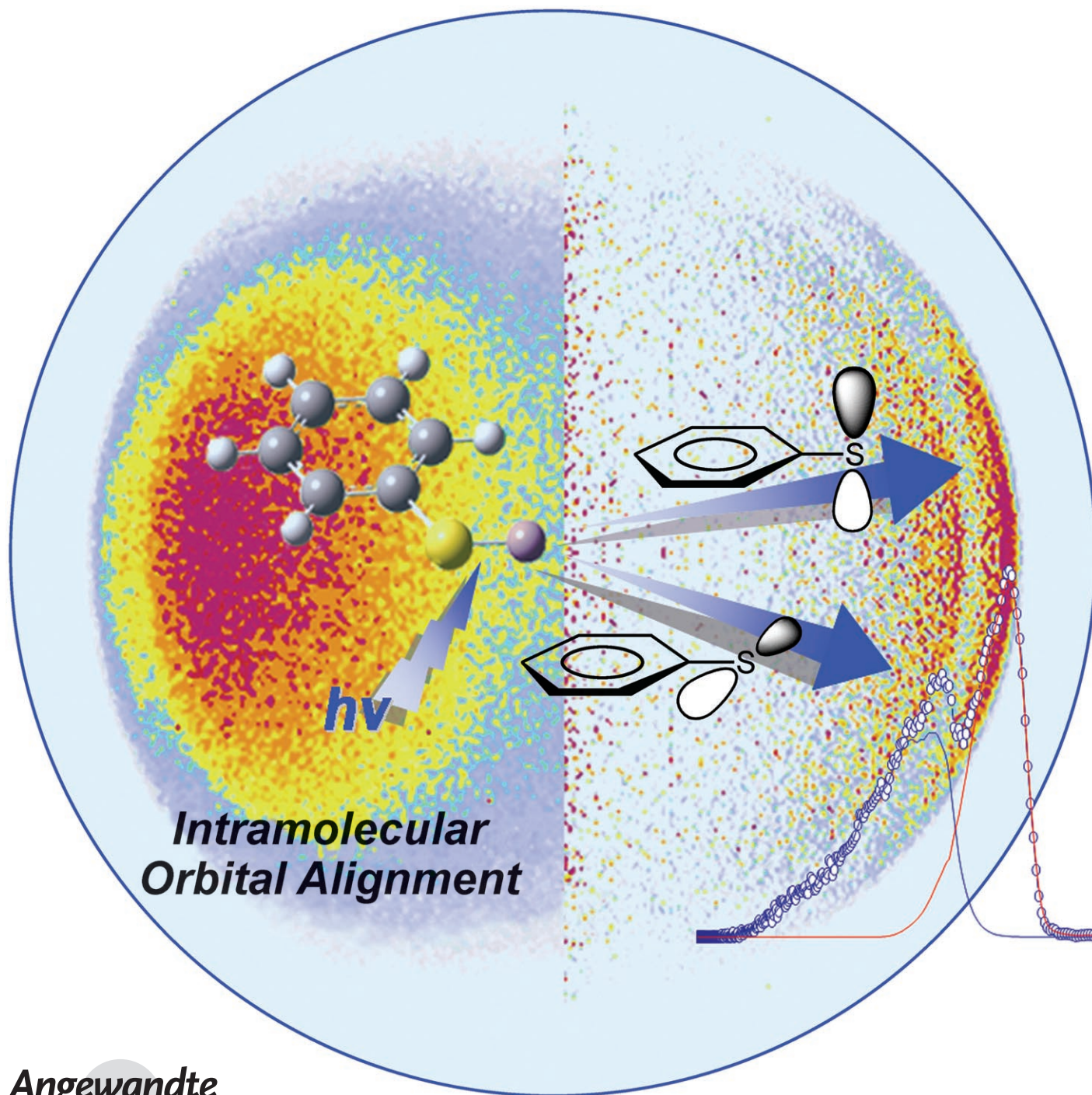


Intramolecular Orbital Alignment Observed in the Photodissociation of [D₁]Thiophenol**

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One of the most active topics in stereodynamics is the orientation and alignment of molecules with respect to the laboratory or recoil frame. Steric effects have long been recognized as an important factor for the explanation of the experimentally measured rate constants with theoretical models based on the simple version of collision theory. The basic concept behind the steric factor is that the chemical reactivity in bimolecular reactions is significantly affected by the relative orientation of the reactants at the moment of collision.

Brilliant experiments have been carried out^[1–11] to demonstrate the molecular alignment, and excellent review articles in the area of chemical dynamics have appeared.^[12–20] In particular, a major effort has gone into the development of experimental and theoretical tools for the alignment of reactants in the laboratory frame. One of the most commonly utilized tools is based on the manipulation of the nuclear framework in the laboratory-fixed axes, which arise from the interaction of the molecular permanent (or transition) dipole moments with an external electric (or optical) field.^[8] A typical example is the collision between a free metal atom and an oriented symmetric-top molecule, such as potassium or rubidium atoms and oriented methyl iodide.^[9,14] In that case, one obtains a different yield according to the orientation of the symmetric-top molecule, which enables one to explore stereoselective chemistry in terms of the chemical shape.^[17]

A conceptually different kind of alignment is known for open-shell systems.^[10–13] In this case, the electronic orbital is aligned either in the laboratory or recoil frame subsequent to the reactive (or inelastic) collision, photodissociation, or gas-surface collision. Typically, diatomic molecules have been subjected to such experiments.^[10,11] For example, the relative population in Λ -doublet states of diatomic fragments such as $\text{OH}(\dots\sigma^2\pi^3;X^2\Pi)$, $\text{NO}(\dots\sigma^2\pi^1;X^2\Pi)$, and $\text{NH}^*(\dots\sigma^1\pi^3;c^1\Pi)$ have been used as a clue for determining the planarity of the photodissociation process. This is attributed to the fact that the singly occupied molecular orbital (SOMO) in the classical limit is either parallel or perpendicular to the rotating plane.^[11]

As an extension, one may consider a rather different case of orbital alignment. Here, one recognizes and maintains the essential ingredients of the recoil frame orbital alignment with the exception of the reference frame with respect to

which the orbital alignment is achieved. In other words, one introduces a frame of reference within the molecule so that an intramolecular orbital alignment is achieved on the molecular frame defined by symmetry. As the orbital alignment is genuinely provided and maintained within the molecule, one eliminates the need to work with rotating planes. One of the easiest examples of such cases is hydrogen-abstracted planar aromatic radicals. These species have been known to exist in so-called π and σ structures,^[21] which arise from the relative orientation of the SOMO with respect to the molecular plane defined by the benzene moiety. However, there is no report of experimental generation of such orbital-aligned species because an experimental observation of electronically forbidden transitions is difficult.^[22]

Herein, we investigate the deuterium-detachment photodissociation of jet-cooled $[\text{D}_1]$ thiophenol ($\text{C}_6\text{H}_5\text{SD}$) by the velocity map ion imaging technique using the (2+1) ionization of D at 243.0 nm. The speed and angular distribution of the nascent D fragment provide the first experimental observation for the photoinduced products of phenylthiyl radical ($\text{C}_6\text{H}_5\text{S}$) species. Through our theoretical work we show that these radical species are characterized by the relative orientation of the SOMO with respect to the molecular frame.

The raw and reconstructed images of the photodissociated deuterium ion are shown in Figure 1. A detailed description of the experimental setup and data analysis was reported

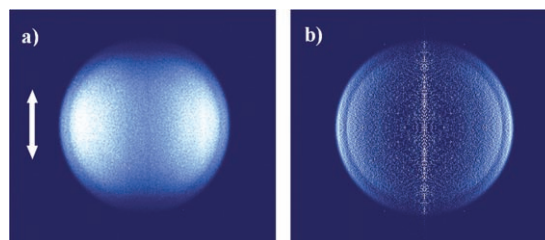


Figure 1. a) 2D projection of the raw 3D distribution and b) the central slice of the reconstructed 3D distribution of the deuterium ion from the photodissociation of $\text{C}_6\text{H}_5\text{SD}$ at 243.0 nm. The vertical arrow indicates the polarization of the pump laser pulse.

earlier.^[23] Both images consisting of two energy distributions give rise to two peaks in the total translational energy distribution which are located at 24.7 and 32.4 kcal mol⁻¹, respectively (Figure 2). The corresponding anisotropy parameters, β , are -1 and -0.76 for the respective large and small total translational energies.^[24] It is inferred that the observed peaks arise from two different quantum states of phenylthiyl radical which may be reached by at least two distinct dissociation pathways. The observation of two different quantum states are clearly supported by the deconvoluted translational energy distribution plot shown in Figure 2, which was obtained using Equation (1), where $\beta(E)$ is the anisotropy parameter as a function of the translational energy E , $P_1(E)$ and $P_2(E)$ represent the population of the D fragment belonging to $\beta = -1$ and $\beta = -0.76$ channels, respectively, with $P_1(E) + P_2(E) = 1$.

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[**] This research was supported by the Pure Basic Science Research Groups of Korea Research Foundation (KRF-2005-070-C00063), CNMM of KIMM (M102KN010010-05K1401-01010), and the Supercomputing Center of KISTI.

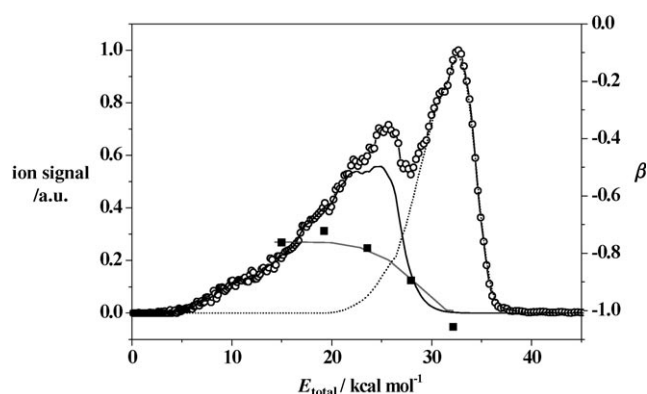


Figure 2. Plot of the total translational energy (E_{total}) distribution and the anisotropy parameter, β . The plot shows the overall distribution (\circ), deconvoluted $\tilde{X}(B_1)$ state (\cdots), and $\tilde{A}(B_2)$ state (—) of the C_6H_5S radical. The averaged anisotropy parameter (β : \blacksquare) is plotted versus the transitional energy. The fit using Equation (1) is shown as a gray line.

$$\beta(E) = (-1.00)P_1(E) + (-0.76)P_2(E) \quad (1)$$

Our multireference ab initio calculation revealed that there are indeed two close-lying electronic states of the phenylthiyl radical which correspond to the ground state, $\tilde{X}(B_1)$, and the first excited state, $\tilde{A}(B_2)$, separated by 2674 cm^{-1} , as determined at the CASPT2 (complete active space second-order perturbation theory) level in agreement with the experimental value of $2605 \pm 84 \text{ cm}^{-1}$. As shown in Figure 3, the essential difference between the radical species arises from the relative orientation of the SOMO with respect to the benzene moiety that defines the molecular plane. The $\tilde{A}(B_2) \leftarrow \tilde{X}(B_1)$ transition is essentially a promotion of an electron from the nonbonding $\sigma(\text{HOMO}-1)$ orbital to the nonbonding $\pi(\text{SOMO})$ orbital of the ground state. This transition results in an energetic promotion of the in-plane nonbonding orbital and a corresponding demotion of the out-

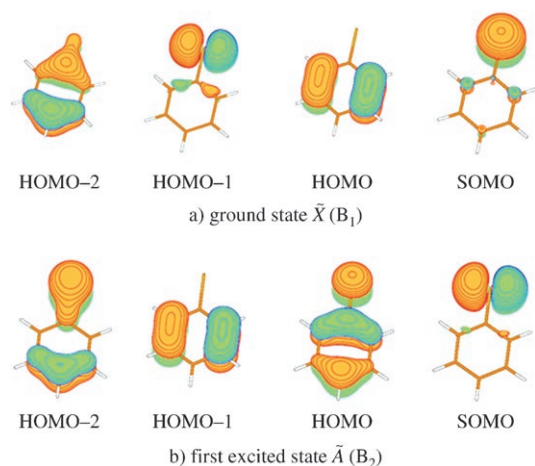


Figure 3. Natural orbitals obtained in a CASSCF(6,6) calculation for the singly occupied (SOMO) and highest doubly occupied molecular orbitals (HOMO), the second HOMO (HOMO-1), and the third HOMO (HOMO-2) of a) the ground state and b) the first electronically excited state of the phenylthiyl radical.

of-plane orbital, which gives the in-plane SOMO for the excited state. During this process the partially bonding $\pi(\text{HOMO}-2)$ orbital of the ground state participates and gives rise to the bonding $\pi(\text{HOMO}-2)$ and antibonding $\pi^*(\text{HOMO})$ orbitals of the excited states. In similar fashion to other hydrogen-detachment reactions of planar aromatic systems such as phenol,^[26] there is a crossing of the potential energy curves (PECs) which leads to these two electronic states of the radical along the S-D dissociation coordinates owing to symmetry conservation. Although such an energetic ordering was predicted almost three decades ago,^[25] the experimental observation in a photodissociation process is given here for the first time.

More striking, however, is the indication that the SOMOs of the phenylthiyl radical in both states are largely localized on the sulfur atom and show little π interaction with the adjacent benzene moiety, as depicted in Figure 3. These nonbonding SOMOs, therefore, maintain to a large degree the characteristics of the corresponding atomic p orbitals on sulfur whose relative orientation gives rise to either a perpendicular $\pi(p_x)$ or a parallel $\sigma(p_y)$ orbital alignment with respect to the molecular plane for the respective $\tilde{X}(B_1)$ and $\tilde{A}(B_2)$ state of the phenylthiyl radical. In contrast to the Λ -doublet species for which the orbital alignment is defined according to the virtual plane induced by a nuclei rotation, the present case reveals a situation where an orbital alignment occurs naturally as photodissociation products result from an electronic excitation (Figure 4). The chemical significance of

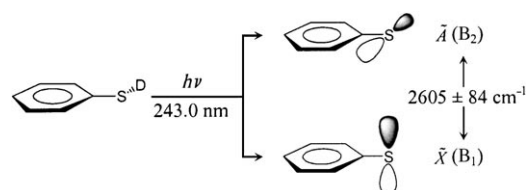


Figure 4. The two close-lying electronic states of the phenylthiyl radical corresponding to the ground and first excited states.

this case lies in the expectation that the molecular-frame-aligned orbital may present a reactive center with atomic-orbital-like characteristics. This may lead to stereoselective chemical reactivity, thus introducing a new stereodynamic feature in chemical reactions. The orbital aligned with respect to the molecular frame can make experimental investigation of stereospecific dynamics quite simple because no laboratory-frame alignment or orientation is necessary.

In conclusion, we have presented an example of a novel case of orbital alignment for the phenylthiyl radical generated by the photodissociation of thiophenol. Clear directionality with well-defined alignment of the orbital makes the present case stand out from the so-called π and σ structures of similar planar aromatic systems.^[26] A small energy difference between the $\tilde{X}(B_1)$ and $\tilde{A}(B_2)$ states of the C_6H_5S radical suggests that the lifetime of the upper state should be long enough for further chemical reactions. Whether or not the intramolecular orbital alignment of the phenylthiyl radical will affect the chemical reactivity will be an important

question, for instance, in bimolecular reactions. It will also be interesting to investigate the effect of orbital alignment in terms of the molecular structure and reactivity upon complexation of the phenylthiyl radical with a metal. A detailed theoretical investigation on the photodissociation dynamics of thiophenol is underway, and the results will be reported soon. This will serve as a guide in the controlled production of molecule-frame orbital-aligned radical species by, for example, tuning the excitation wavelength.

Experimental Section

[D₁]Thiophenol (> 80%) was mixed with He to be expanded into vacuum through a nozzle orifice with a backing pressure of 3 atm. The wavelength of the pump/probe laser pulse ($\Delta t \approx 5$ ns) was continuously scanned over the entire Doppler width of the D fragment while the corresponding image was being taken. The image was averaged over 36000 laser shots. The three-dimensional image was reconstructed by using the BASEX algorithm.^[27]

Received: May 18, 2006

Keywords: ab initio calculations · deuterium · molecular orbitals · photodissociation · radicals

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