Eur. Phys. J. D **20**, 399–402 (2002)
DOI: 10.1140/epjd/e2002-00162-7

THE EUROPEAN PHYSICAL JOURNAL D

Picosecond time-resolved nonresonant ionization detected IR spectroscopy on 7-azaindole dimer

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Received 14 May 2002 / Received in final form 11 June 2002

Abstract. The picosecond time-resolved IR spectrum of the 7-azaindole dimer has been measured by picosecond time-resolved nonresonant ionization detected IR spectroscopy. This new time-resolved technique was developed by combining nonresonant ionization detected IR (NID-IR) spectroscopy with tunable picosecond IR and UV lasers. The time-resolved NID-IR spectrum from 2 600 cm^{-1} to 3 800 cm^{-1} shows a drastic change from 1.5 ps to 11 ps time evolution. A mode-specific vibrational redistribution has been suggested.

PACS. 33.20.Ea Infrared spectra – 33.40.+f Multiple resonances (including double and higher-order resonance processes, such as double nuclear magnetic resonance, electron double resonance, and microwave optical double resonance) – 33.80.Rv Multiphoton ionization and excitation to highly excited states (e.g., Rydberg states)

1 Introduction

A non-equilibrium distribution in the vibrational energy relaxation process in the solution was observed for the first time ten years ago. Because of its importance in chemical and biological reaction dynamics, various experimental approaches have been tried to reveal the mechanism of the vibrational energy relaxation phenomenon [1–7]. One of the most remarkable results has been found in a purely biological system, *i.e.* hem-protein [4–7]. The vibrational redistribution in hem-protein has been measured by time-resolved picosecond Raman spectroscopy, and a mode-specific vibrational redistribution has been clearly found. It is surprising that a non-equilibrium vibrational redistribution exists in an extremely large biological system. Its existence suggests an important role of the mode-specific vibrational energy flow in the precise reaction control of the biological system. However, the detailed mechanism of mode-specific vibrational energy flow has not been fully understood because of its extremely large size. Therefore, it is important to find other examples of mode-specific vibrational redistribution in rather simple molecular systems under well-defined conditions, such as a molecular cluster in a supersonic jet.

Based on the above motivation, we tried to reveal the vibrational energy redistribution in the 7-azaindole dimer in a supersonic jet. The 7-azaindole dimer has been regarded as a model for the hydrogen-bonded base pair of DNA, and has been suggested to provide information about a mechanism involving the mutation of DNA pairs [8–10]. The detailed electronic structure of the 7-azaindole dimer was studied using a supersonic jet, and the mechanism of proton transfer (concerted or stepwise) has been discussed extensively [11–17]. Concerning the vibrational structure, we applied IR Dip spectroscopy to two isomers (reactive and nonreactive) of the 7-azaindole dimer, and revealed that the so-called “nonreactive” dimer is a water-inserted 7-azaindole dimer [18].

In the present work, we developed a new picosecond time-resolved IR spectroscopy, and applied it to the 7-azaindole dimer (only “reactive”) to reveal its intramolecular vibrational energy redistribution (IVR). The observed time-resolved IR spectrum with nonresonant ionization detection (nonresonant ionization detected IR spectroscopy [19–22]) clearly shows a fast time-evolution with a non-equilibrium distribution in the picosecond time domain. The possibility of a mode-specific intracluster vibrational redistribution in the 7-azaindole dimer is briefly reported.

2 Experimental

The experimental setup for measuring the time-resolved NID-IR spectroscopy is essentially the same as that for UV-IR-UV ion dip spectroscopy [27]. The laser system is based on a cw mode-locked Ti:sapphire laser (Spectra Physics, Tsunami) with a pulse duration of 130 fs, pumped by a 5 W diode laser (Spectra Physics, Millennia Vs).

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The output pulses (550 mW; 82 MHz) from the oscillator are amplified at a repetition rate of 10 Hz in a regenerative Ti:sapphire amplifier (Quanta Ray, TSA-10) pumped by the frequency-doubled output of a Nd^{3+}:YAG laser (Quanta Ray, PRO-230). By masking the grating in a regenerative Ti:sapphire amplifier, the time duration and energy of the amplified output pulses were ∼3 ps and 6 mJ/pulse at 800 nm. The output was divided into two beams. One beam (1 mJ/pulse) was used to pump a traveling-wave optical parametric amplifier (OPA) system (light conversion, TOPAS 400) after frequency doubling in BBO and to provide tunable UV light (250–390 nm; >15 μJ) by the second harmonics of the signal (or idler) wave from the OPA. The other (<5 mJ/pulse) was further split into two beams, one of which was introduced into another OPA system (light conversion, TOPAS 800). The second harmonic of the idler wave from the OPA and the remaining fundamental light (<2.5 mJ/pulse) were differentially mixed in a KTA crystal to generate tunable IR light (2 750–4 000 cm^{-1}; >80 μJ). The line width of the UV and IR light beams were ∼10 cm^{-1} and ∼15 cm^{-1}, respectively.

Both the IR laser and the UV laser used in the picosecond laser system were colinearly introduced into a vacuum chamber (Toyama/Hakuto) and crossed a supersonic jet. The IR laser irradiated the sample before/after the UV laser at several delay times. The delay time between the IR laser and the UV laser was varied by an optical delay system (Sigma, LTS-400X; 5 μm/step) which ranged from −500 ps to 1.5 ns. The samples ionized by the UV laser were detected by a channel multiplier (Murata Ceratron) through a quadrupole mass filter (Extrel). The signal was amplified by a preamplifier (EG&G PARC, 5113) and integrated by a digital boxcar (EG&G PARC, 4420/4422). The integrated signal was recorded by a personal computer as a function of the IR laser frequency.

7-azaindole vapor at 378 K was seeded in He gas at 3 atm, and expanded into the vacuum chamber through a pulse nozzle operated at 10 Hz. 7-azaindole was purchased from Tokyo Kasei and used after purification. Here, the sample was carefully dried so as to avoid the water-inserted 7-azaindole dimer, which has been called a "nonreactive" dimer (see Ref. [18]). Under this condition, only the "reactive" dimer was detected in our experimental setup.

3 Results and discussion

To measure the vibrational redistribution sensitively, we developed a time-resolved nonresonant ionization detected IR spectroscopy (in short, time-resolved NID-IR) in the picosecond time domain. It is based on nonresonant ionization detected IR spectroscopy (NID-IR), which was also originally developed by our group [19]. The principle of NID-IR spectroscopy is shown in Figure 1a. Briefly, a sample molecule is excited to a vibrational level in S_0 by an IR laser (ν_{IR}). The vibrationally excited molecule is selectively ionized by a nonresonant two-photon process due to UV laser (ν_{UV}). Selective ionization of the vibrationally excited molecule was achieved by fixing ν_{UV} to an energy slightly lower than half of the ionization potential (IP_0). Under this condition, only the vibrationally excited molecules can be ionized by the two-photon process due to ν_{UV}. Therefore, the ion current is detected only when ν_{IR} is resonant to the vibrational level. Because the background signal is weak and the ions are detected, NID-IR spectroscopy has a very high sensitivity and S/N.

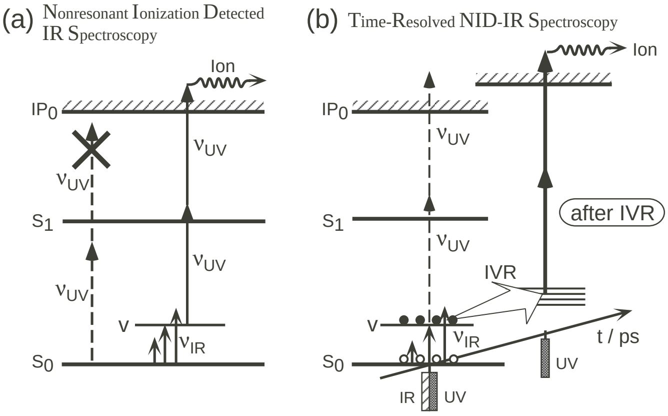

Fig. 1. (a) Principle of nonresonant ionization detected IR (NID-IR) spectroscopy and (b) picosecond time-resolved NID-IR spectroscopy and its relation to IVR.

From the detailed investigations by Ebata and coworkers [23–25] as well as ourselves [20,21,26] it has been found that IVR takes place before ionization in NID-IR spectroscopy. Especially for the phenol molecule in the fundamental vibration region, this mechanism has been directly proved by a picosecond pump-probe experiment [25]. In the present work, we further extended IVR detection of NID-IR spectroscopy by combining picosecond tunable IR and UV lasers. Figure 1b shows the detection scheme of time-resolved NID-IR spectroscopy. The picosecond tunable IR laser excites the sample and its frequency is scanned over the vibrational region. After an appropriate delay time, a picosecond UV laser is introduced to ionize the vibrationally excited samples. According to a previous study, the ionization efficiency becomes higher after IVR. We thus expect that the time-evolution of IVR can be detected by a change in the intensity of a nonresonant ionization signal.

Figure 2 shows the picosecond time-resolved NID-IR spectra of the 7-azaindole dimer at (b) 1.5 ps and (c) 11 ps delay times. For a comparison, the IR dip spectrum of the 7-azaindole dimer that corresponds to the IR absorption spectrum in S_0, is also shown on the top. Here, the IR dip spectrum was measured by the picosecond laser system that was used for time-resolved NID-IR spectra. The obtained IR dip spectrum coincides to our previous work measured by a nanosecond laser system [18], except for a difference in the energy resolution. The vibrational bands in the IR dip spectrum are roughly described as anharmonic coupling between the CH stretching vibration and NH stretching, which is red-shifted due to hydrogen-bond formation. In the picosecond time-resolved NID-IR

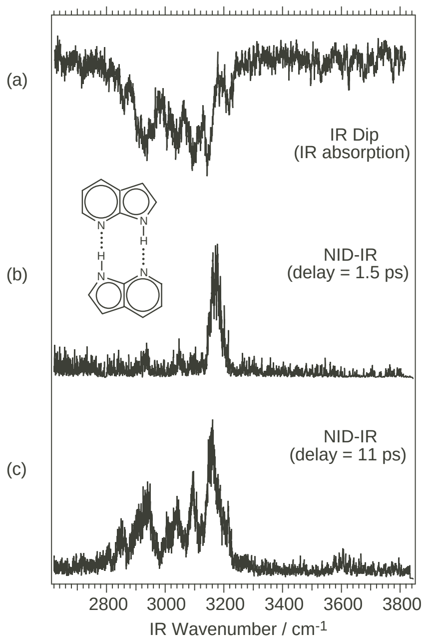

Fig. 2. Picosecond time-resolved NID-IR spectra of 7-azaindole dimer at (b) 1.5 ps and (c) 11 ps delay times. For a comparison, the IR dip spectrum of 7-azaindole dimer, that is corresponding to the IR absorption in S_0, is also shown in (a).

spectra, one very strong band (at 3 172 cm^{-1}) and weak structures at around 3 000 cm^{-1} were observed at a 1.5 ps delay time. The relative intensity of the 3 172 cm^{-1} band rapidly decreased with time, and at an 11 ps delay time the spectral feature of NID-IR was similar to that of the IR dip spectrum. It was quite clear that the drastic time evolution occurred within only 10 ps.

At a delay time of 1.5 ps, both the IR laser and the UV laser overlapped in time because of their pulse duration of 3 ps. Thus, it is not clear that the observed strong band at 3 172 cm^{-1} is a vibrational band in S_0, because a higher excited state which is generated by the two-photon absorption of the UV laser can also give the band by accidental resonance. In this case, the time-evolution corresponds to the decay of the higher excited state. To clarify the origin of the band at 3 172 cm^{-1}, we changed the wavelength of the UV laser from 324 nm to 320 nm so as to avoid any accidental resonance, and measured the time-resolved NID-IR spectrum at 1.5 ps. The strong band appeared at exactly the same position for IR frequency, and no obvious change was found. We therefore concluded that the intense band at 3 172 cm^{-1} is the vibrational band in the ground state, and that the fast time-evolution is due to the dynamics in S_0.

Let us discuss the origin of the observed time-evolution in S_0. 7-azaindole dimer is a well-known example of intracluster proton transfer. However, the proton transfer reaction has been reported only when the dimer is excited to the S_1 state, and no proton transfer has been found in S_0. Thus, the time-evolution should be discussed in terms of the intracluster vibrational redistribution (IVR) and/or predissociation. For a cluster, vibrational predissociation may be a natural interpretation of the time-evolution from the vibrational state, because the vibrational energy of 3 000 cm^{-1} is sufficient to break a single hydrogen bond. Ebata and co-workers have interpreted the decay of the NID-IR signal of the hydrogen-bonded phenol clusters measured by the picosecond laser system with 20 ps resolution [25]. However, this interpretation is not applicable for 7-azaindole dimer, because it has two hydrogen-bonds and their dissociation energy will be expected to be roughly 6 000 cm^{-1} [28]. Therefore, the time-evolution must be explained only in terms of IVR.

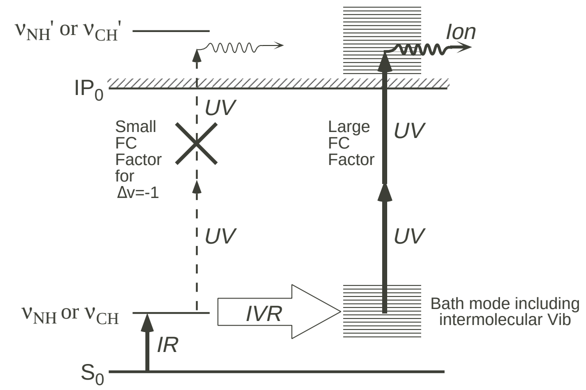

Fig. 3. Schematic diagram of transitions in time-resolved NID-IR spectroscopy for 7-azaindole dimer.

If all of the vibrational state generated after IVR would be ionized, no time-evolution could be observed. Thus, the presence of time-evolution means that only specific vibrational states populated after IVR are ionized by the UV laser. This selectivity can be explained by the Franck-Condon factor for near adiabatic ionization. Let us assume that the cluster is ionized just above the adiabatic ionization potential IP_0, which correspond to the zero vibrational level in the cation (see Fig. 3). The ionization efficiency from the initially prepared vibrational level in S_0 is very low if the geometry is almost the same; the Franck-Condon factor from $v = 1$ to 0 might be low because of the same potential minimum. On the other hand, a significant ionization efficiency (*i.e.* large FC factor) can be expected from the vibrational level to IP_0, if the geometry of the cluster is changed by the ionization along the corresponding vibrational coordinate. Even if ionization occurs with a moderate excess energy, a similar argument can be made.

From several studies on cluster cations, such as PFI-ZEKE spectroscopies [29–35], we know that the geometry of the monomer is generally not changed much after ionization. On the other hand, in general, the cluster shows a drastic change in the geometry along the intermolecular vibrational coordinate, because the cluster cation undergo a charge-induced dipole interaction, which does not exist in the neutral case [35–39]. From this condition, it is highly possible that the ionization from a vibrational state which contains an intermolecular vibrational mode might be high. This means that the NID-IR signal detects the IVR to the intermolecular vibration, and the observed time-evolution reflects the vibrational energy flow into the intermolecular vibrations. If so, the drastic change of the spectral shape from 1.5 ps to 11 ps suggests that the vibrational state at 3 172 cm^{-1} has a significantly faster IVR to the intermolecular mode compared to other vibrational states in the same region.

To confirm this argument, we have to examine several assumptions, such as the geometry of the 7-azaindole dimer cation. Also, assignments of the vibrational bands around the 3 000 cm^{-1} region are also important, because the vibration at 3 172 cm^{-1} has a mode-specific IVR into the intermolecular vibrational mode. Of course, the detailed time-evolution must be measured for each vibrational band around 3 000 cm^{-1}. These experiments and calculations are now in progress.

The present work was financially supported in part by a Grant-in-Aid from the Ministry of Education, Science, Sports and Culture in Japan. Support from the Daiko Foundation is also gratefully acknowledged. The authors thank Mr. Takaya Yamanaka and Mr. Tadashi Ueda in Laser Research Center for Molecular Science for their help in using the picosecond laser facilities.

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