THE DIFFERENCES IN THE ROLE OF O AND S ATOMS IN THE MOLECULAR STRUCTURE AND DYNAMICS OF SOME COMPLEXES

YOSHIYUKI KAWASHIMA, AKINORI SATO and YOSHIO TATAMINTANI, *Department of Applied Chemistry, Faculty of Engineering, Kanagawa Institute of Technology, Atsugi, Kanagawa 243-0292, JAPAN*; NOBUKIMI OHASHI, *Kanazawa University, 920-1192, JAPAN*; JAMES M. LOBUE, *Department of Chemistry, Georgia Southern University, Statesboro, GA 30460, USA*; EIZI HIROTA, *The Graduate University for Advanced Studies, Hayama, Kanagawa 240-0193, JAPAN*.

We have investigated the van der Waals complexes consisting of the one among a rare gas atom (Rg), CO, N_2 or CO_2 combined with one of the two pair molecules: dimethyl ether (DME)/ dimethyl sulfide (DMS) and ethylene oxide (EO)/ ethylene sulfide (ES), by using Fourier transform microwave spectroscopy supplemented by $ab\ initio$ MO calculations, in order to examine how different the role of the O and S atoms is in molecular properties of the complexes. The present talk reports the results on Ar-DMS and CO-EO, in comparison with those on Ar-DME and CO-ES, respectively. For the CO-EO complex, we concluded the CO moiety located in a plane perpendicular to the C-O-C plane and bisecting the COC angle of EO, in sharp contrast with the case of CO-DME, where the heavy atoms lie essentially in a same plane.[a] An $ab\ initio$ MO calculation at the level of MP2/6-311++G(d,p) yielded a structure, which, when optimized, agreed well with the experimental result for the both complexes.

The molecular structures of the pair molecules DME/DMS and EO/ES resemble with each other. However, van der Waals complex formation of these pair molecules with either Rg or CO leads to quite different structures of the complex. In the case of the CO-DMS and CO-ES, the CO moiety is located closer to the CH_3 and CH_2 end of DMS and ES, respectively, whereas to the O end in the cases of CO-DME and CO-EO. Similar differences were found for Rg complexes. Because of the larger atomic radius and lower electronegativity of S than those of O, S behaves as a much weaker nucleophile than O, which explains the differences in molecular structure between the two corresponding complexes. The structures of Rg-DMS and Rg-ES thus considerably deviate from that of the n-type complex proposed by Legon.[b]

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[a] Y. Kawashima, Y. Morita, Y. Tatamitani, N. Ohashi, and E. Hirota, $J.\ Chem.\ Phys.$ 127, 194302 (2007).

[b] A. C. Legon, $Angew.Chem.Int.Ed.$ 38, 2686 (1999).