Research paper

# Angular dependence of ionization probability of $C_2H_2$ in a linearly polarized intense laser field

Hirokazu Hasegawa [a,*], Yuki Ikeda [b], Kotaro Sonoda [a], Takahiro Sato [b], Atsushi Iwasaki [b], Kaoru Yamanouchi [b]

[a] Department of Integrated Sciences, Graduate School of Arts and Sciences, The University of Tokyo, 3-8-1 Komaba, Meguro-ku, Tokyo 153-8902, Japan
[b] Department of Chemistry, School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

A B S T R A C T

The probabilities of the single and double photoionization of acetylene ($C_2H_2$) were derived as a function of the angle between the H-C-C-H molecular axis and the laser polarization direction of a linearly polarized ultrashort intense laser pulse by aligning non-adiabatically the molecular axis of acetylene using another linearly polarized ultrashort intense laser pulse prior to the ionization. The effect of nuclear spin statistics in the alignment processes was discussed by the comparison with the results obtained for isotopologue of $^{12}C^{13}CH_2$.

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## 1. Introduction

By irradiating a molecular ensemble with a linearly polarized ultrashort intense laser pulse, the angular distribution of the molecular axes can be spatially aligned periodically in time after the laser irradiation with a period determined by the rotational constants [1–4]. This phenomenon of the field free alignment, which is also called the non-adiabatic molecular alignment, has been investigated in most cases by recording the ejection angles of the fragment ions generated by a circularly polarized ultrashort intense probe laser pulse [5,6].

On the other hand, by adopting a linearly polarized ultrashort intense laser pulse as a probe pulse inducing the photoionization and by detecting charged parent ions, the angular dependence of the ionization probability can also be obtained in the molecular fixed frame as has been demonstrated for small molecular species such as $N_2$, $O_2$, and $CO_2$ [6,7].

Recently, by adopting this scheme in which a linearly polarized laser pulse is used not only for the alignment but also for the ionization, the angular dependence of the ionization probability of acetylene, $C_2H_2$, which is one of the simplest linear hydrocarbon molecules, was investigated [8], and the ionization probability was found to be larger when the H-C-C-H molecular axis is perpendicular to the laser polarization direction than when it is parallel to the laser polarization direction. The observed yields of singly charged cation $C_2H_2^+$ and doubly charged cation $C_2H_2^{2+}$ were repro-

duced by the numerical simulation in which the angular dependence of the ionization probabilities of $C_2H_2$ to $C_2H_2^+$ and that to $C_2H_2^{2+}$ calculated by a time-dependent density functional theory were adopted.

On the other hand, as demonstrated for $N_2$, $O_2$, and $CO_2$ [6,7], the angular dependence of the ionization probability with respect to a molecular axis can be derived experimentally as long as a linearly polarized laser pulses are adopted not only for the alignment but also for the ionization. In the present study, by adopting this scheme and by detecting singly and doubly charged parent ions of acetylene, $C_2H_2^+$ and $C_2H_2^{2+}$, we experimentally derived functional forms of the angular dependences of the single and double photoionization probabilities of acetylene, which are the relative ionization cross sections represented as a function of the angle between the H-C-C-H molecular axis and the polarization direction of the linearly polarized probe laser pulse. The effect of nuclear spin statistics in the alignment processes is also discussed on the basis of the non-adiabatic alignment of isotopologue of $^{12}C^{13}CH_2$.

## 2. Experiment

A linearly polarized femtosecond laser pulse (800 nm, 1.5 mJ/pulse, 100 fs, 10 Hz) generated by a Ti:Sapphire chirped pulse amplifier system (B. M. Industries, α-10) seeded by a Ti:Sapphire oscillator (Coherent, Mira Seed) is spilt into a pair of pulses by a Michelson interferometer with a delay stage (Sigma Koki, KST (GS)-50X). One of the pulses called a pump pulse and the other called a probe pulse are used respectively to align and ionize sample molecules. The energy of the pump laser pulse is adjusted to be

sufficiently weak so that the photoionization is suppressed by a pair of a half-wave plate and a polarizer placed in an optical path in the interferometer.

The energy of the probe laser pulse and its beam diameter are adjusted to optimize the spatial overlap between pump and probe laser pulses by changing a diameter of an iris placed in an optical path in the interferometer. The temporal delay between the pump and probe pulses, $\tau$, is controlled by moving the positions of the reflection mirrors on the delay stage. The polarization direction of the probe pulse is rotated by another half-wave plate placed in the optical path in the interferometer.

A molecular beam is introduced into a vacuum chamber equipped with a Wiley-McLaren type time-of-flight mass spectrometer (TOF-MS) [9]. The pump and probe laser pulses are focused by a plano-convex lens ($f = 200$ mm) on a supersonic molecular beam of pure acetylene ($C_2H_2$) introduced into a vacuum chamber through a pulsed nozzle (General Valve Inc.) with a stagnation pressure of 1.1 atm. The beam size of the pump laser pulse and that of the probe laser pulse at their focal point are $2.6 \times 10^{-5}$ cm$^2$ and $2.9 \times 10^{-5}$ cm$^2$, respectively, which are estimated by the diameter of the Airy disc. The temporal pulse duration measured by a homemade single-shot autocorrelator is $100 \pm 7$ fs just before the interferometer. On the basis of the beam size, the pulse energy, and the temporal duration, the laser field intensities at the focal point are estimated to be 10 TW/cm$^2$ and 70 TW/cm$^2$ for the pump and probe laser pulses, respectively. By the pump laser pulse, $C_2H_2$ molecules are aligned non-adiabatically, and after a temporal delay, parent ions, $C_2H_2^+$ and $C_2H_2^{2+}$, are generated by the probe laser pulse. The generated parent ions are detected by the TOF-MS. The polarization directions of both of the pump and probe pulses are set to be parallel to the TOF axis.

## 3. Results and discussion

### 3.1. Rotational revival of the yields of $C_2H_2^+$ and $C_2H_2^{2+}$, and $^{12}C^{13}CH_2^+$

By blocking the pump arm in the interferometer, the TOF mass spectrum was recorded by irradiating the sample beam with the probe laser pulse only. In the mass spectrum, distinct peaks were observed. Among them, the peaks appearing at the mass-to-charge ratios of $m/q = 13$ and $26$ are assigned to $C_2H_2^{2+}$ and $C_2H_2^+$, respectively. There are two possibilities in the assignment of the peak at $m/q = 27$, that is, it can be assigned to either $^{12}C^{13}CH_2^+$ or $C_2HD^+$. However, as will be shown later, the peak at $m/q = 27$ is assigned exclusively to $^{12}C^{13}CH_2^+$ based on the revival pattern appearing as a function of the pump and probe time delay.

There are two possible pathways to generate $C_2H_2^{2+}$. The pump pulse induces the alignment of neutral molecules $C_2H_2$, and then, by the delayed probe pulse, the aligned neutral $C_2H_2$ are ionized to $C_2H_2^{2+}$. Alternatively, the pump pulse ionizes neutral molecules $C_2H_2$ to singly charged cations $C_2H_2^+$ whose rotational states are a coherent superposition of their rotational eigenstates, and then, the aligned $C_2H_2^+$ ions are ionized to $C_2H_2^{2+}$ by the delayed probe pulse. If the latter sequential double ionization process is a dominant pathway, it is expected that the signals originating from the transient alignment appear at the delay of multiples of a half of the rotational period of $C_2H_2^+$. However, because the observed transient signals of $C_2H_2^{2+}$ are almost exactly the same as those of $C_2H_2^+$, the former process in which $C_2H_2^{2+}$ is formed directly from neutral $C_2H_2$ is considered to be a dominant pathway. It was also confirmed that the signal ratio of the $C_2H_2^+$ produced only by the pump pulse with respect to that by the pump and probe pulses is as small as 4.9%.

Only from the $m/q$ value, it cannot be judged if the peak at $m/q = 13$ is to be assigned to CH$^+$ or to $C_2H_2^{2+}$. However, CH$^+$ generated from $C_2H_2^{2+}$ through the Coulomb explosion is known to appear as a doublet profile in a TOF mass spectrum [10,11], reflecting its large released kinetic energy. However, any broadening, which could reflect the kinetic energy release of the decomposition of $C_2H_2^+$, was not identified in the profile of the peak at $m/q = 13$ in the TOF spectra. Furthermore, the yield of CH$^+$ produced through the dissociation of $C_2H_2^+$ was estimated to be less than 10% of the yield of $C_2H_2^{2+}$ [10] in the experiment performed under the similar conditions to ours. Therefore, the peak at $m/q = 13$ can securely be assigned not to CH$^+$ but to $C_2H_2^{2+}$.

When the pump-probe delay, $\tau$, was varied, the ion yield of $C_2H_2^+$ exhibited peaks appearing periodically at $\tau = 7.1, 14.2, 21.3,$ and 28.4 ps as shown in Fig. 1(a). This type of revival pattern has been known as the temporal evolution of the field free alignment characteristic of diatomic and linear molecules [8,12,13]. By using the rotational constant, $B_0 = 1.176608$ cm$^{-1}$ [14], of $C_2H_2$, the rotational period $T_{\mathrm{rot}}$ can be calculated to be

$$T_{\mathrm{rot}} = (2cB_0)^{-1} = 14.2 \text{ ps}, \tag{1}$$

where $c$ is the speed of light in vacuum. Consequently, the assignment of the observed peaks can be performed in a straightforward manner, that is, the peaks appearing at $\tau = 14.2$ and 28.4 ps represent a full revival, and the peaks appearing at $\tau = 7.1$ and 21.3 ps represent a half revival. As shown in Fig. 1(b), the ion yield of $C_2H_2^{2+}$ also exhibits revival peaks appearing at $\tau = 7.1, 14.2, 21.3,$ and 28.4 ps, which are exactly the same as those of $C_2H_2^+$ within the experimental uncertainties.

If the alignment is achieved in singly charged parent ions $C_2H_2^+$ having the rotational constant $B^+ = 1.104$ cm$^{-1}$ [15], which is converted to the rotational period of 15.1 ps, the revival peaks should appear at $\tau = 7.6, 15.1, 22.7,$ and 30.2 ps, which are not consistent with the observed peak positions. Therefore, our observation that the revival peaks were observed at $\tau = 7.1, 14.2, 21.3,$ and 28.4 ps for both $C_2H_2^+$ and $C_2H_2^{2+}$ shows that not only the single ionization from $C_2H_2$ to $C_2H_2^+$ but also the double ionization from $C_2H_2$ to $C_2H_2^{2+}$ occurs within the probe laser pulse duration of 100 fs, which is sufficiently shorter than the rotational period of $C_2H_2$.

It is true that an additional alignment is achieved by the rising edge of the probe pulse. However, our theoretical simulation in which the alignment achieved by the probe pulse by the time when the probe laser intensity reaches the ionization threshold shows that the extent of the alignment achieved by the rising edge of the probe pulse is only 17% of that achieved by the pump pulse.

On the other hand, the ion yield of the peak appearing at $m/q = 27$ is found to exhibit recurrence peaks at $\tau = 7.2, 14.5, 21.7,$
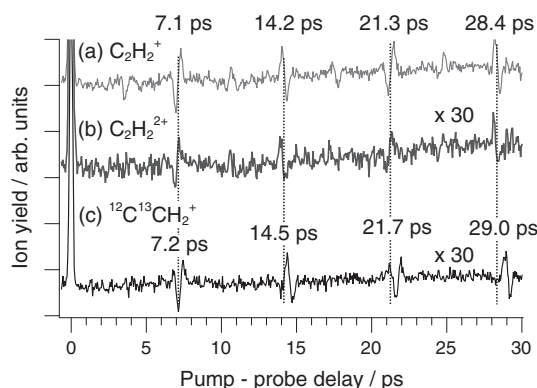


**Fig. 1.** The yields of (a) $C_2H_2^+$, (b) $C_2H_2^{2+}$, and (c) $^{12}C^{13}CH_2^+$ as a function of the pump-probe delay.