

# Design and Reconstruction of Molecular Quantum States of Motion

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Molecules are vital existence. In a gas-phase ensemble at room temperature, they are, in an average, flying away by a few hundred meters, making turns almost reaching to  $10^{11}$  times, and shaking themselves more than  $10^{13}$  times within the duration of only one second. The ultimate goal this research group has been aiming to is to capture the lively figures of molecules moving in such a dynamic manner and to have a perfect command over the molecular motions. Here lasers with ultimate resolution in time and energy domains are employed complementally and cooperatively for this purpose.

## 1. Nonadiabatic Excitation of Molecular Rotation Induced by Intense Ultrashort Laser Fields

When a gaseous molecular sample is irradiated by an intense nonresonant ultrashort laser pulse, the laser field exerts a torque that aligns the molecular axis along the laser polarization vector, due to the interaction with the molecular anisotropic polarizability. Here the field-matter interaction only remains in much shorter duration than the characteristic time for molecular rotation, and thus the rotation of the molecules is coherently excited to create a rotational quantum wave packet (WP). We have developed a method to explore the nonadiabatic excitation in a quantum-state resolved manner and applied it to diatomic and symmetric-top molecules.<sup>1)</sup> It has been shown that the state distribution is a useful experimental source for verifying the excitation process.<sup>2,3)</sup> When a pair of excitation pulses is implemented with appropriate time delay between them, partial control of rotational-state distribution has been achieved.<sup>1,4)</sup> In a favorable case, the double-pulse excitation coupled with the state-selective probe has enabled us to reconstruct experimentally a rotational WP thus created.<sup>5)</sup> If the mutual polarization direction and time delay between the two pulses are adjusted, the sense of rotation around the laser propagation direction can also be controlled, yielding to a rotational WP

exhibiting angular-momentum orientation.<sup>6,7)</sup>

## 2. Coherent Excitation of Intermolecular Vibrations in Molecular Clusters by Nonresonant Intense Ultrashort Laser Fields

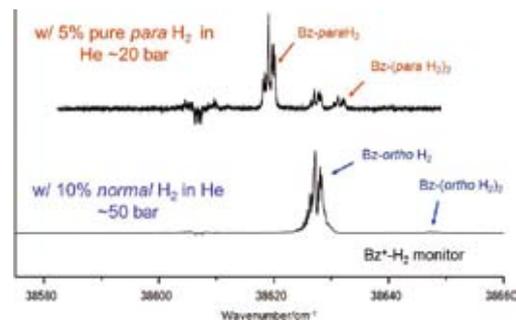
Nonadiabatic interaction with a nonresonant intense ultrashort laser field can also coherently excite vibration of molecule through the structural dependence of the molecular polarizability. We have recently succeeded in creating and observing WPs pertinent to intermolecular vibrations of several molecular clusters in their electronic ground states. So far, NO-Ar, benzene dimer and trimer have been studied. Here, vibrational distribution after nonadiabatic vibrational excitation (NAVEX) is probed in a quantum-state resolved manner. By monitoring the resonant two-photon ionization (R2PI) spectra, substantial decrease of the transition from the vibrationally ground state has been clearly observed when the femtosecond (fs) pump pulse was applied, and in the case of NO-Ar, the observation was accompanied with the emergence of several hot bands, assigned to those from vibrationally excited states pertinent to intermolecular modes. The double fs pulse excitation has also been implemented for examining the real-time quantum interference of the WPs. The observed time-domain signals for NO-Ar were directly compared with the calculation on the WP propagation by numerically solving the time-dependent Schrödinger equation on the intermolecular potential energy surface. For more detailed examination of the NAVEX process and further application to various molecular cluster systems, we are now renovating the experimental setup, in particular, the molecular beam time-of-flight mass spectrometry (TOF-MS) apparatus. The modification includes: Improvement of mass resolution by extending the TOF flight tube, rejection of the interference of strong monomer signals by implementing a mass gate, and realization of more extensive cooling by enlarging the vacuum pumping capabilities.

### 3. High-Resolution Laser Spectroscopy of Benzene Clusters with Atoms and Small Molecules

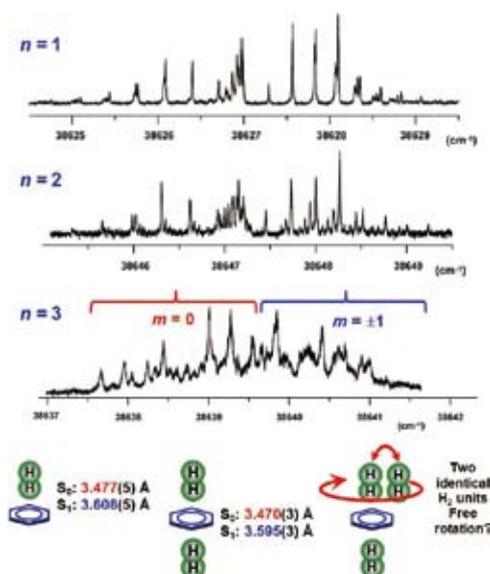
Molecular clusters containing benzene are prototypical systems for elucidating the intermolecular interaction pertinent to aromatic rings. The information on the precise cluster geometry and energy-level structure pertinent to the intermolecular vibration are useful experimental input to reconstruct the intermolecular potential energy surface. We are now focusing on clusters of benzene attached by small numbers of atoms and molecules. So far, electronic spectra of  $C_6H_6$  complexed with one and two He atom(s), two Ar atoms, up to three  $H_2$  molecules, and one  $H_2O$  molecule have been examined via two-color R2PI in the vicinity of the monomer  $S_1-S_0$   $6_0^1$  band. We employed a tripled output from a ns pulsed dye amplifier, which was injection-seeded by the CW output from a Ti:Sapphire laser, as an excitation source. Owing to the narrow band width ( $\sim 250$  MHz) of the laser system and the efficient rotational cooling down to 0.3 K by implementing a high-pressure pulsed valve, rotational structures have been greatly simplified.

Structural parameters of the clusters with He have been substantially refined than those reported previously.<sup>8)</sup> The distances of He above the plane are set to be: 3.602 (+0.063) Å and 3.596 (+0.057) Å, respectively, for the clusters with one and two He atoms, where values in parentheses represent the change by the excitation from  $S_0$  to  $S_1$ . Several vibronic bands with excitation of intermolecular vibrations have also been observed. The vibrational frequencies of benzene( $S_1$ )–He are derived as: 17 and 13  $cm^{-1}$  for the intermolecular stretch and bend modes, respectively. The intermolecular stretch of the cluster with two He is 15.72  $cm^{-1}$ , while no experimental information has been obtained for the bend modes. The vibronic bands of benzene–He exhibit tunneling splitting due to a large-amplitude migration of He above and below the benzene molecular plane. This finding is matched with the prediction based on a high-level *ab initio* calculation. We have also recorded the R2PI spectrum of mono  $^{13}C$  substituted species of benzene–He.

For the clusters with  $H_2$ , two distinguished isomers, correlating to *para* and *ortho*  $H_2$ , are identified. This finding shows that the permutation of the two H atoms in  $H_2$  is feasible in the clusters. When the *normal*  $H_2$  was used as a sample gas, only the clusters of *ortho*  $H_2$  were observed, and thus we had to use a gas sample of pure *para*  $H_2$  to record the clusters with *para*  $H_2$  (see Figure 1). This observation indicates the smaller effective binding energy for benzene–*para*  $H_2$  than that of the *ortho*  $H_2$  cluster. This energy relation has been well known for the clusters with smaller molecules (*e.g.*, HF, HCl, and OCS) attached by  $H_2$ . It is noted the present study is the first experimental report on the coexistence of *para* and *ortho*  $H_2$  isomers in the clusters of aromatic molecules. Rotationally resolved spectra allowed us to fix the cluster geometry unambiguously, as shown in Figure 2. It has shown that the effective intermolecular distances are substantially different from each other between the clusters with *para* and *ortho*  $H_2$ , indicating the change in the average  $H_2$  orientation relative to the benzene plane in the two isomers.



**Figure 1.** Excitation spectra of  $C_6H_6-(H_2)_n$  recorded with the *normal*  $H_2$  sample (bottom) and the pure *para*  $H_2$  sample (top).



**Figure 2.** High-resolution excitation spectra and the experimentally derived cluster geometry of  $C_6H_6-(ortho H_2)_n$ .

We also recorded for the first time rotationally resolved excitation spectrum of the cluster with two Ar atoms lying on the same side of the benzene plane.

#### References

- 1) Y. Ohshima and H. Hasegawa, *Int. Rev. Chem. Phys.* **29**, 619–663 (2010).
- 2) H. Hasegawa and Y. Ohshima, *Phys. Rev. A* **74**, 061401 (4 pages) (2006).
- 3) H. Hasegawa and Y. Ohshima, *Chem. Phys. Lett.* **454**, 148–152 (2008).
- 4) D. Baek, H. Hasegawa and Y. Ohshima, *J. Chem. Phys.* **134**, 224302 (10 pages) (2011).
- 5) H. Hasegawa and Y. Ohshima, *Phys. Rev. Lett.* **101**, 053002 (4 pages) (2008).
- 6) K. Kitano, H. Hasegawa and Y. Ohshima, *Phys. Rev. Lett.* **103**, 223002 (4 pages) (2009).
- 7) Y. Khodorkovsky, K. Kitano, H. Hasegawa, Y. Ohshima and I. Sh. Averbukh, *Phys. Rev. A* **83**, 023423 (10 pages) (2011).
- 8) S. M. Beck, M. G. Liverman, D. L. Monts and R. E. Smalley, *J. Chem. Phys.* **70**, 232–237 (1979).