



Laboratory for Laser Chemistry

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1. Current Research and Principal Research Interests

My current research focuses on high intensity laser chemistry, more specifically, ionization and fragmentation, and Coulomb explosion of organic molecules induced by femtosecond laser pulses. One of the applications called as Femtosecond Laser Mass Spectrometry (FMLS) would be a new method of trace detection of dioxins. Five photon absorption followed by the fluorescence has been found recently. Mechanism of femtosecond pulse induced protein nucleation is started to study. Multiphoton reactions via hot molecules formed by internal conversion using a VUV laser is another subject of interest.

1.1. High-Intensity Laser Chemistry

New research fields have opened related to the interaction between molecules and high-intensity optical fields, where the laser intensity ranges from 10^{12} ~ 10^{16} Wcm⁻². For large molecules, an intact molecular ion with little fragmentation has been found to form in an intensity region around 10^{14} Wcm⁻². The intact ion formation can be used for femtosecond laser mass spectrometry. In an intensity region of 10^{15} Wcm⁻² and more, electrons are stripped from molecules by optical field ionization and the highly charged ions reach a Coulomb explosion. Coulomb explosions of benzene and C₆₀ have been demonstrated and the mechanism can be analyzed by molecular dynamic simulation.

1.1.1 Intact Molecular Ion and Fragment Ion Formation of Organic Molecules on Irradiation with an Intense Femtosecond Laser Pulse

Ionization and fragmentation of several tens of organic molecules have been examined in a high intensity femtosecond laser field. Phenomenologically, it is clear that femtosecond intense laser pulses lead to enhanced formation of molecular ions compared with nanosecond laser excitation, even though the molecules have no electronic absorption at the laser wavelengths. The predominance of parent cations should be of great advantage in the femtosecond laser mass spectroscopy (FLMS) of aromatic hydrocarbons.

We have succeeded in generalizing that the resonance between the laser wavelength and the electronic energy levels of the molecular cations is a key factor in the formation of fragment ions during femtosecond laser excitation, as shown in Fig.1.

The cation of 1,4-cyclohexadiene is resonant at the excitation wavelength of 800 nm, and the spectra show heavy fragmentation. While the cation of 1,3-cyclohexadiene is not in resonance with the laser wavelength, parent ions are produced. Excitation pulses are obtained from a

high-intensity Ti:sapphire femtosecond laser in the intensity region of 10^{14} Wcm^{-2} [*Chem. Phys. Lett.* 2001.].

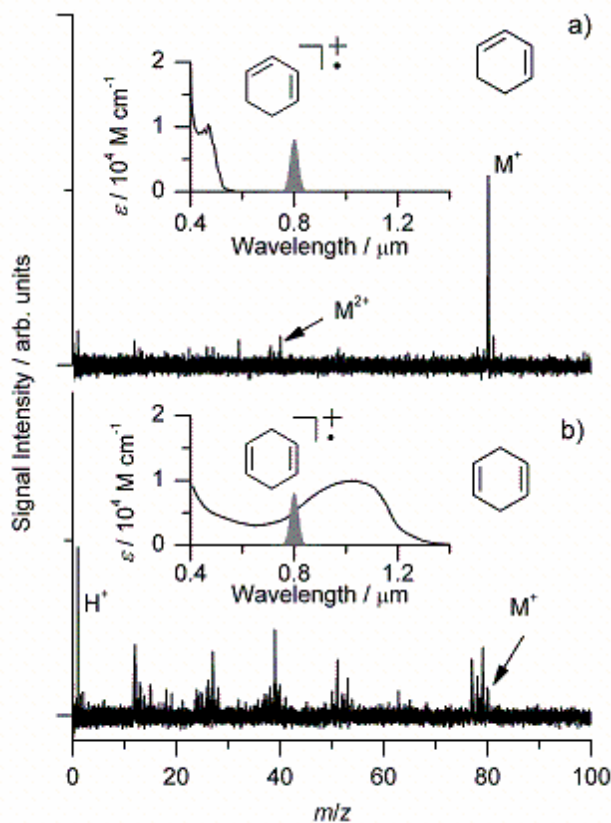


Figure 1. Mass spectra of 1,3-cyclohexadiene (1,3-CHD) and 1,4-cyclohexadiene (1,4-CHD) observed at 800 nm with a 130 fs pulse width at $0.7 \times 10^{14} \text{ Wcm}^{-2}$. The molecular ions are denoted by M^+ , and the doubly charged molecular ions by M^{2+} . 1,3-CHD⁺ is not in resonance with the laser wavelength and results in a high yield of molecular ion formation, while 1,4-CHD⁺ is resonant and results in fragmentation.

1.1.2 Molecular Ion Formation Affected by Various Pulse Parameters: Excitation Wavelength, Pulsewidth, and Laser Polarization

The most effective parameter was found to be wavelength related to resonance with the cation absorption. 2,3-Dimethyl-1,3-butadiene cation with weak intensity of the fragment ions were successfully detected by excitation at the non-resonance wavelength of 1.4 μm . On the contrary, the resonance wavelength of 0.8 μm produced many fragments, as shown in Fig.2. Shorter pulse < 30 fs and linear polarization were better to produce molecular ions at 0.8 μm . The re-scattering by the electron seemed to be minor effect for the fragmentation.

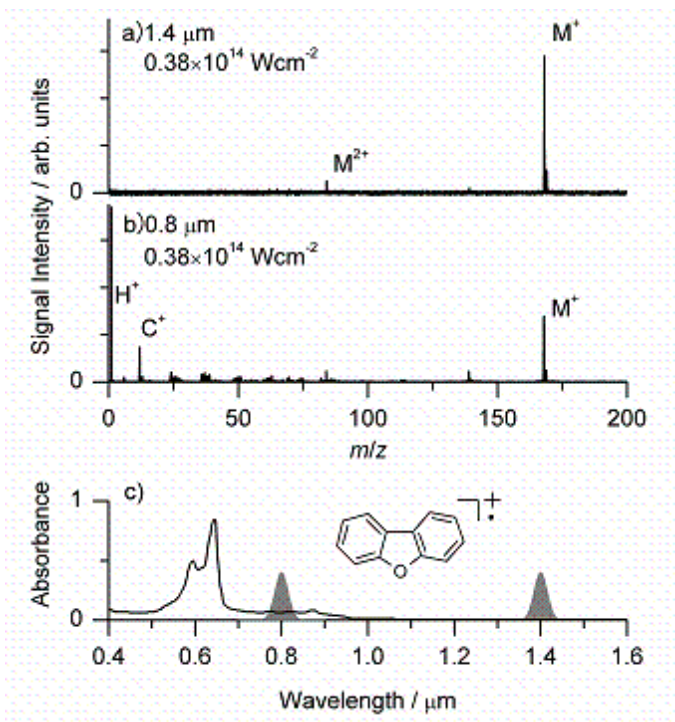


Figure 2. TOF mass spectra of 2,3-dimethyl-1,3-butadiene, by a) 1.4- μm excitation at an irradiation intensity of $1.6 \times 10^{14} \text{ Wcm}^{-2}$ and b) 0.8 μm excitation at an irradiation intensity of $1.6 \times 10^{14} \text{ Wcm}^{-2}$. The molecular ion is indicated by M^+ . The asterisk (*) indicates H_2O^+ signal. c) The absorption spectrum of DB at a low-temperature matrix. The two shaded Gaussian shapes indicate the spectra of the excitation pulses.

1.1.3 Application of FLMS to Dioxins

More than 20 chlorinated compounds including dioxins have been irradiated to produce the molecular ions. Some of them are highly toxic and may not be easily detected by the conventional multiphoton ionization method (REMPI). FLMS is viewed as an alternative method. Chlorinated dioxins have been irradiated and the molecular ions were observed with reasonably high efficiency with small amount of fragments, one of the examples is shown in Fig. 3.

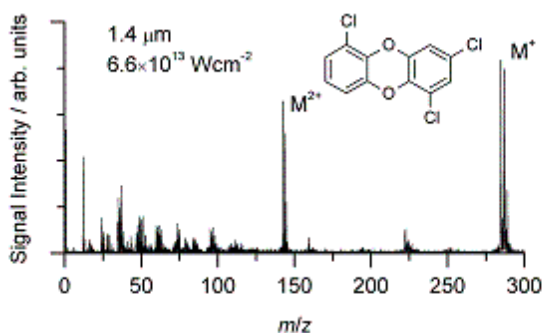


Figure 3. TOF spectra of 1,3,6-trichlorodibenzofuran ionized by 130-fs pulses. The molecular ion intensity, M^+ , was the highest. M^{2+} is the doubly charged molecular ion.

1.3 Coulomb Explosion of Organic Molecules on Irradiation with an Intense Femtosecond Laser Pulse

Coulomb explosion has been found to start in diatomic molecules at a critical internuclear distance larger than R_e , while isotropic explosions involving mega-eV particles have been observed in clusters. C_{60} and benzene can be classified as an intermediate case between two- to three-atom molecules and large clusters. Our results show that the explosion is anisotropic and has no clear critical structure. The irradiation intensity was $1\text{--}8 \times 10^{16} \text{ Wcm}^{-2}$ [*J. Chem. Phys.* 2000, 2002.]. In the case of perfluorobenzene, smooth explosion of the carbon atoms was found to be largely disturbed, because of the heavy F atoms [*Chem. Phys. Lett.* 2005.].

1.4 Multiphoton Absorption, Ionization, and Neucleation of Protein in Solution by an Intense Femtosecond Laser Pulse

High intensity chemistry in solution will be important and interesting. One of the targets is to clarify the mechanism of the neucleation. Five photon excitation was found to occur for terphenyl with 1.4 μm femtosecond pulse excitation even in solution.

2. VUV Laser Chemistry

-Formation of Hot Molecules and their Reactions in the Gas Phase-

VUV photochemistry of organic molecules in the gas phase has been studied from a novel point of view. The highly vibrationally excited state can be formed by efficient internal conversion from an electronically excited state on irradiation with a VUV laser. We call the molecule in the vibrationally excited state a "hot" molecule. The hot molecule has a narrow internal energy distribution and a high equivalent vibrational temperature up to 6000 K. Therefore, hot molecules have been good targets to study the specific reaction rate, collisional relaxation rate constants, and an intermediate of multiphoton reactions. We have studied benzenes, alkylbenzenes, olefins, etc, and have written two reviews [*J. Phys. Chem.* 1989; *Bull. Chem. Soc.* 2001.] .

Two-photon chemistry via hot molecules is interesting. We recently have succeeded in formation of 1,3-hexadiene-5-yne as a dominant photoproduct of benzene instead of fulvene for the case of two-photon hot molecule reaction. The scheme is illustrated in Fig. 4 [*J. Photochem. Photobiol. A* 2005.] .

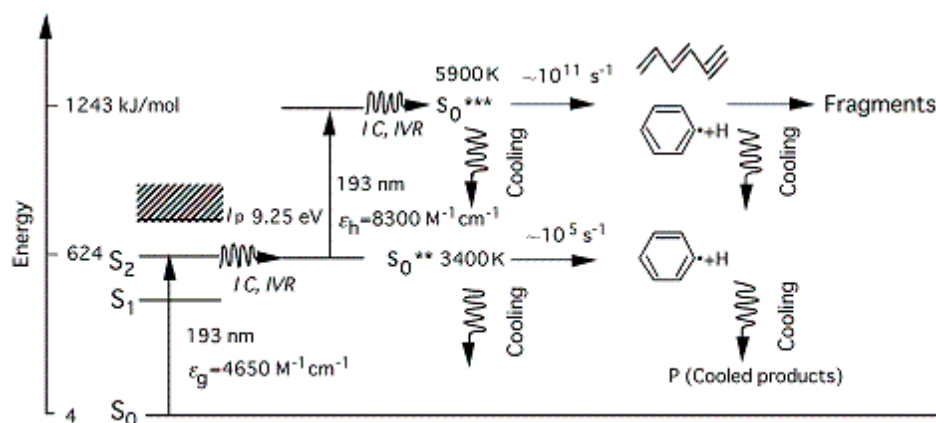


Figure 4. Two-photon reaction via hot benzene produce 1,3-hexadiene-5-yne as a dominant photoproduct. The corresponding vibrational temperature of benzene with two-photon energy of ArF laser light is evaluated to be as high as 5900 K.

2. Selected Publications

- 1."Ionization and Fragmentation of some Organic Molecules with Intense Femtosecond Laser Pulses", N. Nakashima, T. Yatsunami, M. Murakami, R. Mizoguchi, and Y. Shimada, in *Advanced in Multi-photon Processes and Spectroscopy*, the forthcoming volume, edited by S. H. Lin, A. A. Villaeys, and Y. Fujimura (World Scientific, Singapore), in press.
- 2."Ionization and Fragmentation of Anthracene with an Intense Femtosecond Laser Pulse at 1.4

μm ", M. Murakami, R. Mizoguchi, Y. Shimada, T. Yatsuhashi, N. Nakashima, *Chem. Phys. Lett.* **403**, 238-241 (2005).

3. "A Key Factor in Parent and Fragment Ion Formation on Irradiation with an Intense Femtosecond Laser Pulse", H. Harada, S. Shimizu, T. Yatsuhashi, S. Sakabe, Y. Izawa, N. Nakashima, *Chem. Phys. Lett.* **342**, 563-570 (2001).

4. "Anisotropic Coulomb Explosion of C_{60} Irradiated with a High-intensity Femtosecond Laser Pulse", J. Kou, V. Zhakhovskii, S. Sakabe, K. Nishihara, S. Shimizu, S. Kawato, M. Hashida, K. Shimizu, S. Bulanov, Y. Izawa, Y. Kato, N. Nakashima, *J. Chem. Phys.* **112**, 5012-5020 (2000).

5. "Multiphoton Reduction of Eu^{3+} to Eu^{2+} in Methanol using Intense, Short Pulses from a Ti:sapphire Laser", N. Nakashima, S. Nakamura, S. Sakabe, H. Schillinger, Y. Hamanaka, C. Yamanaka, M. Kusaba, N. Ishihara, Y. Izawa, *J. Phys. Chem.* **103**, 3910-3916 (1999).

6. "Role of Hot Molecules Formed by Internal Conversion in UV Single-Photon and Multiphoton Chemistry", (Feature Article) N. Nakashima, K. Yoshihara, *J. Phys. Chem.* **93**, 7763-7771 (1989).

7. "Laser Flash Photolysis of Benzene. VIII. Formation of Hot Benzene from the S_2 State and its Collisional Deactivation", N. Nakashima, Keitaro Yoshihara, *J. Chem. Phys.* **79**, 2727-2735 (1983).

8. "Nanosecond Laser Photolysis of Benzene Monomer and Excimer", N. Nakashima, M. Sumitani, I. Ohmine, K. Yoshihara, *J. Chem. Phys.* **72**, 2226-2230 (1980).

9. "Picosecond Flash Spectroscopy of Solvent-Induced Intramolecular Electron Transfer in the Excited 9, 9'-Bianthryl", N. Nakashima, M. Murakawa, N. Mataga, *Bull. Chem. Soc. Jpn.* **49**, 854-858 (1976).

10. "Picosecond Flash Photolysis and Transient Spectral Measurements over the Entire Visible, Near Ultraviolet and Near Infrared Regions", N. Nakashima, N. Mataga, *Chem. Phys. Lett.* **35**, 487-492 (1975).

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