Orbital Picture in Molecular Inner-Shell Excited States of Rydberg-Valence Mixed Character

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The core-to-σ* excited state is repulsive for the bond elongation; on the other hand, the core ionized state and the core-to-π* state are bound and the core-to-Rydberg states are almost parallel to the potential energy curve of the core ionized state. Thus, the core-electron excitation to the unoccupied σ* orbital can be mixed with the one-electron Rydberg or continuum orbital, as dependent on the bond distance, and even with the unoccupied π* orbital in some cases. Within the framework of one-electron picture, we show σ* orbitals mixed with Rydberg character in the 1s excitation of O2 and CH3F, and Rydberg orbitals mixed with valence character in the 1s excitation of CH4, CO2, and N2O.

I. INTRODUCTION

The atomic and molecular core-to-Rydberg excitation is converging to a certain core ionization threshold (E_{th}). In addition, most molecules have unoccupied molecular orbitals of anti-bonding valence character such as σ* and π*. These anti-bonding orbitals can also accept an excited electron from the inner shell. The potential energy curve of the core-to-σ* valence excited state [1] is repulsive for a specified σ bond; then, the core-to-σ* excited state is lower than the continuum and Rydberg region at the longer bond distance and is embedded in the continuum at the shorter distance. That is, two kinds of interaction involving the valence state should be discussed along the potential energy curve for a specified σ bond[1]: the Rydberg-valence interaction below E_{th} and the continuum-valence interaction above E_{th}. In the present work, we discuss the former interaction within one-electron picture and show how the valence and/or Rydberg orbitals look like through the interactions.

II. RYDBERG CONTRIBUTION IN CORE-TO-σ* EXCITATION

A. O2

N2 has a triple covalent bond and the 3σ_u* molecular orbital is of strong anti-bonding character; then, the N1s excitation to this σ* orbital is observed above E_{th} as a well-known shape resonance. In molecules having weak covalent bonds, the 1s→σ* excited state is possibly observed below E_{th}. We can expect Rydberg-valence (RV) mixings in the case of the same p-symmetry as the 2pσ* orbital. As already discussed [1,2], the strong RV mixing results in new potential energy curves due to the avoided curve crossing of the Rydberg (p-type) and valence (2pσ*) states.

The Rydberg features in the O 1s excitation spectrum of O2 with a triplet ground state (^3Σ_u^+) are very complicated due to two ionization thresholds, ^4Σ^- and ^2Σ^+ [2,3]. The angle-resolved photoion spectroscopy (ARPIS) has shown that the core-to-σ* (3σ_u*) excited states give exchange-split two strong resonances in the Rydberg region [2,3] and that the ^4Σ^- channel gives vibrational enhancements in the 3pσ Rydberg state and the ^2Σ^+ channel has no distinct evidence for the RV mixing [2]. Fig. 1 shows (a) this 3σ_u* orbital before the RV mixing and (b) the RV-mixed 3pσ-3σ_u* orbital in the Franck-Condon region. This kind of the RV mixing is not effective for the s-type or d-type Rydberg states with different symmetry from the 2pσ* orbital.

![FIG. 1: Contour maps of (a) the 3σ_u* orbital obtained before the RV mixing (without any diffuse function) and (b) the RV-mixed 3pσ-3σ_u* orbital in the O1s excitation of O2.](image)

B. CH3F

In N2, the N1s excitation to the π* orbital is located lower than the Rydberg region. Even in saturated molecules, the excitation to the σ* orbital is possibly located below the Rydberg region in the case of very weak σ covalent bonds. In CH3F with a very weak σ covalent bond between CH3 and F, we have observed a broad and strong σ* (6a_1) band below the Rydberg region and a weak shoulder arising from the 3sa_1 Rydberg [4]. The σ* (6a_1) and 3sa_1 Rydberg orbitals are shown in Fig. 2, indicating that the 3sa_1 orbital of the CH3 fragment is deformed by orthogonalization to the valence electrons of the F atom. There might be more or less RV mixing due to the avoided crossing for the same a_1 symmetry.
III. VALENCE CONTRIBUTION IN CORE-TO-RYDBERG EXCITATION

A. CH$_4$

A simple molecular orbital picture predicts that the CH$_4$ molecule has the 2t$_2^*$ and 3a$_1^*$ antibonding molecular orbitals. In the case of inner-shell excitation, the C1s (1a$_1^1$) → 3a$_1^*$ excitation is dipole forbidden but the C1s (1a$_1^1$) → 2t$_2^*$ excitation is dipole allowed. However, no distinct 2t$_2^*$ resonance is observed in the C1s photoabsorption of CH$_4$ [5]. The C1s photoabsorption spectrum shows many distinct Rydberg states, vibronically allowed 3sa$_1^*$, strong npt$_2$ series, and ndt$_2$ series. The Rydberg region in CH$_4$ (C1s) [5] seems to be almost the same as in CH$_3$F (C1s) [4]. It is noticed that the C1s (1a$_1^1$) → 3pt$_2^*$ Rydberg excited state with three-fold degeneracy should be affected by Jahn-Teller (JT) distortion. Fig. 3 shows one of the three degenerate 3pt$_2^*$ Rydberg orbitals in CH$_4$ in comparison with the 3sa$_1^*$ Rydberg orbital. Considering that the 3pt$_2^*$ orbital has no valence contribution and is purely atomic-like, we could expect a very weak JT distortion in the 3pt$_2^*$ Rydberg state [6]. However, recent high-resolution C1s photoabsorption spectra of CH$_4$ [7,8] have shown that the 3pt$_2^*$ Rydberg state shows strong vibrational contributions in addition to the total symmetric vibration. This vibrational enhancement should arise from the JT effect in CH$_4$. Fig. 4 shows (a) the 3pt$_2^*$ orbital obtained without any diffuse function and (b) a C$_3v$-distorted “3pt$_2^*$” orbital in the C1s excitation of CH$_4$. The 2t$_2^*$ valence mixing gives intensities to the vibronically excited states of the C1s (1a$_1^1$) → 3pt$_2^*$ excitation.

B. CO$_2$(C1s)

In the C1s (2σ$_g^*$) excitation spectrum of CO$_2$, the strongest Rydberg state is of 3sσ$_g$ symmetry [8,9]. However, the C1s (2σ$_g^*$) → 3sσ$_g$ Rydberg excitation is dipole-forbidden. Fig. 5 shows a contour map of the 3sσ$_g$ Rydberg orbital (Fig. 5(a)), which is mixed with the 5σ$_v^*$ antibonding orbital (Fig. 5(b)). This valence mixing does not give any intensity from the C1s (2σ$_g^*$). On the other hand, Fig. 6 shows an orbital map for the same 3s Rydberg orbital at a bent geometry. The 3s Rydberg state has a large π$^*$ contribution. The C1s (2σ$_g^*$) → 2π$^*$ valence excited state has a stable bent geometry due to the Renner-Teller effect on electronically degenerate states in linear polyatomic systems [10]. This bending geometry, or bend-
ing motion in terms of molecular dynamics, is related to the vibronically induced $3s\sigma_g$ Rydberg transition. In high-resolution ARPIS spectra, bending vibrational fine structures are resolved in the $C1s (2\sigma_g) \rightarrow 3s\sigma_g$ and $4s\sigma_g$ Rydberg bands [8,9].

![Contour maps of (a) the $5\sigma_g$* valence orbital obtained without any diffuse function and (b) the $3s\sigma_g$ Rydberg orbital in the C1s ($2\sigma_g$) excitation of CO$_2$.](image1)

![Contour maps of (a) the $\pi^*$ orbital and (b) the 3s Rydberg orbital at a bent geometry in the C1s excitation of CO$_2$. The 3s Rydberg orbital has a large $\pi^*$ valence contribution.](image2)

C. N$_2$O and CO$_2$ (terminal N and O)

N$_2$O and CO$_2$ are isoelectronic and the molecular orbitals look similar. The lowest $\sigma^*$ ($8\sigma^*$) and 3s Rydberg orbitals excited from the central N ($N_c$) are shown in Fig. 7. The orbital character is nearly the same as in CO$_2$(C1s) shown in Fig. 5. The $N_c$ 1s excitation of N$_2$O is expected to be similar to the C1s excitation of CO$_2$. Unfortunately, the N1s excitation spectra include contributions from two N 1s edges and do not show clear evidence for bending mode coupling in the $N_c$ manifold [11]. On the other hand, the lowest $\sigma^*$ orbitals ($8\sigma^*$ of N$_2$O in Fig. 7(a) and $5\sigma_g^*$ of CO$_2$ in Fig. 5(a)) have a large $p\sigma$ component on the terminal N ($N_t$) and O. Fig. 8 shows a contour map of the “4s” Rydberg orbital excited from the $N_c$ 1s. The $N_t$ 4s Rydberg orbital has a large $8\sigma^*$ contribution with a $p\sigma$ component as shown in Fig. 7(a) and get its intensity from the $N_t$ 1s $\rightarrow p\sigma$ component [1,11]. Although the $s$-type Rydberg series is generally expected to be weak in the 1s photoabsorption, the Rydberg regions of the $N_t$ 1s and O1s excitations of N$_2$O and CO$_2$ are dominated in the observed spectra [7,8,11] by the $s$-type Rydberg states (4s most dominant) due to the lowest $\sigma^*$ mixing with the $p\sigma$ component on the terminal atoms. However, it is noted that the 1s $\rightarrow 8\sigma^*$ excitation of N$_2$O and 1s $\rightarrow 5\sigma_g^*$ excitation of CO$_2$ are not definitely identified as the 1s $\rightarrow 2t_2^*$ of CH$_4$. In these cases, it is reasonable to think that the valence contribution is dissolved in the Rydberg sea [1,6,12].

![Contour maps of (a) the lowest $\sigma^*$ ($8\sigma^*$) orbital obtained without any diffuse function and (b) the RV-mixed 3s$\sigma$ orbitals in the central N ($N_c$) 1s excitation of N$_2$O.](image3)

IV. SUMMARY

Using molecular orbitals, we have discussed how the 1s $\rightarrow \sigma^*$ excited state looks like in the 1s excitation of O$_2$ and CH$_3$F, and how we know evidence for the 1s $\rightarrow \sigma^*$ contribution in
photoabsorption spectra of CH\textsubscript{4}, CO\textsubscript{2}, and N\textsubscript{2}O. In the former molecules, the excitation to the \(\sigma^*\) orbital is identified in the Franck-Condon region from the ground state; in the latter molecules, the excitation to the \(\sigma^*\) orbital is not clearly identified but its evidence is observed through the Rydberg-valence mixing in the Franck-Condon region. In O\textsubscript{2}, the \(\sigma^*\) (3\(\sigma_u^*\)) orbital is mainly mixed with the 3p\(\sigma_u\) Rydberg orbital converging to the \(4\Sigma^+ (^4\Sigma_u^+)\) ionization. In CH\textsubscript{4}, the excitation to the \(\sigma^*\) (6a\textsubscript{1}) orbital is observed below the 3s\textsubscript{1} Rydberg state. On the other hand, in CH\textsubscript{4}, the Jahn-Teller distortion of the 3p\textsubscript{2} Rydberg transition induces contribution from the \(\sigma^*\) (2t\textsubscript{1}*) orbital component. In the 1s excitations from the terminal atoms in CO\textsubscript{2} and N\textsubscript{2}O, some lower s-type Rydberg states get intensities from the \(\sigma^*\) (5\(\sigma_g^*\) and 8\(\sigma_u^*\)) component. In the 1s excitations from the central atoms in CO\textsubscript{2} and N\textsubscript{2}O, the 1s\rightarrow \sigma^* excited state with \textit{gerade-gerade} transition is a dipole-forbidden (dark) state (not exactly from N\textsubscript{c} in N\textsubscript{2}O). In CO\textsubscript{2}, the C1s excitation to the 3s\textsubscript{g} Rydberg orbital is vibronically enhanced through mixing with the C1s excitation to the \(\pi^* (2\pi_u^*)\) orbital with the Renner-Teller effect.

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