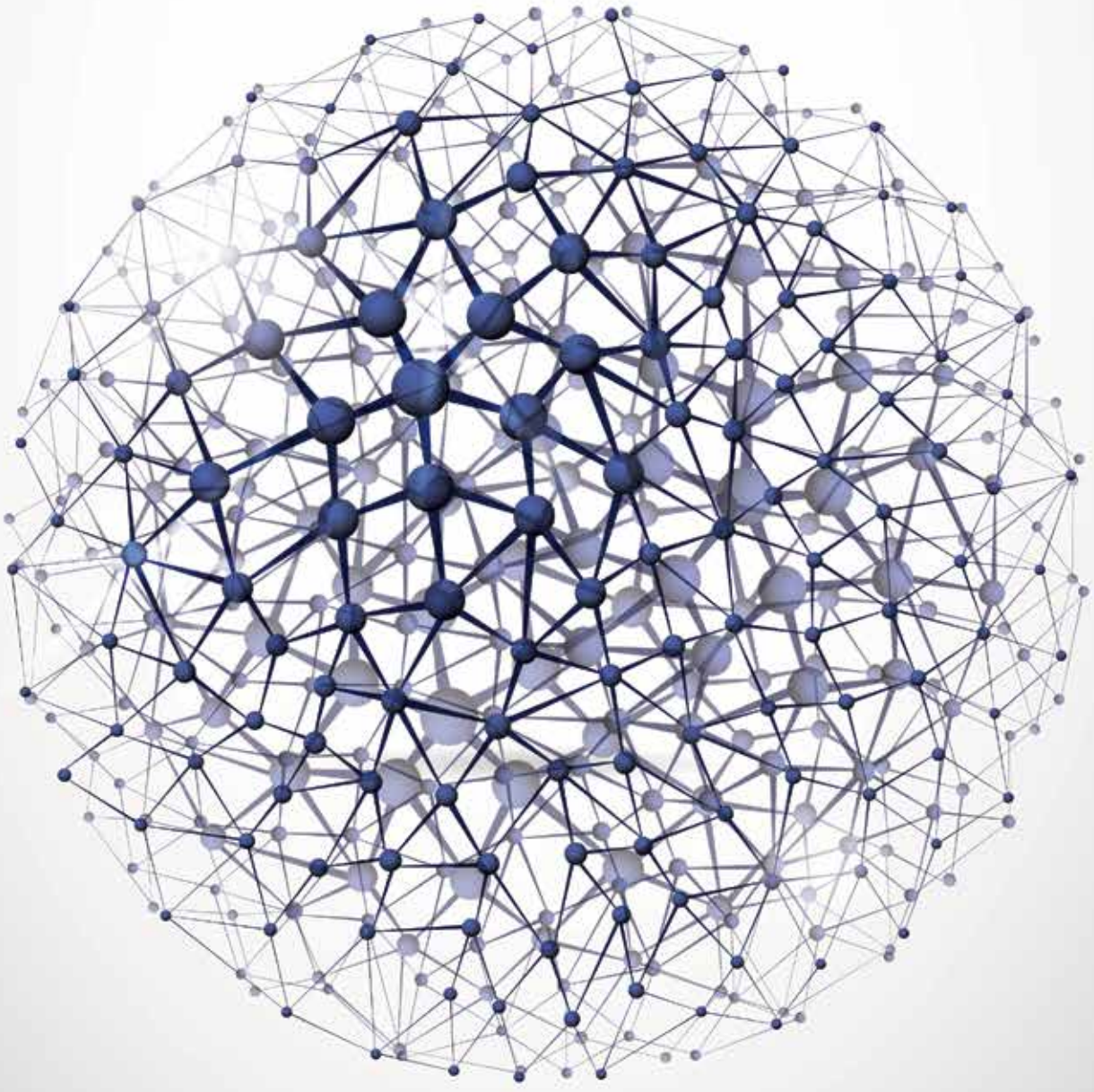
Manipulation of
Molecular Quantum States

Hirofumi Sakai



Scientia

www.scientiapublications.com

Manipulation of Molecular Quantum States

Hirofumi Sakai is associate professor and group leader at the Department of Physics, Graduate School of Science, the University of Tokyo, where he is an expert in high-intensity laser physics, and molecular optics.

How did your research begin in molecular alignment and orientation?

The starting point came with the success of the deflection of neutral molecules using the non-resonant dipole force. Deflection of neutral molecules means controlling the centre-of-mass motion of neutral molecules. This experiment was done in the National Research Council (NRC) of Canada, where I was working as a visiting researcher with Dr. Henrik Stapelfeldt and Dr. Paul B. Corkum.

Through experiments using the non-resonant induced dipole force, I came to know that the non-resonant induced dipole interaction can be used to manipulate neutral molecules, which has many applications and led to rapid progress in molecular alignment and orientation.

After realising that the non-resonant induced dipole interaction can be used to deflect molecules, I was eager to demonstrate the molecular alignment for the first time. A two-dimensional ion imaging apparatus is very useful in evaluating the degrees of alignment based on the angular distributions of the fragment ions, produced from multiply-ionised aligned molecules in a process called Coulomb explosion. At that time, Stapelfeldt, who was one of my collaborators in NRC, started work at Aarhus University, Denmark, and developed a velocity-map ion imaging spectrometer. I worked as a visiting researcher at Aarhus and we succeeded in demonstrating molecular alignment. After leaving, my colleagues there succeeded in demonstrating three-dimensional molecular alignment with an intense non-resonant elliptically polarised laser pulse.

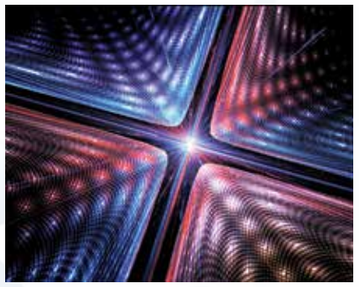
Can you tell us about how your career has progressed since then and what your new results are?

In October 1999 I moved to the University of Tokyo to develop various molecular orientation techniques. Using a theoretical proposal by Friedrich and Herschbach, our group demonstrated one and three-dimensional orientation of ordinary molecules. This was done with linearly and elliptically polarised laser fields, respectively, in a weak electrostatic field (the combined-field approach) in the adiabatic regime. Based on these results, our group proposed and demonstrated laser-field-free molecular orientation with an intense non-resonant laser field, which has a slow turn-on and a rapid turn-off in a weak electrostatic field.

Then in order to increase the degrees of orientation, we used a sample of iodobenzene molecules in their lower rotational states, which were selected by our homebuilt molecular deflector. By applying the plasma shutter technique, we achieved laser-field-free orientation of state-selected asymmetric top molecules. More recently, we have achieved laser-field-free three-dimensional orientation of state-selected asymmetric top (3,4-dibromothiophene) molecules, with an elliptically polarised laser field. This accomplishment marks the acme of molecular orientation techniques based on the combined-field approach because all the desired requirements, such as laser-field-free condition, three-dimensional control and higher degrees of orientation, were successfully achieved. From here we want to develop a novel method to efficiently orient gaseous molecules at higher densities, above $10^{17}cm^{-3}$, and higher rotational temperatures, above 10 Kelvin.

Why were state-selected asymmetric top iodobenzene molecules used in your experiments?

In general, molecular orientation is much more difficult than molecular alignment. The reason for the additional difficulty is that molecules in their initial rotational states are oriented in different directions. In order to overcome this to increase the degree of orientation, it is useful to select molecules in lower rotational states using the molecular deflector we developed. We used state-selected asymmetric top iodobenzene molecules as a sample. The reason for using asymmetric top molecules as a sample is that an asymmetric top molecule is the most general



molecule in the classification based on the magnitude of the moment of inertia.

What other research avenues are you exploring in molecular alignment and orientation?

As an alternative molecular orientation technique, our group has proposed and demonstrated all-optical molecular orientation with an intense non-resonant two colour laser field in the adiabatic regime. The technique relies on the combined effect of the anisotropic hyper-polarisability interaction as well as the anisotropic polarisability interaction. By employing state-selected molecules as a sample and by operating the plasma shutter at the peak of the two-colour pump pulse, completely field-free molecular orientation with higher degrees of orientation will be achieved just after the rapid turn-off of the pump pulse.

What is perhaps the most interesting immediate application of your research?

It is said that "seeing is believing" and many researchers are now interested in making "molecular movies" with X-ray free electron laser radiation to understand ultrafast structural dynamics in laser-molecule interactions. Molecular movies are made from many frame-by-frame X-ray photoelectron diffraction patterns from a sample of aligned/oriented molecules using X-ray free-electron laser pulses.

Rapid Laser Switch-off Leaves Molecules well Orientated

Hirofumi Sakai of the University of Tokyo covers new ground in molecular orientation using combined field techniques, pulse shaping and in-house equipment that he and his group have pioneered.

MOLECULAR ORIENTATION

Hirofumi Sakai is Associate Professor at the Department of Physics, Graduate School of Science, the University of Tokyo. Sakai's group undertakes fundamental research into a wide range of atomic and molecular physics, and quantum optics, with a focus on controlling quantum processes in atoms and molecules. In particular, they research high-intensity laser physics by studying nonlinear and ultrafast phenomena, laser control of ultrafast dynamics using shaped pulses, and imaging the structure and dynamics of molecules. In addition, they aim to "film" so-called molecular movies by means of X-ray photo-electron diffraction. The subject of their most recent research is the development of a laser-field-free technique for the alignment and orientation of asymmetric top iodobenzene molecules. Their approach to state-selected asymmetric top molecules has wide implications, as this field produces the most modern and important applications stemming from quantum physics.

The field of molecular alignment and orientation has been advancing in recent years, with established and innovative techniques that are reaching greater efficiencies and finding novel applications. The goal of molecular alignment and orientation is to manipulate an ensemble of molecules with the use of lasers and electric fields, and to rotate them so that they are lined up along the same axis. Molecular alignment is the condition where the molecules are aligned along the same axis, so some fraction of the molecules will be facing in the opposite direction. Greater control is exhibited in molecular orientation – as opposed to molecular alignment – because the molecules, as well as being aligned, will also be pointing in the same direction.

It all started for Sakai when he was working as a visiting researcher at the National Research Council, Canada, with Dr. Stapelfeldt and Dr. Corkum, on non-resonant manipulation of neutral molecules. It was there he realised that an induced dipole interaction can be used to deflect molecules, and he has since worked in this area with great interest.

NEW RESULTS

In Sakai's recent work he experimentally demonstrated the orientation of iodobenzene molecules, which have the chemical formula C_6H_5I, and possess a benzene ring structure substituted with a single, large iodine atom. The ensemble of iodobenzene molecules was originally primed for orientation by being prepared in particular rotational states by a molecular deflector that was built by Sakai and his group, which filtered out lower-lying rotational states that are easier to orientate. Lower-lying rotational states of molecules have lower rotational energies and are near the ground state.

According to Sakai, one of the reasons for choosing iodobenzene is that this molecule has "a larger anisotropic polarisability, which leads to a larger induced dipole moment, making it relatively easy to handle". In other words, the molecule is polarised, having one electrically positive end and one negative end. The more pronounced the polarisation is, the easier it is for an electric field to get a better grip and rotate the molecule into the desired orientation.

Molecular orientation is induced by an intense nanosecond laser field in a weak electrostatic filed, which is called a combined field approach. Rapidly switching off the laser field leaves the molecules in a laser-field-free state of orientation. The rapid switch-off is done by customising the shape of the laser profile using a plasma shutter technique. Sakai explains that this works with two lasers used together: "a femtosecond Ti:sapphire pulse and a nanosecond Nd:YAG pulse are collinearly focused onto an ethylene glycol jet sheet with a thickness of 50 micrometers. The intense Ti:sapphire pulse triggers the plasma formation at the peak of the YAG pulse. After that, the YAG pulse cannot pass through the plasma so it gets rapidly switched-off, in a falling time of approximately 150 femtoseconds". In other words, as the two parallel lasers are focused onto the jet sheet, the Ti:sapphire rapidly produces a plasma from the sheet that is opaque to the Nd:YAG laser, forcing it to rapidly switch-off in 150 femtoseconds, or 150×10^{-15} seconds, leaving the iodobenzene molecules in a laser-field-free state.

Once the molecules are in a laser-field-free state, they are still being oriented for a while in a dephasing time of 5–10 picoseconds, or $5–10 \times 10^{-12}$ seconds. Although this is an incredibly short period of time, it is actually a long time for molecules to be orientated under these conditions, and almost one hundred times longer than it took to rapidly turn the laser off.

The degree of molecular orientation of the whole ensemble, and the dephasing time taken by the molecules to jostle out of orientation, were measured in an interesting way using Coulomb explosion of the molecules which was detected by a two-dimensional ion imaging detector. This was done with an intense femtosecond probe pulse that was fired into the orientated ensemble to ionise the molecules in a way that caused the component iodine atoms to undergo an explosive electric repulsion from the molecular ions. The positive iodine atoms were accelerated towards a sensitive, two-dimensional detector and the image on the detector was recorded by a CCD camera. The detection position of the iodine ions was used to build up a "molecular map" that shows how the molecules are aligned or oriented by where the ions impact and cluster on the detector. The map will correspond directly to where the iodine atoms are inside the iodobenzene molecules. For a well-orientated ensemble, iodine atoms will be in the same relative positions in the sample of orientated iodobenzene molecules. The iodine atoms can be clearly distinguished from other molecular fragments from the Coulomb explosion, by their longer time of flight due to their comparatively large mass. Using experimental data, Sakai and his team calculated a maximum value of 0.68 out of 1 for the ensemble orientation which shows high orientation.

This is the state of the art in the combined field approach to molecular alignment and orientation.

ORIENTATION TOWARDS THE FUTURE

Altogether, by judiciously choosing the right parameters, such as the pulse shape and intensity of the laser-field, the strength of the electrostatic field, the initial rotational states prepared by the homebuilt deflector, and a number of other important parameters, Sakai and his team will finely tune their apparatus to prepare a better orientated ensemble of iodobenzene molecules.

More recently, and using similar techniques to those that were used here, Sakai and his team have demonstrated three-dimensional orientation of state-selected asymmetric top molecules, this time using 3,4-dibromothiophene molecules, in a laser-field-free state with an elliptically polarised laser and a weak electrostatic field. This is the state of the art in the combined field approach to molecular alignment and orientation.

These results will be of great interest to those working in chemical stereodynamics, where chemical reaction rates that depend on the spatial orientation of molecules are studied. There are many more important areas of research that can benefit from these techniques, such as high-order harmonic generation, non-sequential double ionisation, hot above-threshold ionisation, and two-electron excitation. An interesting and recently considered application is making “molecular movies” using X-ray photo-electron diffraction, for the purposes of displaying molecular dynamics in real-time that can be watched just like a movie. Being able to watch molecular movies may give confirmation and new insights into molecular dynamics. As Sakai has carried out research in these areas, he and his group are well placed to make breakthrough contributions.

Researcher Profile

Dr. Hirofumi Sakai
Department of Physics, Graduate School of Science
The University of Tokyo, Japan

Dr. Hirofumi Sakai is Associate Professor at the University of Tokyo, Japan, and specialises in experimental studies of quantum optics and atomic/molecular physics, the papers of his group in Tokyo gathering worldwide attention and about 1300 times of citations. He received his Ph.D. in science from the University of Tokyo in 1994, after which he remained to continue his research career in quantum optics and atomic and molecular physics. His research interests include the ultrafast-laser control of molecular quantum processes, nonlinear high-intensity laser physics and ultrafast atomic and molecular phenomena.

CONTACT

E: hsakai@phys.s.u-tokyo.ac.jp
T: +81 3 5841 8394
W: http://www.s.u-tokyo.ac.jp/en/lp/sakai_hirofumi/
W: http://www.amo-phys-s-u-tokyo.jp/en/

KEY COLLABORATORS

Prof. Paul B. Corkum, University of Ottawa and National Research Council of Canada, Canada
Prof. Henrik Stapelfeldt, Aarhus University, Denmark
Prof. Eric Constant, Université de Bordeaux, France
Prof. Jakob Juul Larsen, Aarhus University, Denmark
Dr. C. P. Safvan, Inter University Accelerator Centre, India
Dr. Shinichirou Minemoto, The University of Tokyo

Acknowledgements to all the graduate students for molecular orientation and other related studies at the University of Tokyo

FUNDING

Japan Society for the Promotion of Science (JSPS)
Ministry of Education, Culture, Sports, Science, and Technology (MEXT)

REFERENCES

J. H. Mun, D. Takei, S. Minemoto and H. Sakai, Laser-field-free orientation of state-selected asymmetric top molecules, Phys. Rev. A, 2014, 89, 051402(R).

K. Oda, M. Hita, S. Minemoto and H. Sakai, All-optical molecular orientation, Phys. Rev. Lett., 2010, 104, 213901.

A. Goban, S. Minemoto and H. Sakai, Laser-field-free molecular orientation, Phys. Rev. Lett., 2008, 101, 013001.

H. Tanji, S. Minemoto and H. Sakai, Three-dimensional molecular orientation with combined electrostatic and elliptically polarized laser fields, Phys. Rev. A, 2005, 72, 063401.

S. Minemoto, H. Nanjo, H. Tanji, T. Suzuki and H. Sakai, Observation of molecular orientation by the combination of electrostatic and nonresonant, pulsed laser fields, J. Chem. Phys., 2003, 118, 4052.

H. Sakai, S. Minemoto, H. Nanjo, H. Tanji and T. Suzuki, Controlling the orientation of polar molecules with combined electrostatic and pulsed, nonresonant laser fields, Phys. Rev. Lett., 2003, 90, 083001.

SCHOOL OF SCIENCE
THE UNIVERSITY OF TOKYO