

Real-time Probing of Ultrafast Hydrogen Migration in Methanol by Near-IR Few-cycle Laser Pulses

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Abstract: Hydrogen migration in CH₃OH was probed by pump-probe measurements using few-cycle laser pulses. Oscillation in the kinetic-energy release of the fragment ions was interpreted theoretically as the motion of a migrating hydrogen atom in CH₃OH⁺.

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1. Introduction

In our previous study of ultrafast hydrogen migration in methanol by a pump-probe coincidence momentum imaging (CMI) method [1], we showed that the hydrogen migration in singly charged methanol, CH₃OH⁺, was completed within the temporal pulse duration of the intense laser field (38 fs). In order to clarify how fast the hydrogen migration proceeds, we have performed pump-probe CMI measurements with the high temporal resolution of 6 fs using few-cycle laser pulses generated by a hollow fiber technique [2], and identified a characteristic oscillation in the time delay dependence of the kinetic energy releases (KER) of the fragment ions, CH₂⁺ and OH₂⁺, produced through the two-body decomposition process accompanying the hydrogen migration from methyl group to hydroxyl group; CH₃OH²⁺ → CH₂⁺ + OH₂⁺. For examining the observed oscillatory behavior, we have performed a theoretical calculation of two-dimensional wave packet propagation on the potential energy surface of CH₃OH⁺, and found that the result of the theoretical calculation consistently interprets the observed oscillation in terms of a wave packet of a migrating hydrogen atom oscillating near the barrier for the migration prior to the complete migration in the very early time domain (~20 fs) after the irradiation of the pump laser pulse.

2. Experimental

Output pulses of a femtosecond Ti:sapphire laser system (800 nm, 5 kHz, 0.6 mJ, 30 fs) were focused into a 1.5 m hollow-core fiber (inner diameter: 330 μm) filled with an Ar gas (0.4 atm) to broaden the spectral bandwidth through the self-phase-modulation. The spectral bandwidth was about 300 nm at full-width at tenth-maximum at the center wavelength of 770 nm. By compensating the spectral phase dispersion by chirp mirrors (PC70, Ultrafast Innovations) and a pair of wedged glass plate, few-cycle pulses were generated. The spectrum and spectral phase were measured by a home-built 2D spectral shearing interferometer [3], and the temporal pulse duration of the intense laser pulse were measured to be 6 fs. The generated few-cycle laser pulses were introduced into a Mach-Zehnder interferometer to generate a pulse replica, and the length of one arm of the interferometer was varied using PZT controlled optical stage to obtain the variable time delay (τ) in the range between -10 fs to 500 fs. Both the pump and probe pulses were focused onto a molecular beam of methanol in a vacuum chamber by a concave mirror ($f = 150$ mm). The focal intensity at the focal spot per laser pulse was estimated to be 2.7×10^{14} W cm⁻².

The fragment ions generated from methanol were guided by a static electric field toward the two-dimensional position sensitive detector (HEX120, RoentDek) in the velocity map imaging conditions [4]. From the flight time and the position of fragment ions, the momenta of the respective fragment ions were determined. For every laser shot, the momentum data of the fragment ions and the delay time data were collected simultaneously by a data acquisition board (TDC8HP, RoentDek), and after the acquisition, the KER spectra were constructed as a function of the delay time.

3. Results and discussion

The time evolution of the KER spectra of the non-migration pathway and the hydrogen migration pathway are shown in Fig. 1(a) and (b), respectively. In both Figs. 1(a) and (b), two distinct components can be identified; one is a KER distribution in the range between 4 and 7 eV running horizontally in the entire time delay range and the other is a component whose KER decreases as the time delay increases. The constant KER means that the distance between two fragment ions is kept almost constant, and the decrease in the KER means that the distance between the

two fragment ions increases with the time delay. Therefore, the upper and lower KER distributions represent respectively the time evolution of the wave packet trapped in the bound potential in the molecular domain and the wave packet propagating along the dissociation coordinate on the repulsive potential energy surface of CH_3OH^+ prepared by the pump laser field. It should be noted in Fig. 1(b) that the hydrogen migrated species, CH_2OH_2^+ , starts to appear in the very early stage ($\tau \sim 20$ fs) after the irradiation of the pump laser pulse.

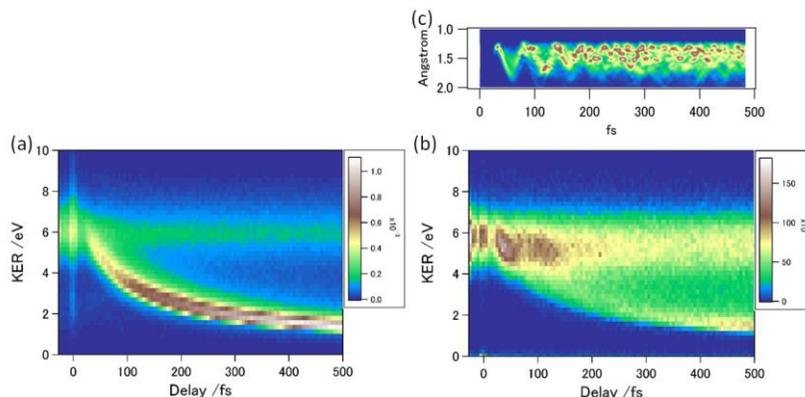


Fig. 1. The time evolution of the KER of (a) $\text{CH}_3\text{OH}_2^+ \rightarrow \text{CH}_3^+ + \text{OH}^+$, (b) $\text{CH}_3\text{OH}_2^+ \rightarrow \text{CH}_2^+ + \text{OH}_2^+$ fragmentation pathway, and (c) the time evolution of the theoretically calculated wave packet.

When we look closely at the early delay time region less than 200 fs in Fig. 1(b), the wide KER distribution exhibit characteristic oscillatory structure, that is, the peak position of the KER distribution periodically changes as a function of the time delay with the period of about 65 fs, indicating that the CO bond distance in CH_3OH^+ is oscillating in time with the period of 65 fs.

In order to investigate the origin of the oscillation, we have performed a two-dimensional wave packet simulation by solving the Schrödinger equation represented in atomic unit,

$$\left[-\frac{1}{2M_{\text{eff}}} \frac{\partial^2}{\partial R_{\text{CO}}^2} - \frac{1}{2M_{\text{H}}} \frac{1}{R_{\text{H}}^2} \frac{\partial^2}{\partial \theta^2} + V(R_{\text{CO}}, \theta) \right] \phi(R_{\text{CO}}, \theta; t) = i \frac{\partial}{\partial t} \phi(R_{\text{CO}}, \theta; t),$$

where M_{eff} is the reduced mass of CH_2 and OH , M_{H} the mass of H, R_{CO} the CO bond length, R_{H} the distance between the center of mass of CO and H, θ the angle between the CO axis and the line connecting the center of mass of CO to H, and $V(R_{\text{CO}}, \theta)$ the two dimensional adiabatic potential energy surface of singly charged methanol. The two dimensional adiabatic potential $V(R_{\text{CO}}, \theta)$ was constructed theoretically by Gaussian09 (UB3LYP/aug-cc-pVTZ) by optimizing the structural parameters other than R_{H} , which is fixed to be 2 Å, R_{CO} and θ .

When the wave packet is placed on the potential energy surface of CH_3OH^+ at the equilibrium geometry of neutral CH_3OH at $\tau = 0$, the time evolution of the probability density distribution of the vibrational wave packet is obtained as shown in Fig. 1(c). The comparison of this Fig. 1(c) and the experimental results shown in Fig. 1(b) shows that the theoretical simulation reproduced well the observed oscillation, indicating that the vibrational wave packet prepared in CH_3OH^+ by the pump pulse partially propagates over the potential barrier located along the θ coordinate in the middle of CH_3OH^+ and CH_2OH_2^+ . The simulation showed that CH_2OH_2^+ is formed at around $\tau = 30$ fs after the oscillatory motion of the wave packet. The time scale of this theoretical hydrogen migration is in good agreement with the experimental observation.

4. References

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