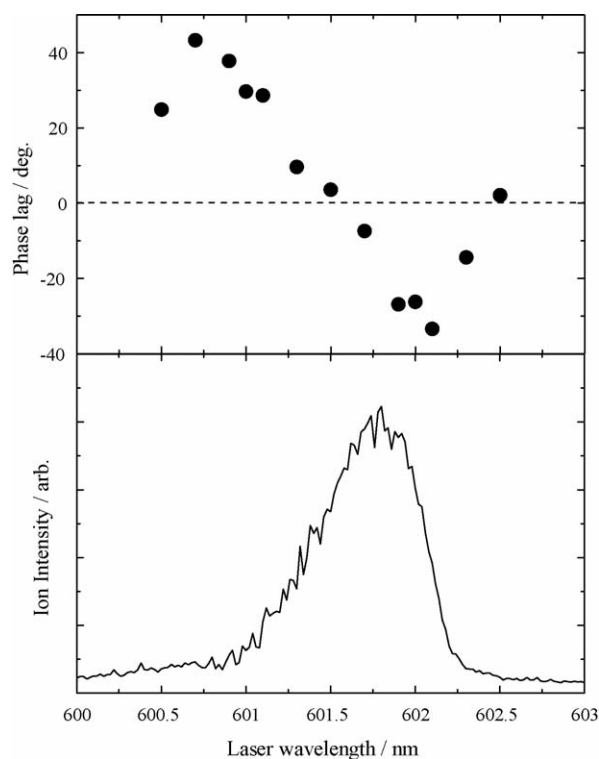

Fig. 3. Phase lag for CD_3I relative to $N(CH_3)_3$ plotted against the excitation wavelength of the fundamental laser. The REMPI excitation spectrum of CD_3I shown in the lower panel was measured with fundamental laser only.

energy dependence of the phase lag of CD_3I with the energy dependence of the molecular phase that will vanish at the resonance with the $\tilde{B}$ state.

4. Conclusions

We have measured the relative phase lags among the phase modulations of the ionization signals of some polyatomic molecules. It is verified that the molecular phase of CH_3I is not zero with observed energy dependence of the phase lags. Our previous result [7] that no phase lag was observed between monomer and cluster of CH_3I suggests that the molecular phase is not affected by the cluster formation.

References

[1] P. Brumer, M. Shapiro, Ann. Rev. Phys. Chem. 43 (1992) 257.
[2] M. Shapiro, J.W. Hepburn, P. Brumer, Chem. Phys. Lett. 149 (1988) 451.
[3] L. Zhu, V. Kleiman, X. Li, S.P. Lu, K. Trentelman, R.J. Gordon, Science 270 (1995) 77.
[4] L. Zhu, K. Suto, J.A. Fiss, R. Wada, T. Seideman, R.J. Gordon, Phys. Rev. Lett. 79 (1997) 4108.
[5] H. Nagai, H. Ohmura, F. Ito, T. Nakanaga, M. Tachiya, J. Chem. Phys. 124 (2006) 034304.
[6] X. Wang, R. Bersohn, K. Takahashi, M. Kawasaki, H.L. Kim, J. Chem. Phys. 105 (1996) 2992.
[7] H. Nagai, H. Ohmura, F. Ito, T. Nakanaga, Chem. Phys. Lett. 383 (2004) 240.
[8] B. Katz, K. Tsukiyama, R. Bersohn, Chem. Phys. Lett. 125 (1986) 19.
[9] I. Tokue, A. Hiraya, K. Shobatake, Chem. Phys. 130 (1989) 401.
[10] P. Limao-Vieira, S. Eden, P.A. Kendall, N.J. Mason, S.V. Hoffmann, Chem. Phys. Lett. 366 (2002) 343.
[11] D.H. Parker, R.B. Bernstein, D.A. Lichtin, J. Chem. Phys. 75 (1981) 2577.
[12] S. Felps, P. Hochmann, P. Brint, S.P. McGlynn, J. Mol. Spectrosc. 59 (1976) 355.
[13] D.H. Parker, R. Pandolfi, P.R. Stannard, M.A. El-Sayed, Chem. Phys. 45 (1980) 27.
[14] J.A. Dagata, M.A. Scott, S.P. McGlynn, J. Chem. Phys. 85 (1986) 5401.
[15] D.J. Donaldson, V. Vaida, R. Naaman, J. Chem. Phys. 87 (1987) 2522.
[16] P.G. Wang, L.D. Ziegler, J. Chem. Phys. 95 (1991) 288.
[17] J.A. Syage, Chem. Phys. Lett. 212 (1993) 124;
J.A. Syage, J. Steadman, J. Chem. Phys. 94 (1990) 7374.
[18] A.P. Baronavski, J.C. Owrutsky, J. Chem. Phys. 108 (1998) 3445.
[19] J.C. Owrutsky, A.P. Baronavski, Chem. Phys. Lett. 222 (1994) 335.
[20] R.J. Gordon, L. Zhu, T. Seideman, J. Phys. Chem. A105 (2001) 4387;
T. Seideman, J. Chem. Phys. 111 (1999) 9168.
[21] T. Nakajima, J. Zhang, P. Lambropoulos, J. Phys. B 30 (1977) 1077.
[22] S. Lee, J. Chem. Phys. 107 (1997) 2734.
[23] H. Lefebvre-Brion, T. Seideman, R.J. Gordon, J. Chem. Phys. 106 (2001) 9402.
[24] H. Lefebvre-Brion, J. Chem. Phys. 106 (1997) 2544.