

Theoretical Study on Molecular Excited States and Chemical Reactions

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Molecules in the excited states show characteristic photo-physical properties and reactivity. We investigate the molecular excited states and chemical reactions which are relevant in chemistry, physics, and chemical biology with developing the highly accurate electronic structure theory. We are also interested in the excited-state dynamics and energy relaxation so that we also develop the methodology of large-scale quantum dynamics. In this report, we report our recent studies on the inner-shell spectroscopy^{1,2)} and catalytic reaction.³⁾

1. Theoretical Study of the Vibration-Induced Suppression of Valence-Rydberg Mixing¹⁾

The vibrational wave function of a molecule is spatially more spread out when the molecule has one or more quanta of vibrational excitation. Thus spectroscopic studies of vibrationally excited molecules can be used to probe different regions of the potential surfaces of electronically excited states. In this work, we examine that vibrational excitation of the electronic ground state significantly affects the amount of valence character observed in the Rydberg series in the x-ray absorption spectrum of N₂O. In the O1s x-ray absorption spectrum of ground state N₂O, the ns σ Rydberg series appears with significant intensity due to a mixing of σ^* valence character in the Rydberg states. But, the excitation of the Rydberg states is significantly suppressed for ground state molecules in excited bending-mode vibrational states.

Figure 1 compares the initial-state specific ARIY (Angle-Resolved Ion Yield) spectra in the vicinity of the O 1s ionization threshold. The absorption spectra were observed at 300/700 K and the vibrationally excited absorption spectrum was extracted assuming the Boltzmann distribution. A key finding is that the intensity of the ns σ Rydberg series and A' state are significantly suppressed and increased for excitation from vibrationally excited states, respectively, whereas the intensity of the ns σ Rydberg series is unchanged. These observations suggest that the decrease in the bond angle causes

a decrease in the mixing in of valence character that enhances the transition probability to the Rydberg states. In order to understand these phenomena, we executed the SAC-CI calculations of the energies and the second moment $\langle r^2 \rangle$ of the O1s excited states varying the bond angle.

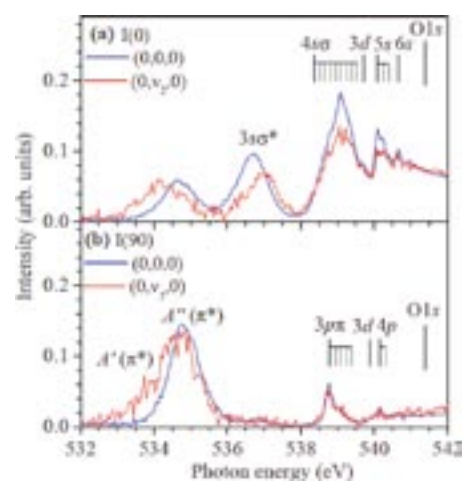


Figure 1. ARIY spectra in the N₂O O1s π^* and Rydberg excitation region. (a) Initial state specific 0°ARIY spectra for the vibrationally ground state (blue) and vibrationally excited states (red). (b) Initial state specific 90°ARIY spectra.

Figure 2 shows cuts of the calculated potential energy surfaces of the O 1s excited states of A' symmetry. The 1A' state is correlated to the π^* state and stabilizes along the bending coordinate. All other states are stable in the linear structure. A characteristic curve crossing occurs between the σ and π Rydberg states along the bending coordinate. These potential curves explain the red shift of the π^* state and the blue shift of 3s σ and 4s σ states. In order to analyze the mixing of the valence character in the Rydberg states, we examined the electronic part of the second moment $\langle r^2 \rangle$, which is anticorrelated to the amount of valence character (Figure 3). The second moments of the 3s σ , 4s σ , and 5s σ states become large as the molecule becomes bent. This indicates that the

mixing of the valence character in these states becomes less as the bond angle decreases. Consequently, the absorption oscillator strength to the ns σ Rydberg states becomes small. These results confirm the interpretation of the intensity changes observed for excitation from vibrationally excited molecules.

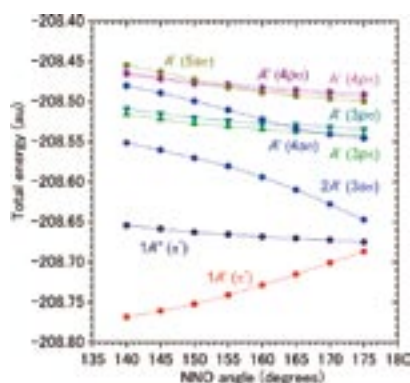


Figure 2. Potential energy curves of the low-lying O1s excited states of N_2O at $R_{NN} = 1.127 \text{ \AA}$ and $R_{NO} = 1.185 \text{ \AA}$.

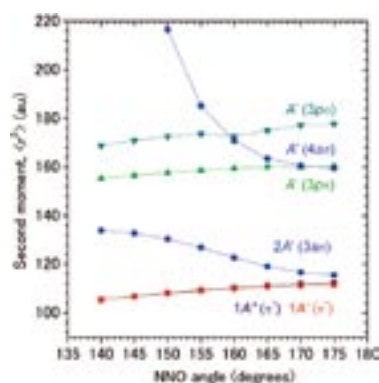


Figure 3. Second moments $\langle r^2 \rangle$ of the low-lying O1s excited states of N_2O at $R_{NN} = 1.127 \text{ \AA}$ and $R_{NO} = 1.185 \text{ \AA}$.

As seen in Figure 2, the $1A'(\pi^*)$ state stabilizes along the bending coordinate whereas the $2A'(3s)$ state destabilizes more than the $1A''(\pi^*)$ state. This anticorrelation indicates that the $1A'(\pi^*)$ and $3sA'$ states are strongly coupled. We believe that this coupling opens a flow of the valence character from the $3sA'$, $4sA'$, and $5sA'$ Rydberg states to the $1A'(\pi^*)$ state. Analyzing the MOs which contribute to the excitations, we concluded that the counterpart of the decrease in the mixing of the valence character in the $3s$, $4s$, and $5s$ states is an increase in the $s\sigma$ -type character of the $a'(\pi^*)$ orbital.

Thus, using an *ab initio* analysis of the electronic part of the second moment $\langle r^2 \rangle$, the suppression is interpreted as being due to a decrease in the mixing of the valence character in the ns σ Rydberg states with decreasing bond angle.

2. Theoretical Study of the Palladium-Catalyzed Regioselective Silaboration of Allene³

Transition-metal catalyzed additions of silicon-containing

σ -bonds to unsaturated bonds of organic molecules have been a major strategy for the synthesis of organosilicon compounds. While Si–Si bond addition has been extensively studied, addition reactions involving silicon–heteroatom bonds such as B, Sn and Ge have become important topics in recent years. Many reactions of these interelement σ -bonds proceed regioselectively, leading to the effective syntheses of regiodefined organosilicon compounds. Recently, effective silaboration reactions of allenes using silylborane have been developed. These reactions proceed in a regio- and stereoselective fashion in the presence of the palladium catalyst, producing synthetically useful β -borylallylsilanes in high yields.

We theoretically investigated this catalytic reaction, the silaboration of allene catalyzed by the Pd complex, to clarify the reaction mechanism and the origin of the regioselectivity (Figure 4). We examined the overall reaction scheme in particular to determine the mechanism of the regioselectivity. The present catalytic reaction is exothermic and the rate-determining step is the insertion of allene into the Pd–B bond of the Pd complex. σ -Allylic and π -allylic complexes exist as intermediates and play an important role in the regioselectivity. Selective insertion of the unsubstituted C=C bond into the Pd–B bond produces the most stable σ -allylic complex, which converts to the π -allylic complex while maintaining the Pd–O coordination. The selective formation of the specific σ -allylic complex and the large activation barrier between two isomeric π -allylic complexes dominantly determines the regioselectivity of the present reaction. The major-product complex is less stable than the minor-product complex, and therefore kinetic control is predominant in the present reaction.

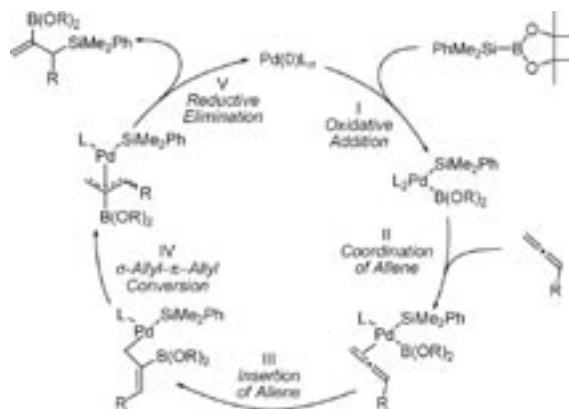


Figure 4. Reaction mechanism of the palladium-catalyzed regioselective silaboration of allene.

References

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