Chemical Physics Letters 678 (2017) 259–264

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Research paper

Theoretical study on the anion photoelectron spectra of Ln(COT)$_2^-$ including the spin-orbit effects

Erika Nakajo, Satoshi Yabushita *

Department of Chemistry, Faculty of Science and Technology, Keio University, 3-14-1 Hiyoshi, Kohoku-ku, Yokohama 223-8522, Japan

ARTICLE INFO

Article history:
Received 6 January 2017
In final form 13 April 2017
Available online 18 April 2017

Keywords:
Lanthanide organometallic complex
Spin-orbit coupling
4f-ligand interaction
Photoelectron spectroscopy

ABSTRACT

The multiplet level splittings for both anion and neutral sandwich complexes Ln(COT)$_2$ (Ln = Ce-Yb, COT = 1,3,5,7-cyclooctatetraene) were calculated with spin-orbit interactions to analyze their anion photoelectron spectra. The theoretically simulated spectra obtained with these energies and the pole strengths are generally consistent with the experimental spectra for the X peak. The magnitudes of the energy splittings, relative peak intensities, and their Ln dependence are reproduced. In comparison to our previous calculations, the inclusion of spin-orbit interactions with the SO-MCQDPT2 method makes the simulated spectra more consistent with the results of the experiment.

1. Introduction

Lanthanide (Ln) elements, which have progressively filled 4f electrons, are important in various applications, such as optical and magnetic materials. Particularly, the large magnetic moment and its anisotropy have attracted much attention because of its potential property of single-molecule magnets [1–3]. In contrast to transition metal complexes, lanthanide complexes generally show a negligible contribution of the open-shell 4f orbitals to the bonding [4]. Because the 4f orbitals are localized in the inner-shell, and the possible interactions with ligands are effectively shielded by the outer 5s and 5p closed-shell electrons, they remain as open-shell unpaired orbitals and are weakly perturbed by the ligands. The combination of the spin-orbit coupling (SOC) and weak ligand field effect makes the electronic structure of Ln complexes highly complicated. Thus, their theoretical study is one of the most challenging subjects in current quantum chemistry.

Recently, we have performed an ab initio study of the metal-ligand interaction in the anion and neutral Ln(COT)$_2$ complexes to analyze their anion photoelectron spectra (PES) [5–7]. Most of these complexes are believed to consist of a trivalent Ln^{3+} sandwiched with two aromatic rings of COT^{2-} (COT = 1,3,5,7-cyclooctatetraene) [7]; thus, they can be considered a 4f analogue of metallocene. The computed results show that the anion Ln (COT)$_2^-$ complexes have the D_{8h} structure, and the highest occupied molecular orbital (HOMO) essentially consists of the ligand π_{e2u} group orbital with the irreducible representation (irrep) of e$_{2u}$. As previously described, the Ln 4f orbitals are split notably weakly into fourfold levels with a$_{2u}$, e$_{1u}$, e$_{2u}$, and e$_{3u}$ irreps, and even the 4f$_{e2u}$ orbital hardly participates in the HOMO with the identical irrep of e$_{2u}$. (In the following text, the HOMO is denoted by e$_{2u}$ as in [5].) However, the situation drastically changes in the neutral Ln(COT)$_2$ complexes, which have the major electronic configuration of $4f^n e_{2u}^3$ with a hole in the HOMO. Some ligand field split components are stabilized by a specific configuration interaction with minor configurations of $4f^{n-1} e_{2u}^4$ [8–16]. Since this minor configurations are derived by a one-electron excitation from the 4f$_{e2u}$ orbital to the e$_{2u}$ orbital, this configuration mixing represents a resonance interaction between the formal charge structures Ln^{3+}(COT$^{1.5-}$)$_2$ and Ln^{4+}(COT^{2-})$_2$. We consider this relaxation effect as the origin of the interesting experimental results that the lowest X peak of PES is only split for the middle-range Ln complexes [7]. In the previous paper, we discussed the splitting mechanism and its Ln dependence using group theory [5]. The theoretical results based on the state-averaged complete active space self-consistent field (SA-CASSCF) and the second-order multi-configuration quasi-degenerate perturbation theory (MCQDPT2) calculations were consistent with the experimental PES [7]. The theoretically obtained splitting values were reasonably consistent with the experimental values, although the spin-orbit (SO) effect was not considered. However, following the general consensus in lanthanide chemistry, the SO effect is stronger than the ligand field effects and becomes important particularly in the late Ln series [17]. Studies on the neutral Ce(COT)$_2$ [9,18,19] and entire series of the anion Ln(COT)$_2^-$ complexes [20] reveal that the SO effect is not crucial in the electronic ground states, but it is expected to considerably affect the optical process and magnetic properties.

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* Corresponding author.
E-mail address: yabusita@chem.keio.ac.jp (S. Yabushita).

http://dx.doi.org/10.1016/j.cplett.2017.04.049
0009-2614/

Therefore, the inclusion of the SO effect can be essential to accurately describe the PES.

This letter reports an ab initio study on the X peaks of PES by including the SO effect. The multiplet split energies are calculated with the SO-MCQDPT2 method [21], and the so-called pole strengths are evaluated to simulate the relative intensities. The results are compared with the experimental PES and the MCQDPT2 calculations.

2. Calculation methods

2.1. Electronic structure of anion and neutral $Ln(COT)_2$

Before the calculation methods are presented, the electronic structure of the complexes is briefly explained. Since the experimental PES for the X peaks were taken at the 355 nm detachment laser wavelength [7], photodetachment only occurs from the HOMO (e_{2u}) of $Ln(COT)_2^-$ as follows,

$$Ln(COT)_2^-(4f^n e_{2u}{}^4) + h\nu \rightarrow Ln(COT)_2(4f^n e_{2u}{}^3) + ke^- \qquad (1)$$

where e_{2u}^4 denotes the closed-shell electrons in the doubly degenerate HOMO, and ke^- is the detached photoelectron. Reflecting the strong ionic bonding character, the electronic ground state of the anion complexes follows the weak ligand field regime. Thus, it is approximated as the product of two wave functions: one for the ground state multiplet terms $^{2S+1}L_J$ of the Ln^{3+} ion and the other for two weakly perturbing closed-shell COT^{2-} ligands [5]. Therefore, without SOC, the Ln portion is characterized by the set of quantum numbers (L, S, M_L, M_S) of the free Ln^{3+} ion. Here, M_L denotes the split

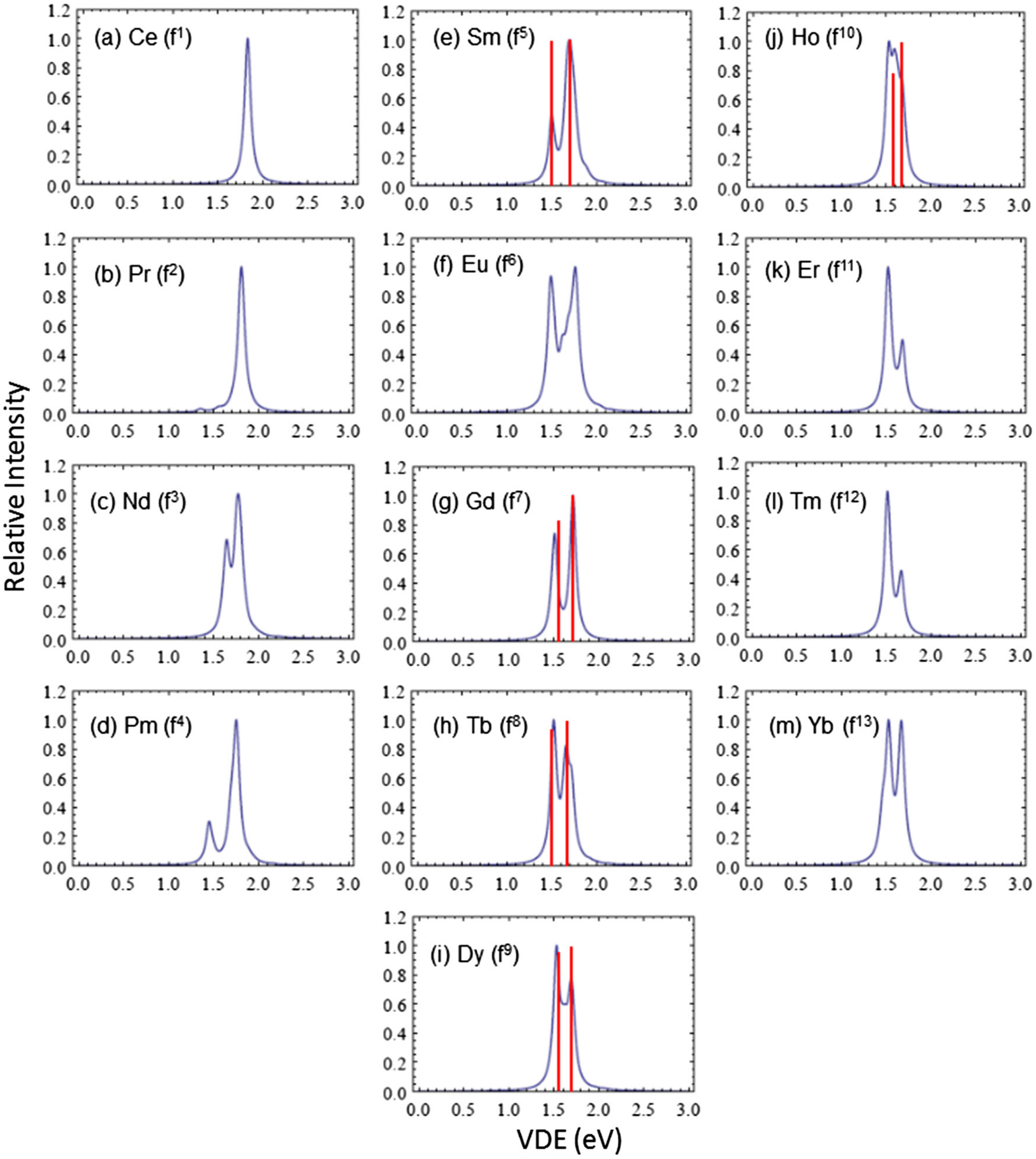

Fig. 1. Calculated anion PES using the SO-MCQDPT2 method. All peaks correspond to the photodetachment from the HOMO, and the initial states are the electronic ground states of $Ln(COT)_2^-$. The experimental PES is approximated by giving the Lorentzian linewidth of the full width at half maximum of 0.08 eV to each line in Fig. S1. Two red bars in each panel are shown for the Ln complexes, where the peak splitting was observed, to compare the peak position and height. The experimental peak positions are shifted so that the experimental X′ peak coincides with the calculated one on the higher-energy side. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)