

III-E Spectroscopy and Dynamics of Vibrationally Excited Molecules and Clusters

This research group is studying structure and dynamics of molecules and clusters by two-color double resonance spectroscopy. New spectroscopic methods will also be developed to observe the higher vibrational state under collision-free condition.

A molecular cluster is a microscopic system of solution and/or crystal, and is thought to provide detailed information on relaxation and reaction dynamics in condensed phase. However the previous studies are concentrated to stable clusters which has no reaction pathway after photo-excitation. Consequently, spectroscopic information which concerns the reaction mechanism has not been obtained sufficiently. In this research project started from 2000, we will apply various laser spectroscopies to the reactive clusters to reveal detailed mechanism of intracuster reaction.

For the study of the ground state, the structure of the cluster can be determined by the combination of the IR dip spectroscopy and *ab initio* MO calculations.¹⁾ The IR dip spectroscopy is a kind of IR-UV double resonance spectroscopy which provides the spectrum which corresponds to the infrared absorption spectrum of the cluster (see Figure 1). A tunable IR laser is introduced to the clusters and is scanned its frequency over the fundamental vibrational region (typically 2400 ~ 4000 cm^{-1}). Then a tunable UV laser, of which the frequency is fixed to the S_1 origin of a specific cluster, is introduced and resonant enhanced multiphoton ionization signal *via* S_1 is monitored. When the IR laser is resonant to a vibrational level of the cluster, the ion signal decreases much because of loss of the population in the vibrational ground state. Thus, the IR absorption spectrum of the cluster can be measured by this depletion spectroscopy. The same spectrum can be obtained when the fluorescence intensity from S_1 is monitored instead of the ion current.

The IR spectrum in the excited state S_1 can also be measured by the depletion spectroscopy, when the UV laser is introduced before the IR laser (the UV-IR fluorescence dip spectroscopy; see Figure 2). The molecule is excited to S_1 by the UV laser, and the fluorescence intensity is monitored as well as the IR dip spectroscopy for S_0 . Then the S_1 molecules are further excited to the vibrationally excited level in S_1 by the IR laser. In general, the fluorescence quantum yield decreases in the higher vibronic level. Thus, the total fluorescence intensity decreases when the IR laser frequency is resonant to the vibrational level in S_1 .

Similarly, the IR spectrum of the ionic cluster can be measured by the depletion spectroscopy (mass-selected ion dip spectroscopy; see Figure 3). The ionic cluster can be prepared by the multiphoton ionization *via* S_1 , and the ion current due to the cation cluster of the specific size can be measured through a mass-filter. When the ionic cluster is vibrationally excited by the IR laser, the cluster is dissociated by the vibrational predissociation. Therefore, the IR transition can be measured by the decrease of the parent cluster. The same spectrum can be obtained by monitoring the enhancement of fragments (mass-selected multiphoton dissociation spectroscopy). In addition to these "dip" spectroscopies, the nonresonant ionization detected IR spectroscopy²⁾ and the PFI-ZEKE photoelectron spectroscopy³⁾ are also important tool to obtain the spectral information in the cation and the overtone states. Based on these spectroscopic techniques, we have measured the IR spectra of solvated clusters,⁴⁾ such as phenol/ammonia,⁵⁾ naphthol/alcohol,⁶⁾ carbazole/water⁷⁾ and 7-azaindole dimers,⁸⁾ and have discussed the relation among geometrical structure, electronic state and intracuster reactions.

From 2001, we have been developing the new ultrafast time-resolved IR spectroscopy for the reactive clusters. The pico second time-resolved vibrational spectroscopy is one of the ideal way to reveal the reaction mechanism directly. Here, we will demonstrate its usefulness by applying the hydrogen transfer reaction in photoexcited PhOH-

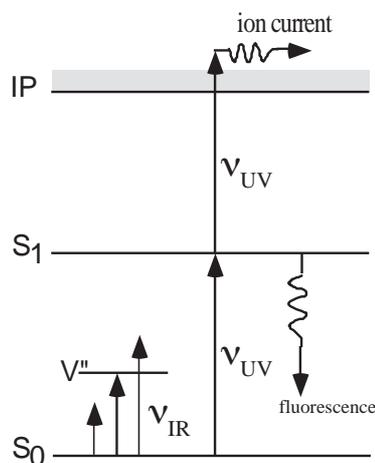


Figure 1. Principle of the IR Dip Spectroscopy. The IR transition in the ground state cluster can be measured.

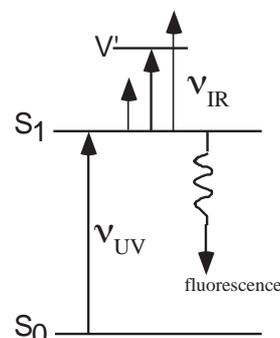


Figure 2. Principle of the UV-IR Fluorescence Dip Spectroscopy. The IR transition of the cluster in the S_1 state can be obtained.

(NH₃)_n cluster.⁹⁾ Figure 4 shows the principle of the picosecond time-resolved UV-IR-UV ion dip spectroscopy. The reactive cluster (PhOH-(NH₃)_n in present case) is excited to S₁ by a picosecond UV laser ν_{UV} and the photochemical reaction (hydrogen transfer) is triggered. The final reaction product, *i. e.* (NH₃)_{n-1}NH₄, is ionized by a nanosecond UV laser ν_{ION} which is irradiated after 100 ns from ν_{UV} and the population of the reaction product is monitored as a mass peak of (NH₃)_{n-1}NH₄⁺. A picosecond tunable IR laser ν_{IR} is irradiated after *t* ps from ν_{UV} and is scanned over vibrational region. If ν_{IR} is resonant to vibrational levels of the transient species, the population of the final reaction product decreases due to the vibrational predissociation of the transient species. Therefore, the vibrational transitions of the transient species at *t* ps can be observed as decrease of ion current of the final reaction product.

Time resolved UV-IR-UV ion dip spectra of phenol-(NH₃)₃ are shown in Figure 5. The numbers in the left hand sides of each spectrum indicate the delay time from ν_{UV} to ν_{IR} . Here the spectrum at -20 ns corresponds to the IR spectrum of PhOH-(NH₃)₃ in S₀, in which the sharp bands around 3400 cm⁻¹, the broad bands at ~ 3200 cm⁻¹ and the very broad background are assigned to the degenerated antisymmetric stretch vibration ν_3 in NH₃, the totally symmetric stretch vibration ν_1 in NH₃ and the OH stretch vibration ν_{OH} in phenol, respectively. The spectrum at +180 ns shows the vibrational transitions of the final reaction product *via* S₁, *i. e.* (NH₃)₂NH₄, and 1) two intense bands at 3180 cm⁻¹ and 3250 cm⁻¹ and 2) a broad band at 2700 ~ 3100 cm⁻¹ which have been assigned to

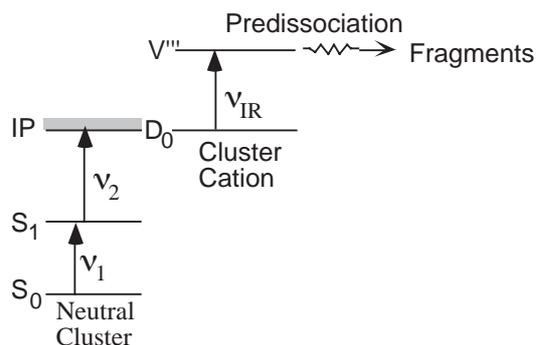


Figure 3. Principle of the mass-selected IR Ion Dip Spectroscopy. The IR transition of the cluster cation can be measured by the depletion of the parent cluster cation. The same spectrum can be measure by monitoring the enhancement of the fragments produced by the IR predissociation.

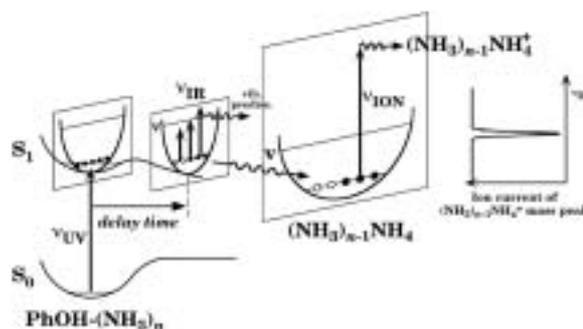


Figure 4. Principle of picosecond time-resolved UV-IR-UV ion dip spectroscopy. Potential curves of S₀ and S₁ are schematically drawn along O-H stretch coordinate. Potential curves in different sections on the S₁ O-H stretch coordinate are drawn along arbitrary N-H stretch coordinates.

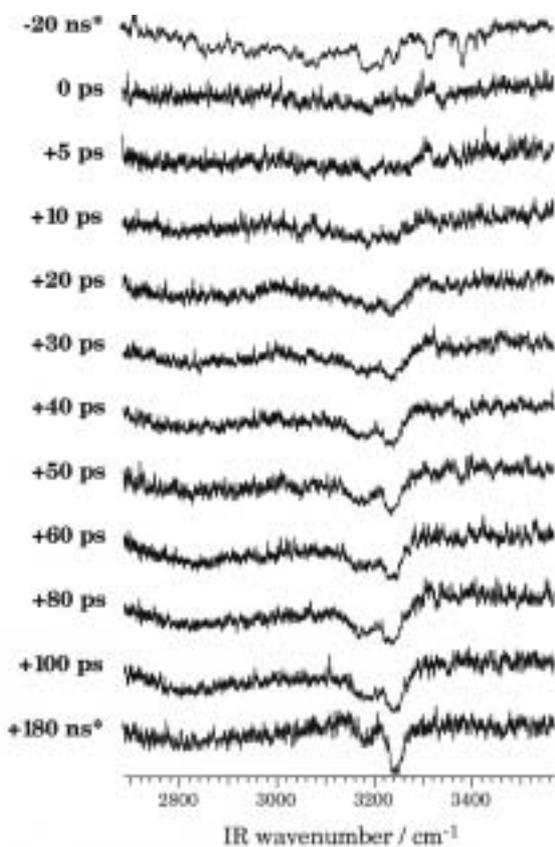


Figure 5. Picosecond time-resolved UV-IR-UV ion dip spectra of the transient species from the electronically excited PhOH-(NH₃)₃ which was observed by fixing ν_{UV} to the low vibronic band in the S₁ state of PhOH-(NH₃)₃ (281.49 nm) and monitoring (NH₃)₂NH₄⁺ due to ν_{ION} (355 nm). Times indicated at the left side of each spectrum mean the delay times between ν_{UV} and ν_{IR} . The spectra whose delay times are -20 ns and +180 ns (indicated by *) are obtained by nanosecond laser system, which have been reported in the previous paper.⁵⁾

vibrational transitions concerned with NH_4 .

One can see that the vibrational bands rise with increasing delay time. The spectral feature at +100 ps is already similar to that of the final reaction product (+180 ns). Here, the intense band at 3250 cm^{-1} rises slower than the band at 3180 cm^{-1} . The relative intensities of the two bands become comparable at 40 ps, thereafter, the higher band at 3250 cm^{-1} clearly grows further. Thus, the rising time constant of the band at 3250 cm^{-1} is apparently different from that of the 3180 cm^{-1} -band. This remarkable difference between the two intense bands suggests that each vibrational transition is derived from different species. The existence of two transient species are naturally interpreted by considering the isomers of $(\text{NH}_3)_2\text{NH}_4$; the most stable $\text{NH}_3\text{-NH}_4\text{-NH}_3$ and the meta-stable $\text{NH}_4\text{-NH}_3\text{-NH}_3$. The co-existence of isomers is strongly supported by *ab initio* calculations.

As described above, we have successfully measured the picosecond time resolved IR spectra of the transient species for the ESHT of $\text{PhOH-(NH}_3)_3$ for the first time. It proves that the picosecond UV-IR-UV ion dip spectroscopy is a powerful tool to explore the dynamics of the intracuster reaction.

References

- 1) R. Yoshino *et al.*, *J. Phys. Chem. A* **102**, 6227 (1998).
- 2) T. Omi *et al.*, *Chem. Phys. Lett.* **252**, 287 (1996); S. Ishiuchi *et al.*, *Chem. Phys. Lett.* **283**, 243 (1998).
- 3) K. Takazawa *et al.*, *Chem. Phys. Lett.* **189**, 592 (1992); K. Müller-Dethlefs *et al.*, *Z. Naturforsch. Teil A* **39**, 1089 (1984); K. Müller-Dethlefs and M. C. R. Cockett, "Zero Kinetic Energy (ZEKE) Photoelectron Spectroscopy," Chapter 7, "Nonlinear Spectroscopy for Molecular Structure Determination," R. W. Field *et al.*, Eds., (Blackwell Science, Oxford, 1998), and references therein.; E. W. Schlag, "ZEKE Spectroscopy" (Cambridge University Press, Cambridge, 1998), and references therein.
- 4) K. Suzuki, Y. Emura, S. Ishiuchi and M. Fujii, *J. Electron Spectrosc.* **108**, 13 (2000), K. Suzuki, S. Ishiuchi and M. Fujii, *Faraday Discuss.* **115**, 229 (2000), K. Sakota, N. Yamamoto, K. Ohashi, H. Sekiya, M. Saeki, S. Ishiuchi, M. Sakai and M. Fujii, *Chem. Phys. Lett.* **341**, 70 (2001).
- 5) S. Ishiuchi, M. Saeki, M. Sakai and M. Fujii, *Chem. Phys. Lett.* **322**, 27 (2000).
- 6) M. Saeki, S. Ishiuchi, M. Sakai and M. Fujii, *J. Phys. Chem. A* **105**, 10045 (2001).
- 7) M. Sakai, K. Daigoku, S. Ishiuchi, M. Saeki, K. Hashimoto and M. Fujii, *J. Phys. Chem. A* **105**, 8651 (2001).
- 8) H. Yokoyama, H. Watanabe, T. Omi, S. Ishiuchi and M. Fujii, *J. Phys. Chem. A* **105**, 9366 (2001).
- 9) S. Ishiuchi, M. Sakai, K. Daigoku, T. Ueda, T. Yamanaka, K. Hashimoto and M. Fujii, *Chem. Phys. Lett.* **347**, 87 (2001).

III-E-1 Photochemistry of Phenol- $(\text{NH}_3)_n$ Clusters: Solvent Effect on a Radical Cleavage of an OH Bond in an Electronically Excited State and Intracuster Reactions in the Product $\text{NH}_4(\text{NH}_3)_{n-1}$ ($n < 5$)

DAIGOKU, Kota¹; ISHIUCHI, Shun-ichi²; SAKAI, Makoto³; FUJII, Masaaki⁴; HASHIMOTO, Kenro⁵
(¹Tokyo Metropolitan Univ.; ²Tokyo Inst. Tech./JST-PRESTO; ³Tokyo Inst. Tech.; ⁴IMS and Tokyo Inst. Tech.; ⁵Tokyo Metropolitan Univ./ACT-JST)

[*J. Chem. Phys.* **119**, 5149–5157 (2003)]

The potential energy surfaces of $\text{PhOH-(NH}_3)_{0,1}$ and $\text{NH}_4(\text{NH}_3)_{1-4}$ have been investigated theoretically by *ab initio* methods. Intermolecular stretching in PhOH-NH_3 assists in the radical cleavage of an OH bond occurring through a $\pi\pi^*/\pi\sigma^*$ potential crossing. Thus, excited state hydrogen transfer (ESHT) is expected to take place by a solvent-assisted mechanism even in the larger $\text{PhOH-(NH}_3)_n$. Because sufficient energy is obtained by ESHT from $\text{PhOH-(NH}_3)_n$ ($\pi\pi^*$) to $\text{PhO-NH}_4(\text{NH}_3)_{n-1}$ ($\pi\sigma^*$) ($n \leq 5$), hydrogen relocation and/or ammonia migration in the product $\text{NH}_4(\text{NH}_3)_{n-1}$ can readily follow ESHT, which is responsible for observing isomer bands in the absorption spectra of the photoinduced reaction products of $\text{PhOH-(NH}_3)_n$.

III-E-2 Four-Color Hole Burning Spectra of Phenol/ammonia 1:3 and 1:4 Clusters

ISHIUCHI, Shun-ichi¹; DAIGOKU, Kota²;

HASHIMOTO, Kenro³; FUJII, Masaaki⁴

(¹Tokyo Inst. Tech./JST-PRESTO; ²Tokyo Metropolitan Univ.; ³Tokyo Metropolitan Univ./ACT-JST; ⁴IMS and Tokyo Inst. Tech.)

[*J. Chem. Phys.* **120**, 3215–3220 (2004)]

The hole burning spectra of phenol/ammonia (1:3 and 1:4) clusters were measured by a newly developed four-color (UV-near-IR-UV-UV) hole burning spectroscopy, which is a kind of population labeling spectroscopy. From the hole burning spectra, it was found that single species is observed in an $n = 3$ cluster, while three isomers are observed simultaneously for $n = 4$. A possibility was suggested that the reaction efficiency of the hydrogen transfer from the electronically excited phenol/ammonia clusters, which was measured by a comparison with the action spectra of the corresponding cluster, depends on the initial vibronic levels.

III-E-3 S_1 - S_0 Electronic Spectrum of Jet-Cooled *m*-Aminophenol

SHINOZAKI, Minako¹; SAKAI, Makoto²;
YAMAGUCHI, Shigeru¹; FUJIOKA, Tomoo¹;
FUJII, Masaaki³

(¹Tokai Univ.; ²Tokyo Inst. Tech.; ³IMS and Tokyo Inst. Tech.)

[*Phys. Chem. Chem. Phys.* **5**, 5044–5050 (2003)]

The S_1 and S_0 states of *m*-aminophenol have been investigated using laser induced fluorescence and

dispersed fluorescence spectroscopy in a supersonic jet. The dispersed fluorescence spectra, obtained by exciting the bands at 34 109 and 34 469 cm^{-1} , show the same vibronic structure, which suggests the coexistence of rotational isomers in *m*-aminophenol. A quantum chemical calculation also supports the coexistence of rotational isomers. From the relative intensities in the spectrum and the calculated stabilization energies of isomers, the bands are assigned to the origin of the *cis*- and *trans*-isomers, respectively. The dispersed fluorescence spectra obtained by exciting the S_1 vibronic bands were analyzed by comparing with the calculated vibrational frequencies and IR and Raman spectra. From the analysis, the S_1 vibronic bands have been assigned. It was found that a one-to-one correspondence between the S_1 and S_0 vibrations is broken, and vibrational mixing due to Fermi resonance or the Duschinsky effect is suggested.

III-E-4 Predicted Spatial Resolution of Super-Resolving Fluorescence Microscopy Using Two-Color Fluorescence Dip Spectroscopy

IKETAKI, Yoshinori¹; WATANABE, Takeshi²; ISHIUCHI, Shun-ichi³; SAKAI, Makoto²; OMATSU, Takashige⁴; YAMAMOTO, Kimihisa⁵; FUJII, Masaaki⁶

(¹Olympus Optical Co. Ltd.; ²Tokyo Inst. Tech.; ³Tokyo Inst. Tech./JST-PRESTO; ⁴Chiba Univ.; ⁵Keio Univ.; ⁶IMS and Tokyo Inst. Tech.)

[*Appl. Spectrosc.* **57**, 1312–1316 (2003)]

The theoretical spatial resolution of the novel super-resolution fluorescence microscopy was investigated. This microscopy is based on the fluorescence depletion process observed by two-color fluorescence dip spectroscopy. For the investigation, we measured the optical properties of Rhodamine 6G concerning the fluorescence depletion process. Using the obtained data, the spatial resolution of the microscopy is theoretically forecast when a first order of the Bessel beam is used for the erase beam. It is found that the resolution overcomes the diffraction limit in the nanometer scale region. The investigation shows that the microscopy gives a spatial resolution better than 100 nm using a nanosecond laser with a pulse energy of \sim nJ/pulse. The microscopy is expected to be an appropriate novel tool for observing samples with nanometer scale structures.

III-E-5 Vibrational Energy Relaxation of the 7-Azaindole Dimer in CCl_4 Solution Studied by Picosecond Time-Resolved Transient Fluorescence Detected IR Spectroscopy

SAKAI, Makoto¹; FUJII, Masaaki²

(¹Tokyo Inst. Tech.; ²IMS and Tokyo Inst. Tech.)

[*Chem. Phys. Lett.* in press]

The picosecond time-resolved IR spectra of the 7-azaindole dimer in a carbontetrachloride solution was measured by using picosecond time-resolved IR/UV double resonance spectroscopy. This spectroscopy

selectively detects the IR transition by transient fluorescence due to an electronic transition from a vibrationally excited level. The time-evolution of the IR spectrum is a single exponential with a 19 ps lifetime, which does not correspond to fast nonstatistical decay due to the intramolecular vibrational redistribution found in a gas-phase cluster. From a comparison with the time-resolved IR spectrum of a jet-cooled dimer, this decay is assigned to vibrational cooling from the dimer to the solvent.

III-E-6 Pulsed Field Ionization—ZEKE Photoelectron Spectrum of *o,m,p*-Tolunitrile

SUZUKI, Kazunari¹; ISHIUCHI, Shun-ichi²; SAKAI, Makoto³; FUJII, Masaaki⁴

(¹Waseda Univ.; ²Tokyo Inst. Tech./JST-PRESTO; ³Tokyo Inst. Tech.; ⁴IMS and Tokyo Inst. Tech.)

[*J. Electron Spectrosc.* in press]

Pulsed field ionization—ZEKE photoelectron spectroscopy has been applied to *o*-, *m*- and *p*-tolunitrile in a supersonic jet. The PFI-ZEKE photoelectron spectra of *m*- and *p*-tolunitrile show well-resolved anharmonic structures in the low frequency region, which are assigned to bands due to internal rotational motion of the methyl group in the cation. Level energies and relative transition intensities are reproduced well by a one-dimensional rotor model with a three-fold axis potential. Potential curves for the internal rotation have been determined. For *o*-tolunitrile, no band due to internal rotation was found in PFI-ZEKE spectrum. It is suggested that the *o*-tolunitrile cation has the high barrier for internal rotation and the stable conformation that is the same as that in S_1 and S_0 . The barrier height and the conformation are compared with other toluene derivatives, and the relation between the electronic character of -CN and the internal rotational motion has been discussed.

III-E-7 Two-Point-Separation in Super-Resolution Fluorescence Microscope Based on Up-Conversion Fluorescence Depletion Technique

WATANABE, Takeshi¹; IKETAKI, Yoshinori²; OMATSU, Takashige³; YAMAMOTO, Kimihisa⁴; SAKAI, Makoto¹; FUJII, Masaaki⁵

(¹Tokyo Inst. Tech.; ²Olympus Optical Co. Ltd.; ³Chiba Univ.; ⁴Keio Univ.; ⁵IMS and Tokyo Inst. Tech.)

[*Opt. Express* **11**, 3271–3276 (2003)]

We have demonstrated a realistic super-resolution scanning fluorescence microscope using conventional nanosecond lasers. This super-resolution microscope is based on the combination of two-color fluorescence dip spectroscopy and shape modulation to a doughnut beam. Only by introducing a doughnut erase beam, the resolution of the laser fluorescence microscope breaks the diffraction limit by two times without using any mechanical probe.

III-E-8 Super-Resolution Fluorescence Microscopy in Nano-Meter Scale Region Using Two-Color Laser Beams

IKETAKI, Yoshinori¹; WATANABE, Takeshi²;
SAKAI, Makoto²; ISHIUCHI, Shun-ichi³;
OMATSU, Takashige⁴; YAMAMOTO, Kimihisa⁵;
FUJII, Masaaki⁶

(¹Olympus Optical Co. Ltd.; ²Tokyo Inst. Tech.; ³Tokyo Inst. Tech./JST-PRESTO; ⁴Chiba Univ.; ⁵Keio Univ.; ⁶IMS and Tokyo Inst. Tech.)

[*J. Surf. Sci. Soc. Jpn.* **24**, 392–399 (2003)]

A super-resolution fluorescence microscopy using two-color laser beams was proposed. The microscopy is based on the combination of two-color fluorescence dip spectroscopy and a phase modulation technique for the laser beam. By applying the proposed technique to a laser-scanning microscope, a fluorescence image of a sample can be observed with a spatial resolution overcoming the optical diffraction limit. To demonstrate validity of the microscopy, we constructed a scanning microscope system using commercial nano-second pulse lasers. An image of micro beads containing dye molecules was observed by the microscopy. We succeeded in obtaining the image with a resolution overcoming the diffraction limit in nano-meter scale region. The experimental data showed that the resolution was improved three times at least. The microscopy is expected to be an appropriate analysis method for samples with nano-meter scale structure.

III-E-9 Formation of Doughnut Laser Beam for Super-Resolving Microscopy Using a Phase Spatial Light Modulator

WATANABE, Takeshi¹; IGASAKI, Yasumori²;
FUKUCHI, Norihiro²; SAKAI, Makoto¹;
ISHIUCHI, Shun-ichi³; FUJII, Masaaki⁴; OMATSU,
Takashige⁵; YAMAMOTO, Kimihisa⁶; IKETAKI,
Yoshinori⁷

(¹Tokyo Inst. Tech.; ²Hamamatsu Photonics K. K.; ³Tokyo Inst. Tech./JST-PRESTO; ⁴IMS and Tokyo Inst. Tech.; ⁵Chiba Univ.; ⁶Keio Univ.; ⁷Olympus Optical Co. Ltd.)

[*Opt. Eng.* **43**, 1136–1143 (2004)]

The formation of a doughnut-shaped laser beam is presented. To generate the beam, we used an optically addressed parallel-aligned nematic liquid-crystal phase spatial light modulator (PAL-SLM), and observed the shape of the focused beam. By using a compensating technique for wave aberration, the beam had a symmetric doughnut shape with a hole size of $1\mu\text{m}\phi$ on the focal plane. The experimental result shows that the generated beam can be expected to be applicable to super-resolving microscopy based on the fluorescence depletion process.