

Intense Field Ionization of C_2H_2 and $^{12}C^{13}CH_2$ Aligned in Field-free Space

Hirokazu Hasegawa¹, Yuki Ikeda², Kotaro Sonoda¹, Takahiro Sato²,
Atsushi Iwasaki², and Kaoru Yamanouchi²

¹Department of Integrated Sciences, Graduate School of Arts and Sciences, the University of Tokyo
3-8-1 Komaba, Meguro-ku, Tokyo 153-8902, Japan

²Department of Chemistry, School of Science, the University of Tokyo
7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan
chs36@mail.ecc.u-tokyo.ac.jp

Abstract: Intense field ionization of nonadiabatically aligned C_2H_2 was investigated by a pump-probe technique. The yield of parent ions revealed that the ionization occurs preferentially when the molecular axis is perpendicular to the laser polarization direction.

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1. Introduction

The interaction of molecules with an intense laser field induces a variety of dynamical processes, which are essentially triggered by ultrafast responses of electrons within a molecule to the intense laser field. Among these processes, ionization of molecules in the gas phase is particularly important and has been intensively studied, because it reflects electronic responses of molecules more directly than in other processes. However, because molecules rotate freely in space in the gas phase, the information on the ionization process is blurred by the averaging over the rotational angles of molecular axes with respect to the laser polarization direction.

A molecular alignment is a promising technique free from this rotational averaging effect [1-3]. When linear molecules are irradiated with a linearly polarized ultrashort intense laser pulse, a rotational wave packet, which is a superposition of rotational eigenstates, is impulsively created by the interaction between the laser field and an induced dipole moment of molecules. After the interaction, molecules can be aligned parallel and perpendicular to the laser polarization direction periodically in field-free space. This phenomenon is known as the nonadiabatic molecular alignment or the field-free molecular alignment [1-3]. In the present study, we investigate the ionization process of C_2H_2 in an intense laser field by taking advantage of this nonadiabatic molecular alignment. In addition, we show that this method provides us with a powerful tool to extract spectroscopic information of rotation of molecules in their electronic ground state.

2. Experiment

A linearly polarized femtosecond laser pulse generated by a Ti:Sapphire chirped pulse amplifier system is split into a pair of pulses by passing through a Michelson interferometer with a delay stage. One of the pulses called a pump pulse and the other called a probe pulse are used to align and ionize molecules, respectively. The temporal delay between the pump and probe pulses, τ , can be controlled by the delay stage in the pump beam arm in the interferometer. The pump and probe laser pulses are focused by a plano-convex lens ($f = 200$ mm) on a supersonic molecular beam. The pulse width is measured to be 100 fs by a single-shot autocorrelator. The laser field intensity at the focal point is estimated to be 10 TW/cm² and 70 TW/cm² for the pump and probe pulses, respectively. A pulsed supersonic molecular beam of pure acetylene (C_2H_2) with the stagnation pressure of 1.1 atm was introduced into a vacuum chamber equipped with a Wiley-McLaren type time-of-flight mass spectrometer (TOF-MS). The nonadiabatic alignment of C_2H_2 is achieved by the interaction with the pump pulse. Parent ions generated by the probe pulse after the temporal delay are detected by the TOF-MS. The polarization of the pump pulse is set to be parallel to the TOF axis, and the polarization directions of the pump and probe pulses are set to be parallel with each other.

3. Results and discussion

Figure 1 shows the dependence of the yield of $C_2H_2^+$ on the pump-probe delay, τ . The transient peaks are observed clearly at $\tau = 7.1$ and 14.2, and these peaks can be regarded as typical field-free alignment signals [3]. Since the rotational period T_{rot} of C_2H_2 is calculated to be $T_{rot} = 1 / (2cB_0) = 14.2$ ps using the rotational constant, $B_0 = 1.176608$ cm⁻¹ [4], it is found that the delay time between the two neighboring peaks corresponds to a half of the rotational period, $T_{rot}/2$, showing that these peaks appear through the nonadiabatic molecular alignment.

In order to compare the observed ion yield with the molecular axis distribution, the expectation value of $\cos^2\theta$, $\langle \cos^2\theta \rangle = \langle \psi(t) | \cos^2\theta | \psi(t) \rangle$, are calculated by numerically solving a time-dependent Schrödinger equation, where θ stands for the angle between the molecular axis and the polarization direction, $|\psi(t)\rangle = \sum_J A_J e^{i\delta_J} e^{-i\omega_J t} |J, M\rangle$ is a rotational wave packet generated by the pump pulse, a real number A_J is a probability amplitude, a real number δ_J is a initial phase, ω_J is a energy phase defined by $\omega_J = hcB_0 J(J+1)/\hbar$, and $|J, M\rangle$ stands for a rotational eigenstate. The $\langle \cos^2\theta \rangle$ calculated by taking account of the initial rotational state

distribution of 50 K agrees well with the positions of spiky peaks in the observed signal, but the phases of the respective peaks are out of phase by 180° . Since the angular dependence of the ionization probability on the relative angle between the molecular axis and the polarization direction influences the ion yield, the observed out-of-phase behavior implies that the ionization probability is higher when the laser polarization direction is perpendicular to the molecular axis. If we assume that the angular dependence of the ionization probability $W(\theta)$ is proportional to $\sin^2\theta$, the observed yield of $C_2H_2^+$ may be expressed as $\int_0^\pi W(\theta)|\psi(\theta, t)|^2 \sin\theta d\theta = \langle \sin^2\theta \rangle$, where $\psi(\theta, t)$ represents a polar coordinate representation of the rotational wave packet.

The expectation value, $\langle \sin^2\theta \rangle$, thus calculated is plotted by the dashed curve shown in Fig. 1, which reproduces well not only the positions of peaks but also the phase of the respective peaks. If the ionization proceeds by the tunneling ionization, $W(\theta)$ is expected to reflect the shape of the highest occupied molecular orbital (HOMO). Since the electronic configuration of C_2H_2 in the electronic ground state is $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(1\pi_u)^4$, the HOMO is $1\pi_u$ as shown in the inset in Fig. 1, which comprises a linear combination of the $2p_x$ atomic orbitals located at the respective two carbon atoms and the degenerated counterpart of the $2p_y$ atomic orbitals, and its electron density distribution spreads along the perpendicular direction to the molecular z axis. Therefore, the good agreement between the observed delay time dependence of the yield of $C_2H_2^+$ and the dashed curve in Fig. 1 suggests that the ionization proceeds via the tunneling ionization from the HOMO $1\pi_u$ orbital of C_2H_2 .

On the other hand, the Fourier transformation (FT) of the pump-probe signals of $C_2H_2^+$ and $^{12}C^{13}CH_2^+$ gives valuable information on molecular constants in the electronic ground state. Such FT spectra of the molecules such as N_2 , O_2 , and N_2O were reported previously [4,5]. Figure 2 shows the FT spectra for $C_2H_2^+$ (lower trace) and $^{12}C^{13}CH_2^+$ (upper trace), in which the abscissa represents the frequencies in units of $cB_0 = 35.3$ GHz for $C_2H_2^+$ and $cB_0 = 34.4$ GHz for $^{12}C^{13}CH_2^+$. All peaks are assigned to the rotational energy differences between the rotational eigenstate $|J+2, M\rangle$ and $|J, M\rangle$, *i.e.*, these peaks form the S-branch of the rotational transitions. These energy differences are denoted by $S(J)$ in Fig. 2. It should be noted that the spectra reflect both the rotational state distributions and the angular dependences of the ionization probability. In the case of $C_2H_2^+$, a clear intensity alternation can be found between even J s and odd J s, which can be ascribed to the nuclear spin statistics of protons. Because the nuclear spin I of a proton is $I = 1/2$ and C_2H_2 belongs to the $D_{\infty h}$ point group, the statistical weight of the nuclear spin functions for the odd J states is three times larger than that for the even J states. Interestingly, the intensity alternation could not be recognized in the case of $^{12}C^{13}CH_2^+$. This is because there is no center of symmetry in $^{12}C^{13}CH_2^+$. This FT analysis of the time-domain non-adiabatic rotational alignment signals is an efficient and universal technique to extract the information of rotational levels of molecules with high spectral resolution.

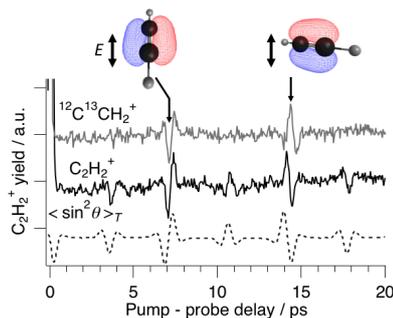


Fig. 1. The observed $C_2H_2^+$, $^{12}C^{13}CH_2^+$ yields, and the expectation value of $\sin^2\theta$ against the pump-probe delay.

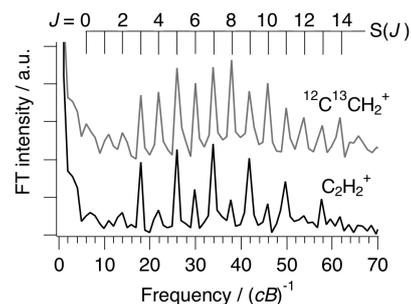


Fig. 2. The Fourier transformed spectra of the observed ion signals.

4. References

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