VIBRATIONAL EXCITATION OF AMMONIA MOLECULES BY FEL-SUT

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Abstract

Free Electron Laser at Tokyo University of Science (FEL-SUT) was employed for exciting single vibrational modes of ammonia molecules. FEL is tuned to 10.5 μ m, corresponding to the X ${}^{1}A_{1}' 2^{1} \leftarrow 2^{0}$ transition of NH₃. The population of the vibrationally excited states is probed by the (2 + 1) resonance enhanced multiphoton ionization (REMPI) technique via the B ${}^{1}E''$ Rydberg state. Excitation efficiency of the $2^{1} \leftarrow 2^{0}$ transition was about 30 %. Rotational analyses of the spectra revealed that vibrational ladder climbing up to X 2^{2} in NH₃ was realized for the first time. IR-FEL excitation spectra were also recorded.

INTRODUCTION

For chemical physicists, the most serviceable advantage of the infrared free electron laser (IR-FEL) over conventional laser light sources is its spectral range. Since the mid infrared (MIR) spectral region falls in the range of excitation energy of a specific molecular vibrational mode, IR-FEL is considered to be a powerful tool for spectroscopic study in the MIR region and bond-selective photochemistry. Our group [1] reported on vibrational excitation of CO molecules as the first result of experiment on gas-phase molecules employing IR-FEL at Tokyo University of Science (FEL-SUT). The 4.7-µm FEL, corresponding to the X ${}^{1}\Sigma^{+} v'' = 1 \leftarrow 0$ transition of CO, generated vibrationally excited CO molecules which were probed by (2 + 1) resonance-enhanced multiphoton ionization (REMPI) technique via B ${}^{1}\Sigma^{+}$ state. We found that ~10 % of the population in v'' = 0 was excited to v'' =1, but no sequential excitation to the $v'' \ge 2$ vibrational levels was observed.

As a next stage, this paper describes preliminary results on vibrational excitation of ammonia (NH₃) molecules. Ammonia and its isotopomers are one of the most representative small gas-phase molecules. From the view point of vibrational excitation, Akagi et al. [2] reported bond-selective dissociation of partially deuterased ammonia excited to the overtone state of N-H or N-D stretching mode. When the $5 v_{NH}$ overtone state (excited by 650-nm visible laser) of NHD₂ was photodissociated by UV laser, the NH dissociation cross section was ~5 times as large as the ND dissociation cross section per bond. Report on the vibrational excitation of single quantum has also been made by Ying et al. employing FEL at Vaderbilt University [3]. Their main purpose was to observe absorption spectrum corresponding to $X^{-1}A_{1}$ " $2^1 \leftarrow 2^0$. In the current study we attempted to generate a large amount of the vibrationally excited ammonia

molecules and to investigate whether the ladder climbing exists or not. We employed (2 + 1) REMPI schemes via the B ¹E" Rydberg state to detect vibrationally excited ammonia, because the observation of the B ¹E" using REMPI schemes has been thoroughly studied [4-8].

EXPERIMENT

The experiment was performed at laboratory III in IR-FEL Research Center at Noda campus of Tokyo University of Science. The status of the FEL-SUT facility was reported elsewhere [9-11]. Figure 1 displays a schematic diagram of the experimental system. The system consists of a reflectron-type time-of-flight spectrometer (Jordan D-651) with a pulsed valve (Jordan C-211AL), a beam duct and several mirrors for the guidance of the FEL beam to the TOF system, a nanosecond dye laser (Continuum ND6000) pumped by a Q-switched YAG laser (Lotis TII), and a microcomputer unit for data storage and control of the dye laser wavelength. A main chamber is evacuated by two turbo molecular pumps (SHIMADZU TMU1500 and TMU 150): The background pressure is below 10^{-7} Torr. The pulsed valve with a skimmer nozzle produces a supersonic molecular beam with 60 µs duration. Molecular beam is supplied with 5 % NH₃ in Ar at the back pressure of 1 atm. This molecular beam is intersected by two counterpropagating laser lights. Both laser beams are focused with a lens (f = 30 cm; BaF₂ for IR and quartz for UV). The polarization plane of the IR-



Figure 1: Experimental apparatus.

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FEL is parallel to the TOF axis and the UV laser polarization is perpendicular to them.

The synchronization among the pulsed molecular beam, FEL macropulse and YAG-laser pulse was controlled electrically by the use of several digital delay generators (SR DG535). The repetition rates of macropulse and micropulse are 5 and 2856 MHz, respectively. As long as the dye laser pulse is sitting in a macropulse of $\sim 2 \mu s$ duration, the dye laser pulse of 3 ns duration contains several micropulses which have 350 ps interval. Because a fast detector for MIR radiation is not available, we monitored the temporal profile of visible harmonics with a photodiode (Electro-Optics Technology, ET-4000).

The wavelength of FEL was tuned around 10.5 μ m, corresponding to the X ${}^{1}A_{1}$ " 2 2 0 transition of NH₃. Typical bandwidth of the IR laser, monitored by using monochromator and a HgCdTe detector, was ~0.16 μ m (~14 cm⁻¹, FWHM). In front of the window of the main chamber, the macropulse energy at this wavelength was measured to be 8-15 mJ which is several times greater than that in the earlier experiment [1]. On the other hand, 315-340 nm light required for (2 + 1) REMPI via the B 1 E" state of NH₃ was obtained as a second harmonic of the dye laser output. The output of the dye laser was frequency doubled in a KDP crystal. The UV pulse energy was measured to be ~1 mJ.

RESULTS AND DISCUSSION

The B \leftarrow X REMPI excitation spectrum obtained by scanning UV wavelength in the range of 315-340 nm was governed by the vibronic progression of v_2 as seen in earlier reports [4-8]. This fact is based on the large change of equilibrium geometry. Whilst the ground state is pyramidal (point group C_{3v}) the Rydberg states are all planar (point group D_{3h}).

Figure 2a) shows a portion of the REMPI excitation spectrum corresponding to the B \leftarrow X 2^{1}_{0} transition without introduction of IR-FEL. Rotational assignments are performed using known molecular constants [4]. The $B \leftarrow X$ two-photon transition belongs to the perpendicular band and the selection rule for K is $\Delta K =$ \pm 1. The ^rS₀(0) and ^pR₁(1) lines cannot be resolved by our laser bandwidth. Missing of the transition from the $J_K = 1_0$ level is explainable as follows. Due to the inversion doubling, each v_2 state in the ground state has s and a components having A1' and A2" vibronic symmetry, respectively. In the B state, the vibronic symmetry is either E" or E', for even or odd v_2 level, respectively. Two-photon transitions connect lower and upper states according to the schemes $E'' \leftarrow A_1'(s)$ and $E' \leftarrow A_2''(a)$. Owing to the nuclear spin statistics, the A₁' component in the X state has only odd-numbered J for K = 0. Inversely, the A_2 " component has only even-numbered J for K = 0. For B \leftarrow X 2¹₀ transition, the lower state doesn't have J_K = 1_0 level since the vibronic symmetry is A_2 ".

Figure 2a) could be reproduced consistently by a simulation taking into account rotational line strengths [12], rotational degeneracy, rotational temperature, and



Figure 2: REMPI spectra in the region of the B \leftarrow X 2¹₀ two-photon transition of NH₃ a) without and b) with irradiation of the IR-FEL (10.5 µm). Rotational assignments added in traces a) and b) belong 2¹₀ and 2²₁ bands, respectively.

nuclear spin statistics in the ground state. Rotational temperature was found to be ~8 K. This calculation indicated that over 99 % of population was fell in the $J_K = 0_0$ and 1_1 in the X(*a*) state.

Figure 2b) is the REMPI spectrum obtained by the irradiation of both the IR-FEL and UV laser. The center wavelength of the IR-FEL was fixed to 10.5 μ m (952 cm⁻¹). Newly appeared peaks were assigned to the rotational lines in the B $\leftarrow X(s) 2^2_1$ two-photon transition, demonstrating that the vibrational excitation of NH₃ corresponding to the X(s) $2^1 \leftarrow X(a) 2^0$ transition in the ground state was achieved. Simultaneous observation of rovibronic transitions from the X(s) $2^1 J_K = 1_0$ and 2_1 levels indicate that the broad spectral width of IR-FEL covers the transition energies of the $a^q R_0(0)$ (951.78 cm⁻¹) and $a^q R_1(1)$ (971.88 cm⁻¹) [13]. Note that the selection rules for the rovibrational transition are A₁'(s) - A₂"(a) and $\Delta K = 0$ (parallel band).

Efficiency of the vibrational excitation was estimated comparing Fig. 2a) and b). The intensity of the each peak in Fig. 2a) apparently decreased in Fig. 2b). Average of the decrease in peak intensities for ${}^{p}Q_{1}(1)$, ${}^{r}R_{1}(1)$, ${}^{r}S_{1}(1)$, and ${}^{p}S_{1}(1)$ peaks suggests that 30 % of the total population in the X(*a*) $2^{0} J_{K} = 1_{1}$ was pumped to the X(*s*) $2^{1} J_{K} = 2_{1}$. Here the strongest peak constructed by two rotational lines was not involved in the calculation.



Figure 3: REMPI spectra in the region of the $B \leftarrow X 2_{1}^{0}$ and 2_{2}^{1} two-photon transition of NH₃. a) Observed spectrum with irradiation of both the IR-FEL (10.5 µm) and UV laser. b)c) Simulation for $B \leftarrow X$ b) 2_{1}^{0} and c) 2_{2}^{1} transitions.

Figure 3a) displays REMPI spectra in the region of the $B \leftarrow X \ 2^{0}_{1}$ and 2^{1}_{2} two-photon transition of NH₃ obtained with irradiation of both the IR-FEL and UV laser. Since this energy region is below the $B \leftarrow X$ band origin (~59300 cm⁻¹), no signal appeared without the IR-FEL. Figure 3b) represents the calculated spectrum corresponding to the $B \leftarrow X \ 2^{0}_{1}$ transition. This trace reproduces ten peaks in Fig. 3a) almost perfectly. The disagreement of their intensities is mainly caused by the fluctuation of the FEL macropulse intensity. The rotational levels in the X 2¹ state are identified to be $J_K = I_0$ and 2_1 , showing that the rotational lines in the X(s) $2^1 \leftarrow X(a) \ 2^0$ band are ${}^qR_0(0)$ and ${}^qR_1(1)$, as same in Fig. 2.

Additionally, the signals corresponding to the $B \leftarrow X$ 2^{1}_{2} transition appeared in this region. The calculated spectrum displayed in Fig. 3c) clearly shows that the X(a) $2^{2} J_{K} = 0_{0}$ and 2_{1} levels are populated. These two levels are excited from the X(s) $2^{1} J_{K} = 1_{0}$ and 2_{1} through the ^qP₀(1) (929.61 cm⁻¹) and ^qQ₁(2) (947.88 cm⁻¹) branches, respectively. This observation demonstrates for the first time that the ladder climbing up to $v_2 = 2$ was realized in the NH₃ system. The complete paths of the vibrational excitations are written as (i) X(a) $2^2 J_K = 0_0 \leftarrow X(s) 2^1$ $J_K = 1_0 \leftarrow X(a) 2^0 J_K = 0_0$, and (ii) X(a) $2^2 J_K = 2_1 \leftarrow$ X(s) $2^1 J_K = 2_1 \leftarrow X(a) 2^0 J_K = 1_1$. No signals could be observed corresponding to the subsequent climbing to X(s) 2^3 : the transition energy of the X(s) $2^3 \leftarrow X(a) 2^2$ band (~ 500 cm⁻¹) is far from the IR-FEL wavenumber used.

Figure 4 shows the examples of IR-FEL excitation spectra recorded by scanning IR-FEL wavelength. The UV laser frequencies are fixed to the a) ${}^{9}R_{0}(1)$ and b) ${}^{p}R_{1}(1)$ branches of the B $\leftarrow X 2^{0}{}_{1}$ transitions; the probed levels by the UV laser are X(s) $2^{1} J_{K} = 1_{0}$ and 1_{1} , respectively. These two levels were pumped through the $a^{q}R_{0}(0)$ and $a^{q}Q_{1}(1)$ branches of the X(s) $2^{1} \leftarrow X(a) 2^{0}$ vibrational band. Though the spectral features are very broad owing to the condition of FEL-SUT, the spectral positions are consistent with the transition energies (calculated from ref. [14]) indicated by down arrows.

In summary, we succeeded in detecting vibrationally hot NH_3 molecules populated by light pulses from FEL-SUT. MIR FEL was tuned to 10.5 µm which corresponds



Figure 4: IR-FEL excitation spectra corresponding to the $X(s) 2^1 \leftarrow X(a) 2^0$ of NH₃. The UV laser frequencies are fixed to the ${}^{q}R_0(1)$ and b) ${}^{p}R_1(1)$ branches of the B $\leftarrow X 2^{0}_{1}$ transition. Down arrows represent the known transition energies.

to the X $2^1 \leftarrow X 2^0$ band. The population of the vibrationally excited state was probed by (2 + 1) REMPI method. Efficiency of the vibrational excitation of the X 2^1 state is as large as 30 %. Spectral assignments revealed that vibrational ladder climbing up to $v_2 = 2$ in NH₃ was realized for the first time. Experiment on the vibrational excitation of the v_4 vibrational mode of NH₃ molecules is under way.

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