

Theoretical Spectroscopy of Inner-Shell Electronic Processes and Photochemistry of Fluorescent Molecules

Masahiro Ehara and Hiroshi Nakatsuji

Abstract The SAC-CI method has been applied to the theoretical spectroscopy of the inner-shell electronic processes and the photochemistry of the organic light-emitting diodes (OLED) and biological chemosensors. Wide varieties of the core-electronic processes such as core-electron ionizations, shake-up satellites, vibrational excitations, valence–Rydberg coupling, and its thermal effect have been investigated by the SAC-CI calculations. The method has also been applied to the electronic spectra and the excited-state dynamics of the polymer materials of OLED such as poly *para*-phenylene vinylene and fluorene-thiophene. The photochemistry of the biological chemosensor has been elucidated in particular for the photo-induced electron transfer mechanism of the acridine-type fluorescent probe.

Keywords: SAC-IC · Theoretical spectroscopy · Inner-cell electronic processes · Organic-light emitting diodes · Priological chemosensors

1 Introduction

Recently, investigations of the core-electronic processes invoked renewal of interest, because significant developments in both high-resolution soft X-ray spectroscopy and accurate state-of-the-art theoretical methods have made us possible to obtain precise knowledge of the core-electronic processes. One can observe vibrational structures in the core-level photoelectron spectrum and thereby discuss the excited-state dynamics. This situation has motivated intensive cooperative researches on the core-electron processes from the experimental and theoretical sides.

Masahiro Ehara (✉)

Institute for Molecular Science, 38 Nishigo-Naka, Myodaiji, Okazaki 444-8585, Japan; JST, CREST, Sanboncho-5, Chiyoda-ku, Tokyo 102-0075, Japan, e-mail: ehara@ims.ac.jp

Hiroshi Nakatsuji

Quantum Chemistry Research Institute, Kyodai Katsura Venture Plaza 106, Kyoto 615-8245, Japan; JST, CREST, Sanboncho-5, Chiyoda-ku, Tokyo 102-0075, Japan, e-mail: h.nakatsuji@qcri.or.jp

The photochemistry of fluorescent molecules like organic light-emitting diodes (OLED) and biological chemosensors is an attractive and important subject. The OLED is recognized as one of the promising candidates for the next generation electro-optical devices. Theoretical interpretation and prediction of the photo-physical properties of the OLED molecules are relevant for developing the new materials. The fluorescent probe which works as biological chemosensor has also been focused and extensively investigated, since it enables the direct and real-time measurements of the enzyme activities. The fluorescence change by the interaction with the enzyme is essential and the elucidation of the electronic mechanism of the fluorescence and the color-tuning are important for developing new fluorescent probes.

In the series of our recent works, we have investigated the theoretical spectroscopy of the inner-shell electronic processes and the photochemistry of organic light-emitting diodes and biological chemosensors with the SAC-CI method. The SAC-CI method [1–3] has been successfully applied to the wide varieties of chemistry in particular for the molecular excited states. The method has been established as an accurate molecular excited-state theory applicable to the various kinds of electronic processes in the wide energy region [3–5]. In this chapter, we review our recent SAC-CI studies on the inner-shell electronic processes [6–18] and the organic light-emitting diodes [19, 20] and biological chemosensors.

2 Theoretical Spectroscopy of Inner-Shell Electronic Processes

Core-electron ionization spectra contain the information not only about inner-core electrons but also valence electrons and chemical bonds. Extensive experimental studies have measured the core-electron binding energies of numerous molecules [21, 22] and the recent development of X-ray photoelectron spectroscopy (XPS) has enabled the detailed analysis of the satellites accompanied by the inner-shell ionization [8, 11–13]. The high-resolution XPS has also been applied to observe the vibrational structure to investigate the geometry change and the dynamics in the inner-shell electronic processes [6, 9–17].

The SAC-CI method is useful to study both the main and satellite peaks in the core-electronic spectra as well as valence spectra. In the series of studies [6–18], the SAC-CI method have been successfully applied to the various kinds of core-electron processes; the core-electron binding energies [7]; the inner-shell ionization satellite spectra of CH_4 , NH_3 [7], H_2O [11], formaldehyde [8]; and the vibrational spectra of the core-hole state of H_2O [6], CO [10], N_2 [12], CO_2 [14], and N_2O [16]. The g - u splitting of homonucleus molecules like N_2 , C_2H_2 , C_2H_4 , and C_2H_6 has been well predicted [7, 12]. The overlapping vibrational spectra of the low-lying shake-up satellite states of CO [9, 13] and N_2 [12] were also successfully interpreted by the present method; the potential energy curves of the inner-shell shake-up states were accurately calculated. The method has also been applied to the core-electronic excited states [15, 17, 18]. The irregular Rydberg behavior observed for the $\text{O}1s$

