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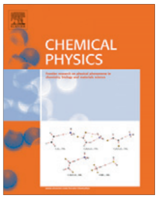

Analytical theory of the nuclear-spin-induced optical rotation in liquids

Guo-hua Yao, Ming He [1], Dong-ming Chen *, Tian-jing He, Fan-chen Liu *

Department of Chemical Physics, University of Science and Technology of China, Hefei, Anhui 230026, PR China

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Based on the thought on the antisymmetric polarizability induced by nuclear magnetic moments and theory of the Faraday effect, an analytical theoretical expression is derived for the nuclear-spin-induced optical rotation (NSOR) of diamagnetic saturated molecules in a circular cylinder. That consists of two parts, $\phi^{(I)}$ and $\phi^{(B)}$, induced by the intramolecular and intermolecular hyperfine interaction, respectively. By using them and the Verdet constants, NSOR for ^{1}H in water, hexane, cyclohexane and methyl–alcohol in liquid and H_2 gas have been calculated. The calculated NSOR for water agrees with the experiment and for three hydrocarbons predicts the same order of magnitude as water. For the samples studied except H_2 gas, $\phi^{(I)}$ and $\phi^{(B)}$ are comparable in magnitude.

1. Introduction

In a recent publication, Savukov et al. reported the detection of nuclear magnetic resonance (NMR) signals of ^{1}H in water using nuclear-spin optical rotation (NSOR) method [1]. This outstanding result literally shines a new light on NMR signal detection [2]. Ikäläinen et al.'s efficient first-principle calculations for isolated water, ethanol, nitromethane, urea and 11-*cis*-retinal protonated Schiff base molecules reveal a range of NSOR for different molecules and inequivalent nuclei, indicating the existence of an optical chemical shift [3]. Pagliero et al. extended the experiment results with observations of ^{19}F- and ^{1}H-induced optical Faraday rotation in a set of model ^{19}F- and ^{1}H-rich liquid samples at high magnetic field [4]. They carried out a optical-chemical-shift resolved characterization of the admixture of hexafluorobenzene and perfluorohexane, which verified experimentally the optical chemical shift for different molecules predicted in Ref. [3]. Lu et al. explored and studied theoretically the relation between the optical detection of NMR signals by the nuclear-spin-induced Faraday and Cotton–Mouton effects in fluids and the nuclear spin–spin coupling tensors [5].

The understanding of the mechanisms that define NSOR is of interest. For this purpose the interplay of experiment, theory and computation is important. However, to date an analytical theory of NSOR in liquids has not been developed yet. The formal description of NSOR may be based on consideration of the influence of intra- and intermolecular magnetic interactions on molecular antisymmetric polarizability. Buckingham et al. gave in full detail the theories of the influence of the nuclear magnetic moment [6] and external magnetic field [7] on the antisymmetric polarizability in Refs. [6,7], respectively. Based on these theories, we attempt to deduce an explicit practical expression of NSOR for diamagnetic saturated molecules in fluids. As examples, we use it to calculate magnitudes of NSOR for ^{1}H in water, three hydrocarbons in liquid, and hydrogen molecule gas, respectively.

In subsequent sections, Section 2.1 proves by quantum theory that NSOR results from two contributions, $\phi^{(I)}$ and $\phi^{(B)}$, from the antisymmetric polarizabilities induced by intramolecular and intermolecular hyperfine interaction (hfi), respectively. Then $\phi^{(B)}$ is derived by classical electromagnetics in Section 2.2. In Section 2.3, $\phi^{(I)}$ is studied through three steps. First the Section 2.3.1 justifies the dominant contribution from the orbital term in hfi to $\phi^{(I)}$ for closed-shell saturated molecules. Second, in Section 2.3.2, $\phi^{(I)}$ is shown to be proportional to an effective part of the Verdet constant, $n_A V_A$, which is due to n_A atoms A with nucleus I of interest in the molecules. Third, based on the atomic addition rule of the Verdet constants, Section 2.3.3 gives fundamental expression of $\phi^{(I)}$ and total NSOR. By using the expression of NSOR, the Section 3 calculates NSOR for ^{1}H in water (in Section 3.1), the saturated hydrocarbons (in Section 3.2), and hydrogen H_2 gas (in Section 3.3), respectively. The calculated results are discussed in Section 3.4.

2. Theory

2.1. Antisymmetric polarizabilities induced by intramolecular and intermolecular hyperfine interactions $\alpha'^{(I)}_{xyz}$ and $\alpha'^{(B)}_{xyz}$

The Hamiltonian of the electronic system of a considered molecule Q with the prepolarized nucleus I is given by

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* Corresponding authors.
E-mail addresses: dmchen@ustc.edu.cn (D.-m. Chen), fcliu@ustc.edu.cn (F.-c. Liu).
URL: http://www.changning.net (M. He).

[1] Present address: Center, 1220-2 Hua Shan Road, Shanghai 200052, PR China.

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$$\hat{H} = \frac{1}{2m}\sum_j \left(\hat{\vec{p}}_j + e\hat{\vec{A}}_j\right)^2 + V_{el}, \tag{1}$$

where $\hat{\vec{p}}_j$ is the generalized momentum and $\hat{\vec{A}}$ is the vector potential due to magnetic fields, j is denotation of the electron in a molecule Q, V_{el} is the electrostatic potential energy term.

We temporarily assume that each molecule in the sample contains only one prepolarized nucleus. The prepolarized nuclear magnetic moment lies in the +*z* direction, and the origin of the coordinates is chosen at the nucleus *I* considered. We have [8(a)]

$$\hat{\vec{A}}_j = \left(\frac{\mu_0}{4\pi}\right)\frac{\vec{\mu}_I \times \vec{r}_j}{|\vec{r}_j|^3} + \left(\frac{\mu_0}{4\pi}\right)\sum_N \frac{\vec{\mu}_N \times \vec{r}_{Nj}}{|\vec{r}_{Nj}|^3}, \tag{2}$$

where μ_0 is the permittivity of a vacuum, $\vec{\mu}_I$ is the magnetic moment of the nucleus *I* in the molecule Q, subscript *N* in this paper is denotation of nuclei in the other molecules. $\vec{r}_j$ is the radius vector from the nucleus *I* to the position of the electron *j* in the molecule Q, and $\vec{r}_{Nj}$ is the radius vector from the nucleus *N* to the position of the electron *j*. The first term in Eq. (2) represents the intramolecular magnetic interactions between the electron *j* and nucleus *I* in the molecule Q. The second term in Eq. (2) expresses the intermolecular magnetic interactions between the electron *j* in the molecule Q and the nuclei *N* in the other molecules.

Substituting Eq. (2) into Eq. (1) and by routine derivations [8(a),9(a)] the Hamiltonian $\hat{H}$ can be written as

$$\hat{H} = \hat{H}_0 + \hat{H}_{hfi} + \hat{H}_B. \tag{3}$$

In Eq. (3) the zeroth-order Hamiltonian $\hat{H}_0$ includes all electrostatic and magnetic interactions internal to the electron system. $\hat{H}_{hfi}$ and $\hat{H}_B$ are attributed to the first and second term in Eq. (2), respectively. $\hat{H}_{hfi}$ is the intramolecular hyperfine interactions (hfi) between the electron *j* and the considered nucleus *I* in the molecule Q and $\hat{H}_B$ is the intermolecular hfi between the electron *j* in the molecule Q and the nuclei *N* in the other molecules.

The intramolecular hfi is

$$\hat{H}_{hfi} = -\mu_{I\alpha}\hat{B}^{(I)}_{el\alpha}. \tag{4}$$

In Eq. (4) (infra), the repeated indices imply the summation. The Greek suffix α, β, γ and English suffix x, y, z with the unit vector $(\vec{i}, \vec{j}\ \vec{k})$ denote the molecule-fixed coordinates and space-fixed coordinates, respectively. The operator $\hat{B}^{(I)}_{el\alpha}$ in Eq. (4) is the magnetic field at the nucleus *I* produced by the electrons in the molecule Q and expressed by [6(b)]

$$\hat{B}^{(I)}_{el\alpha} = -\frac{2\mu_0\mu_B}{4\pi}\left[\sum_j \hat{l}_{j\alpha}r_j^{-3} + \frac{8\pi}{3}\delta\left(\vec{r}_j\right)\hat{S}_{j\alpha} + \frac{\left[3r_{j\alpha}r_{j\beta} - r_j^2\delta_{\alpha\beta}\right]}{r_j^5}\hat{S}_{j\beta}\right], \tag{5}$$

where μ_B is the Bohr magneton, $\hbar\hat{l}_{j\alpha}$ the orbital angular momentum operator of the *j*th electron about nucleus *I*, $\hbar\hat{S}_{j\alpha}$ the spin angular momentum operator of the *j*th electron, and $\delta(\vec{r}_j)$ the Dirac delta function. Corresponding to the three terms in Eq. (5) three types of hfi are included in Eq. (4), i.e., the orbital term $\hat{H}_L$, the Fermi contact term $\hat{H}_F$, and the spin-dipole term $\hat{H}_D$, and

$$\hat{H}_{hfi} = \hat{H}_L + \hat{H}_F + \hat{H}_D. \tag{4$'$}$$

The intermolecular hfi in Eq. (3) can be written as [8(a),9(a)]

$$\hat{H}_B = -\sum_{N,j}\hat{m}_{j\alpha}B^{(j)}_{N\alpha}, \tag{6}$$

where $\hat{m}_{j\alpha}$ is the magnetic moment of the *j*th electron in the molecule Q, $B^{(j)}_{N\alpha}$ is the magnetic field at the electron j in the molecule Q due to the nuclear magnetic moment of the nucleus *N* in the other molecules [8(a),9(a)]

$$B^{(j)}_{N\alpha} = \frac{\mu_0}{4\pi}T^{Nj}_{\alpha\beta}\mu_{N\beta} = \frac{\mu_0}{4\pi}\left[-\frac{\mu_{N\alpha}}{r^3_{Nj}} + \frac{3(\mu_{N\beta}r_{Nj\beta})r_{Nj\alpha}}{r^5_{Nj}}\right]. \tag{7}$$

Definition of the tensor $T^{Nj}_{\alpha\beta}$ is $T^{Nj}_{\alpha\beta} = \nabla_\alpha\nabla_\beta r^{-1}_{Nj}$. If O is the origin of the molecule-fixed coordinate, $\vec{r}_{Nj}$ can be written by the molecule-fixed frame, $\vec{r}_{Nj} = \vec{r}_{NO} + \vec{r}_{Oj}$. Based on definition of $T_{\alpha\beta}$ and $\vec{r}_{Nj}$ and the differential quotient rules, it can be derived [10(a)] that $\vec{r}_{NO}$ may replace $\vec{r}_{Nj}$ in Eq. (7). Thus Eqs. (6) and (7) become, respectively,

$$\hat{H}_B = -\sum_j \hat{m}_{j\alpha}B_\alpha, \tag{6$'$}$$

where $B_\alpha = \sum_N B^{(O)}_{N\alpha}$, and $B^{(O)}_{N\alpha}$ is

$$B^{(O)}_{N\alpha} = \frac{\mu_0}{4\pi}T^{NO}_{\alpha\beta}\mu_{N\beta} = \frac{\mu_0}{4\pi}\left[-\frac{\mu_{N\alpha}}{r^3_{NO}} + \frac{3(\mu_{N\beta}r_{NO\beta})r_{NO\alpha}}{r^5_{NO}}\right]. \tag{7$'$}$$

$\hat{H}_{hfi}$ and $\hat{H}_B$ can make a small perturbation on the antisymmetric polarizability α'_{xy} of the molecule Q and can be written as [5–7] (see Section 2.3)

$$\alpha'_{xy} = \alpha'^{(0)}_{xy} + \alpha'^{(B)}_{xyz}B_Z + \alpha'^{(I)}_{xyz}\mu_{IZ}. \tag{8}$$

The nuclear-spin-induced optical rotation of the plane of polarization in the path-length *Z* for the prepolarized samples is determined by the antisymmetric polarizability α'_{xy} in Eq. (8) [6,7]

$$\phi = \frac{2\pi N\omega Z}{4\pi\varepsilon_0 c}\left\langle\alpha'_{xy}\right\rangle = \frac{2\pi N\omega Z}{4\pi\varepsilon_0 c}\left[\left\langle\alpha'^{(B)}_{xyz}\right\rangle B_Z + \left\langle\alpha'^{(I)}_{xyz}\right\rangle\mu_{IZ}\right], \tag{9}$$

where *N* is the number of molecules in unit volume. The notation ⟨ ⟩ represents the isotropic average. The first and second part of Eq. (9) are denoted as $\phi^{(B)}$ and $\phi^{(I)}$, respectively, $\phi = \phi^{(B)} + \phi^{(I)}$. $\left\langle\alpha'_{xyz}\right\rangle$ in Eq. (9) is [6]

$$\left\langle\alpha'_{xyz}\right\rangle = \alpha'_{\alpha\beta\gamma}\langle i_\alpha j_\beta k_\gamma\rangle = \frac{1}{6}\varepsilon_{\alpha\beta\gamma}\alpha'_{\alpha\beta\gamma},$$

where $\varepsilon_{\alpha\beta\gamma}$ is the unit skew-symmetric tensor. i_α is the direction cosine between the molecule- and space-fixed frames. For Eqs. (2), (8), and (9), we have assumed that a molecule Q only contains an atom *A* with nucleus *I*. If the molecule Q studied has n_A atoms *A* with the nucleus *I*, Eq. (9) becomes

$$\phi = \phi^{(B)} + \phi^{(I)} = \frac{2\pi N\omega Z}{4\pi\varepsilon_0 c}\left[\left\langle\alpha'^{(B)}_{xyz}\right\rangle B_Z + \left\langle\alpha'^{(I)}_{xyz}\right\rangle n_A\mu_{IZ}\right]. \tag{10}$$

Eq. (10) is applicable to molecules with n_A identical prepolarized nuclei *A*. For multinuclear molecules with distinguishable polarized nuclei or inequivalent sites, Eq. (10) may be extended to sum up the additive contributions of various polarized nuclei to NSOR.

Thus the nuclear-spin optical rotation (NSOR) for the prepolarized fluid samples results from two contributions, $\phi^{(I)}$ and $\phi^{(B)}$, due to intramolecular and intermolecular hfi, respectively, i.e. $\phi^{(I)}$ from the magnetization field at the nucleus *I* produced by the electrons in the molecule Q considered, and $\phi^{(B)}$ from the magnetization field of nuclear magnetic moments of the other molecules at the electrons in the molecule Q. As far as we know, these two contributions, $\phi^{(B)}$ and $\phi^{(I)}$, have not been distinguished from each other in the related literature yet. We shall separately study them in Sections 2.2 and 2.3.

2.2. The magnetization field of prepolarized nuclear magnetic moments and its contribution to NSOR, $\phi^{(B)}$

Analogous to the treatment of the magnetization field of paramagnetic ions by Dickinson [11(a)], to give the expression for the local magnetization field B_Z of prepolarized nuclear magnetic moments, we follow the method introduced by Debye and also described in Ref. [11(b)]. Here we consider the local magnetic field at a molecule Q (not the macroscopic magnetic field) which