A GROUP THEORY ANALYSIS OF ESR SPECTRUM OF TERT-BUTYL RADICAL AT LOW TEMPERATURES

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ESR spectra of tert-butyl radical produced by γ-irradiation in organic matrices showed equally-spaced 19 spectral lines with 9 satellite peaks at liquid He temperatures. The spectra also showed drastic temperature dependence. The spectral structure must be a result of complicated interactions between internal rotation of three methyl groups and umbrella motion of carbon skeleton. In a previous paper[a], we have interpreted the spectral structure by taking into account the internal rotation of three methyl groups only, assuming the carbon skeleton is rigidly planar. The simulated spectral structure was close to the observed spectral structure, but not perfectly matched. Here, we have tried to interpreted the spectral structure by taking into account the umbrella motion of carbon skeleton in addition to the internal rotation of three methyl groups. The analysis is based on the permutation-inversion group G_{324} for nine protons. Spectral structure has been simulated by adjusting several parameters in a model Hamiltonian in order to reproduce the observed spectral structure. Roles of umbrella motion in the ESR spectrum will be discussed.

[a] S. Kubota, M. Matsushita, T. Shida, A. Abu-Raqabah, M. C. R. Symons, and J. L. Wyatt, Bull. Chem. Soc. Jpn. **68**, 140 (1995).