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Dissymmetry Factor of Anisotropic Circular Dichroism and A Theory of Anisotropic Elliptical Dichroism: Application to A Quantum Chemical Study on Single-molecule Chiroptical Response

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Abstract

Technique of single-molecule measurement is expected to disentangle the information hidden behind the ensemble average measurements. Anisotropic circular dichroism has potential to be a helpful tool for investigations of chemical phenomena. Nowadays it is possible to compute with some accuracy the electronic wavefunctions of ground and excited state of molecules, hence circular dichroism spectra of isotropic bulk samples can be predicted theoretically. Recently, the single-molecule circular dichroism measurements are reported by a couple of groups. The first group reported the unexpected light-matter interaction dissymmetry between left- and right-circularly polarized light at single molecule level. In order to get an insight into the results, Starting with the classic electromagnetism and quantum mechanics, the anisotropic dissymmetry factor, g is derived. The precise coefficient and formulation of g as a function of propagation direction of light toward an orientationally fixed system is required for accurate evaluation by quantum chemical calculation. To take into account the effect of distortion of circularly polarized light and purity of photon ensembles in the measurements, the absorption rate difference between any pair of photon ensembles are formulated. The linear dichroism contaminant have been the most concern in those groups. However, it is found theoretically that the interference between two orthogonal basis polarization vectors should be payed attention. Also the extensively defined dissymmetry factor, $\tilde{g}$ associated with two kinds of polarization states of light is formulated. The theory is applied to the single-molecule circular dichroism measurements in practice. It is theoretically predicted that a dissymmetery factor can be both positive and negative value even for a given diastereomer. The majority of them fall into the range from -0.01 to 0.01, which agree with the small molecule limit, however, the value becomes large under certain condition where the electric dipole transition moment and incident direction of light is arranged such that the absorption is comparatively small. For the theoretical evaluation of anisotropic $\tilde{g}$, the parameters which determine the elliptically polarizations and purity of photon ensemble are estimated based on the reported information on the light beams used for the measurements. It is suggested that the contaminant of linear component is large when the electric dipole transition moment and incident direction of light is around perpendicular. This effect can be reduced if the orientation of ellipse of two light beams are identical or close to each other. These theory can be used for reflection on dissymmetry factor of anisotropic circular dichroism and elliptical dichroism in general.