Fourier-transform spectroscopy of D_2^+ using intense near-infrared few-cycle laser pulses

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[Abstract] In order to obtain vibrational spectrum of D_2^+, we performed pump-probe measurements of D_2 by using intense near-infrared few-cycle laser pulses. The ion yields of D_2^+ and D^+ are recorded up to the pump-probe time delay of 527 ps. The ion yields oscillate as a function of the time delay and the oscillations reflect the motion of the vibrational wavepackets of D_2^+ created by the pump laser pulses. The vibrational level separations of D_2^+ are obtained with the uncertainties less than 0.01 cm^{-1} from the Fourier transform spectrum of the ion yields. The experimental vibrational level separations are in good agreement with the theoretically calculated values, showing a potential application of the strong-field pump-probe measurements to high-resolution spectroscopy of molecular cations.

[Introduction] Recent advances in ultrashort pulsed laser technologies have enabled us to generate few-cycle intense laser pulses and a vibrational wave packet of hydrogen molecular ions was probed in real time by using few-cycle intense laser pulses [1]. By monitoring the motion of the vibrational wave packet in the time domain, we can obtain the vibrational frequencies from the Fourier transform.

The vibration frequencies of hydrogen molecular ions have been determined by optical spectroscopy of molecular ions in an ion trap [2] and by PFI-ZEKE spectroscopy [3]. In the case of HD$^+$, the vibrational transition frequencies were determined with the precision of $\delta\nu/\nu = 10^{-9}$ by frequency-comb spectroscopy of HD$^+$ in a cold trap [2]. On the other hand, in the case of H_2^+ and D_2^+ having no dipole moment, the fundamental vibration frequencies were determined by PFI-ZEKE spectroscopy with an uncertainty of around 1 cm^{-1} [3].

In the present study, we determine the vibrational frequency of D_2^+ in the electronic ground $2\Sigma_g^+(1s\sigma_g)$ state with the uncertainties less than 0.01 cm^{-1} from the Fourier transform of the ion yields of D_2^+ and D^+ obtained by pump probe measurements using intense near-infrared few-cycle laser pulses.

[Methods] Linearly-polarized few-cycle intense laser pulses (5 fs, 780 nm) were generated by using a hollow-core fiber compression technique. The few-cycle laser pulses were introduced into a Mickelson interferometer to produce pump and probe laser pulses. The delay time between the two pulses, Δt, was scanned up to 527 ps by using an optical stage in the interferometer. The pump and probe pulses were focused onto an effusive molecular beam of D_2 in a time-of-flight mass spectrometer. The focal intensity was estimated to be 3.2×10^{14} W/cm^2. The ion yields of D_2^+ and D^+ were recorded as a function of Δt. The ion yields of D_2^+ and D^+ in the range of 370 fs $< \Delta t <$ 527 ps are Fourier transformed.

[Results and Discussion] In the pump-probe measurement, the pump-pulse ionizes D_2 and prepares a vibrational wavepacket at the Franck-Condon region of the electronic ground $1s\sigma_g$ state of D_2^+, and then, the probe pulse creates light-dressed potential energy curves (PECs) as shown in Fig. 1(a), leading to the dissociation into $D + D^+$ through the three-photon crossing at $R = 3.2$ a.u. Because the vibrational wavepacket at the outer turning point of the PEC of the $1s\sigma_g$ state of D_2^+ dissociates through the three-photon crossing with a higher probability than the wavepacket at the inner turning point, the temporal variations in the yields of D_2^+ and D^+

should reflect the motion of the vibrational wavepacket. By Fourier transform of the delay time dependence of the difference in the ion yields of D_2^+ and D^+, we are able to obtain the FT spectrum in the frequency domain, from which we derive the vibrational level separations of D_2^+ as shown in Fig. 1(b).

In Table 1, the vibrational energy intervals, $\Delta G(v^+ + 1/2)$, obtained from the high-resolution FT spectrum are summarized, which agree well with the theoretical values whose accuracy is considered to be 1×10^{-4} cm^{-1} [4], showing that the strong field Fourier transform spectroscopy using few-cycle near-IR laser pulses is a promising method for the determination of vibrational level energies of molecular cations.
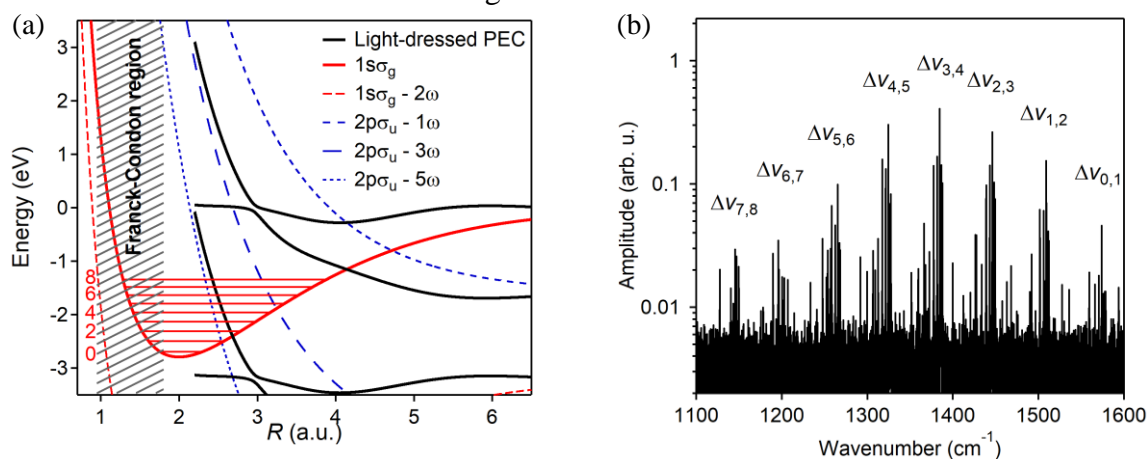
Figure 1. (a) The light-dressed PECs of D_2^+ interacting with a near-IR (775 nm) laser field at the laser field intensity of 3.2×10^{14} W/cm^2. The Fourier transform of the difference in the ion yields of D_2^+ and D^+ in the wave number range of 1100-1600 cm^{-1}.

Table 1. Comparison of the vibrational energy intervals (cm^{-1}), $\Delta G(v + 1/2)$, of D_2^+.

v	Present Experiment	Calculation [4]				Exp. - Calc.
		Non-adiabatic	Relativistic	Radiative	Total	
0	1577.0911(72)	1577.0706	0.0266	-0.0067	1577.0904	0.0007
1	1512.4033(19)	1512.3810	0.0245	-0.0063	1512.3993	0.0040
2	1449.3426(11)	1449.3261	0.0228	-0.0060	1449.3429	-0.0003
3	1387.7523(6)	1387.7365	0.0209	-0.0056	1387.7518	0.0005
4	1327.4621(9)	1327.4475	0.0193	-0.0053	1327.4614	0.0007
5	1268.3099(22)	1268.2975	0.0175	-0.0051	1268.3100	-0.0001

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