

# Fourier transform vibrational spectroscopy of D<sub>2</sub><sup>+</sup> by few-cycle near-infrared laser pulses

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**Abstract.** By strong-field Fourier transform spectroscopy using intense pump and probe few-cycle laser pulses, the vibrational level separations of D<sub>2</sub><sup>+</sup> were determined with high precision by taking advantage of the dressed-state formation by the probe pulse.

## 1 Introduction

As was demonstrated by our recent study [1], spectroscopic information of molecules can be extracted by conducting pump-probe measurements using few-cycle intense laser pulses. For example, in the case of methanol, the vibrational frequency of the C-O stretching mode of methanol cation, CH<sub>3</sub>OH<sup>+</sup>, was determined by the Fourier transform of the pump-probe delay-time dependence of the H<sub>3</sub><sup>+</sup> fragment ions.

This strong field FT approach can in principle be applied to any kinds of molecular species and the energy resolution of the level energy data can be very high as long as the pump-probe delay range is taken to be sufficiently long. Therefore, it would be meaningful to conduct the strong field pump-probe measurements for obtaining high-resolution spectroscopic information that could not be obtained by conventional spectroscopic measurements.

In the previous measurements of the vibrational level energies of the electronic ground  $^2\Sigma_g^+(1s\sigma_g)$  state of H<sub>2</sub><sup>+</sup>, the smallest uncertainty of 1.2 cm<sup>-1</sup> was achieved by the zero-kinetic energy photoelectron spectroscopy [2]. When we apply the strong field FT method to the determination of the vibrational level energies of H<sub>2</sub><sup>+</sup> in the electronic ground  $^2\Sigma_g^+$  state, we can take advantage of the fact that the electronic ground  $^2\Sigma_g^+(1s\sigma_g)$  state and the first electronically excited  $^2\Sigma_u^+(2p\sigma_u)$  state are coupled strongly in an intense near IR laser field. Within the quasi-stationary Floquet picture [3], the energy range of the vibrational levels in the ground  $^2\Sigma_g^+$  state, from which the dissociation proceeds through the coupling with the one-photon dressed  $^2\Sigma_u^+$  state and the three-photon dressed  $^2\Sigma_u^+$  state becomes wider when the light field intensity increases. Therefore, by increasing the field intensity of probe pulses inducing the dissociation into H and H<sup>+</sup>, we are able to determine the energies of the vibrational levels in the wider energy range.

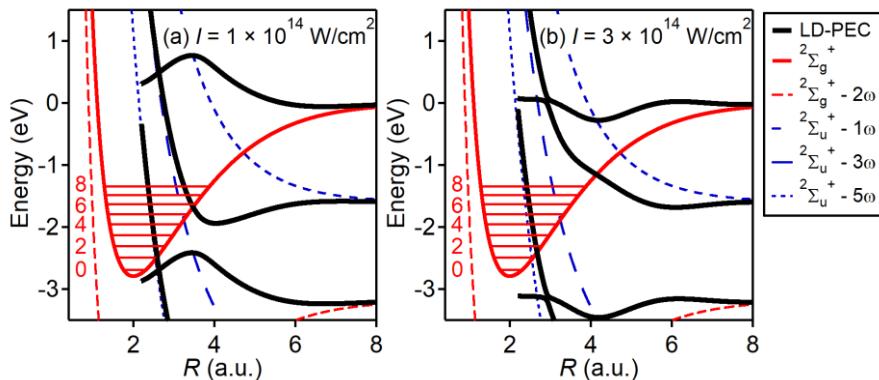
## 2 Experiment

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The detail of the experimental method is summarized in Ref. [4]. Linearly-polarized few-cycle intense laser pulses (5 fs, 780 nm) were introduced into a Michelson interferometer to produce pump and probe laser pulses. The delay time between the two pulses,  $\Delta t$ , 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 ion yield of  $D_2^+$  and  $D^+$  were recorded simultaneously as a function of  $\Delta t$ . The difference of the ion yield of  $D_2^+$  and  $D^+$  in the range of  $370 \text{ fs} < \Delta t < 527 \text{ ps}$  are Fourier transformed.

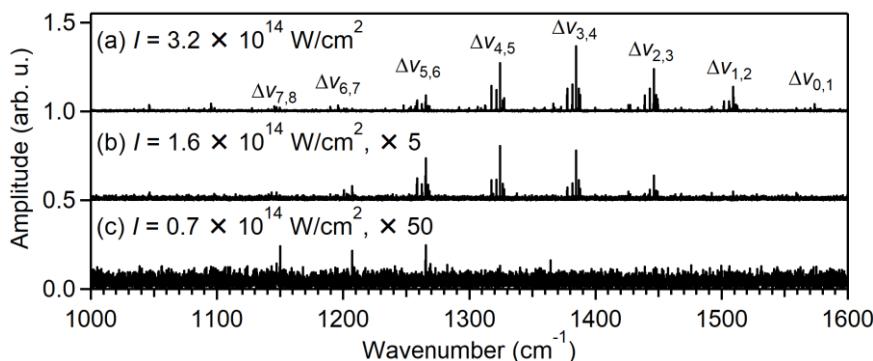
### 3 Results and discussion

In the pump-probe measurement, the pump pulse ionizes  $D_2$  and prepares a vibrational wave packet at the inner turning point of the electronic ground  $^2\Sigma_g^+$  state, and then, the probe pulse creates light-dressed potential energy curves (LD-PECs) as shown in Fig. 1, leading to the dissociation into  $D + D^+$  through the one-photon crossing at  $R = 4.7 \text{ a.u.}$  and the three-photon crossing at  $R = 3.2 \text{ a.u.}$  When the probe laser field intensity is relatively weak ( $I = 1 \times 10^{14} \text{ W/cm}^2$ ), the dissociation is expected to proceed from the higher-lying vibrational levels ( $v > 4$ ) through the energy gap at the one-photon crossing. When the probe laser field intensity is increased ( $I = 3 \times 10^{14} \text{ W/cm}^2$ ), the dissociation is expected to proceed through the energy gap created by the three-photon crossing. By Fourier transform of the delay-time dependence of the ion yield of  $D^+$ , we are able to obtain the FT spectrum in the frequency domain from which we derive the vibrational level energies of  $D_2^+$ .



**Fig. 1.** The LD-PECs of  $D_2^+$  interacting with the near-IR (780 nm) laser field at the two different laser field intensities, (a)  $1 \times 10^{14} \text{ W/cm}^2$  and (b)  $3 \times 10^{14} \text{ W/cm}^2$ , as a function of the internuclear distance  $R$ . Red solid curve: the potential energy curve (PEC) of the ground  $^2\Sigma_g^+$  state. Black curves: LD-PECs. Broken curves: PECs of  $^2\Sigma_g^+$  shifted in energy by  $-2\hbar\omega$  (red) and  $^2\Sigma_u^+$  shifted in energy by  $-3\hbar\omega$ , and  $-5\hbar\omega$  (blue). The one-photon crossing point between  $^2\Sigma_g^+$  and  $^2\Sigma_u^+-\hbar\omega$  is located around  $R = 4.7 \text{ a.u.}$  and the three-photon crossing point between  $^2\Sigma_g^+$  and  $^2\Sigma_u^+-3\hbar\omega$  is located around  $R = 3.2 \text{ a.u.}$

The experimental FT spectra obtained at the three different laser field intensities are shown in Fig. 2. The peaks around  $1570 \text{ cm}^{-1}$  are assigned to the fundamental vibration of  $D_2^+$ ,  $\Delta v_{0,1}$ . The peaks in the lower wavenumber region are assigned to the energy difference between the higher-lying vibrational levels. As the laser field intensity decreases, the intensity of the peaks assigned to the lower vibrational levels decreases, which is consistent with the above interpretation in terms of the energy gaps created between the light dressed PECs.



**Fig. 2.** Fourier transform of the difference between the ion yields of  $\text{D}_2^+$  and  $\text{D}^+$  at the three different focal intensities, (a)  $3.2 \times 10^{14} \text{ W/cm}^2$ , (b)  $1.6 \times 10^{14} \text{ W/cm}^2$ ,  $\times 5$ , and (c)  $0.7 \times 10^{14} \text{ W/cm}^2$ ,  $\times 50$ . The interval of the date point of the Fourier spectra is  $0.0633 \text{ cm}^{-1}$  and the uncertainty of the frequencies can be estimated to be the half of the interval,  $0.032 \text{ cm}^{-1}$ .

In Table 1, the vibrational energy intervals,  $\Delta G(v + 1/2)$ , obtained from the high-resolution FT spectra are summarized, which agree with the theoretical values, whose accuracy is considered to be  $1 \times 10^{-4} \text{ cm}^{-1}$  [5], within the uncertainty of the measurements ( $0.032 \text{ cm}^{-1}$ ), 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 ions with high precision.

**Table 1.** Comparison between the observed and calculated vibrational energy spacings ( $\text{cm}^{-1}$ ),  $\Delta G(v + 1/2)$ , of  $\text{D}_2^+$ .

| $v + 1/2$ | Obs.     | Calc. [5] | Obs. – Calc. |
|-----------|----------|-----------|--------------|
| 0.5       | 1577.110 | 1577.0904 | 0.020        |
| 1.5       | 1512.381 | 1512.3993 | -0.018       |
| 2.5       | 1449.362 | 1449.3429 | 0.019        |
| 3.5       | 1387.737 | 1387.7518 | -0.015       |
| 4.5       | 1327.442 | 1327.4614 | -0.019       |
| 5.5       | 1268.287 | 1268.3100 | -0.023       |

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