Chemical Distinction by Nuclear Spin Optical Rotation

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Nuclear spin optical rotation (NSOR) arising from the Faraday effect constitutes a novel, advantageous method for detection of nuclear magnetic resonance, provided that a distinction is seen between different chemical surroundings of magnetic nuclei. Efficient first-principles calculations for isolated water, ethanol, nitromethane, and urea molecules at standard laser wavelengths reveal a range of NSOR for different molecules and inequivalent nuclei, indicating the existence of an optical chemical shift. ^{1}H results for $H_2O(l)$ are in excellent agreement with recent pioneering experiments. We also evaluate, for the same systems, the Verdet constants of Faraday rotation due to an external magnetic field. Calculations of NSOR in ethanol and a 11-*cis*-retinal protonated Schiff base imply an enhanced chemical distinction between chromophores at laser wavelengths approaching optical resonance.

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The effects of light impinging on a sample in nuclear magnetic resonance (NMR) experiments have been discussed in various studies [1–9]. Magneto-optic phenomena may furnish novel, sensitive methods for NMR detection [8]. Nuclear spin optical rotation (NSOR) arises from the Faraday effect, in which the magnetic field due to spin-polarized nuclei causes the plane of polarization of an incident beam of linearly polarized light to rotate. In the corresponding inverse Faraday effect, circularly polarized light induces shifts in NMR frequencies. First-principles investigations [5–7] imply that, away from regions of optical resonance, the shifts are too small to be measured. In contrast, experimental NSOR has been reported in the liquid state for ^{1}H in water and ^{129}Xe [8]. Arising from the same microscopic property, the dependence of optical polarizability on the nuclear magnetic moment, the laser-induced shift and NSOR can be easily interconverted. The theoretical shifts [6] agree reasonably with the experimental ^{129}Xe NSOR [8,10].

To provide a viable alternative to the conventional magnetic detection of NMR, NSOR should convey distinct signals for inequivalent nuclei in different chemical surroundings. In this Letter we demonstrate via first-principles response-theory calculations of small molecules that this indeed is the case. We reproduce the experimental results for $^1H_2O(l)$ and prove, for ethanol and a 11-*cis*-retinal protonated Schiff base (PSB11), the concept of enhanced chemical distinction between nuclei in different chromophores when approaching optical resonances. The methods are verified by comparison of the Verdet constants parametrizing the Faraday rotation due to an external magnetic field $\boldsymbol{B}_0$, with experimental data.

Consider linearly polarized light propagating in the Z direction through a medium with refractive index $n_r \approx 1$, at frequency ω distinct from optical resonances. The magnetic optical rotation (OR) angle Φ per unit of sample length l can be written as [11,12]

$$\frac{\Phi}{l} = \frac{1}{2}\omega \mathcal{N} \mu_0 c \mathrm{Im}\langle \alpha'_{XY}\rangle, \tag{1}$$

with $\mathcal{N}$ the number density of molecules possessing the average, complex antisymmetric polarizability $\langle \boldsymbol{\alpha}' \rangle$. For $\boldsymbol{B}_0$ and nuclear spin $I_{K,Z}$ along the beam [1,9],

$$\alpha'_{XY} = \alpha'^{(B_0)}_{XY,Z} B_0 + \alpha'^{(I_K)}_{XY,Z} I_{K,Z} + \mathcal{O}(B_0^3, I_K^3). \tag{2}$$

Isotropic molecular tumbling leads to the average

$$\langle \alpha'_{XY,Z}\rangle = \frac{1}{6}\sum_{\epsilon\tau\nu} \varepsilon_{\epsilon\tau\nu}\alpha'_{\epsilon\tau,\nu} = \frac{1}{3}(\alpha'_{xy,z} + \alpha'_{yz,x} + \alpha'_{zx,y}), \tag{3}$$

where $\varepsilon_{\epsilon\tau\nu}$ is the Levi-Civita symbol and (x, y, z) are coordinates in the molecule-fixed Cartesian frame.

In the notation of quadratic response theory [5,13],

$$\alpha'^{(B_0/I_K)}_{\epsilon\tau,\nu} = -\langle\langle \mu_\epsilon; \mu_\tau, h_\nu^{\mathrm{OZ/PSO}}\rangle\rangle_{\omega,0}, \tag{4}$$

the expression of conventional electric dipole polarizability, $\boldsymbol{\alpha}(\omega) = -\langle\langle \boldsymbol{\mu}; \boldsymbol{\mu}\rangle\rangle_\omega$, modified by the presence of a third, static magnetic operator $\boldsymbol{h}$. For OR caused by $\boldsymbol{B}_0$, the latter is the orbital Zeeman interaction of electrons i

$$H_{\mathrm{OZ}} = \sum_{\nu} h_{\nu}^{\mathrm{OZ}} B_{0,\nu}; \qquad h_{\nu}^{\mathrm{OZ}} = \frac{e}{2m_e}\sum_{i} \ell_{iO,\nu}, \tag{5}$$

where $\boldsymbol{\ell}_{iO} = -i\hbar(\boldsymbol{r}_i - \boldsymbol{R}_O) \times \nabla_i$ with respect to gauge origin $\boldsymbol{R}_O$. Hence, $\Phi = VB_0 l$, where the Verdet constant

$$V = -\frac{1}{2}\omega \mathcal{N} \mu_0 c \frac{e^3}{2m_e} \frac{1}{6} \sum_{\epsilon\tau\nu} \varepsilon_{\epsilon\tau\nu} \mathrm{Im}\langle\langle r_\epsilon; r_\tau, \ell_{O,\nu}\rangle\rangle_{\omega,0} \tag{6}$$

parametrizes the Faraday OR in external field. The respective NSOR arises via the orbital hyperfine interaction

$$H_{\mathrm{PSO}} = \sum_{\nu} h_{\nu}^{\mathrm{PSO}} I_{K,\nu}; \qquad h_{\nu}^{\mathrm{PSO}} = \frac{e\hbar}{m_e}\frac{\mu_0}{4\pi}\gamma_K \sum_{i} \frac{\ell_{iK,\nu}}{r_{iK}^3}, \tag{7}$$

where γ_K is the gyromagnetic ratio and $\boldsymbol{\ell}_{iK}$ and $\boldsymbol{r}_{iK}$ are referenced to the location $\boldsymbol{R}_K$ of nucleus K. For unit concentration $[\ ] = \mathcal{N}/N_A$ of the polarized nuclei K,

$$\frac{\Phi_{\mathrm{NSOR}}}{[\ ]l} = -\frac{1}{2}\omega N_A c \langle I_{K,Z}\rangle \frac{e^3\hbar}{m_e} \times \frac{\mu_0^2}{4\pi}\gamma_K \frac{1}{6}\sum_{\epsilon\tau\nu}\varepsilon_{\epsilon\tau\nu}\mathrm{Im}\left\langle\left\langle r_\epsilon; r_\tau, \frac{\ell_{K,\nu}}{r_K^3}\right\rangle\right\rangle_{\omega,0}, \tag{8}$$

where $\langle I_{K,Z}\rangle$ is the average spin polarization.

In a circularly polarized light beam with intensity I_0, the NMR frequency shift Δ also arises from $\boldsymbol{\alpha}^{\prime(I_K)}$ of Eq. (4) [1,5–7]. The relation with NSOR can be written as [8]

$$\frac{\Phi_{\mathrm{NSOR}}}{[\ ]l} = -h\omega N_A \langle I_{K,Z}\rangle \frac{\Delta}{I_0}. \tag{9}$$

First-principles quadratic response-theory calculations of Φ_{NSOR} and V were carried out at standard visible or near-infrared laser frequencies for water, nitromethane (CH_3NO_2), ethanol (C_2H_5OH), urea [$(NH_2)_2CO$], and PSB11. Φ_{NSOR} was computed for ethanol and PSB11 at frequencies around optical resonances. We employed the implementations of quadratic response functions [14] for the Hartree-Fock (HF), density-functional theory (DFT), and coupled cluster (CC) methods in the DALTON program [15]. DFT was calibrated against the rigorous but more expensive *ab initio* CC singles and doubles (CCSD) and the more approximate CC2 [16] levels. The completeness-optimized (co) basis-set paradigm [17] was used to provide results close to the Gaussian basis-set limit [7,18]. The co sets are generated by maximizing overlap with a test Gaussian primitive with exponent ζ sweeping a wide range. As no characteristics of specific atoms are used, the basis sets are universal provided the adequacy of the range [17]. The primitive co-1 and co-2 sets developed for efficient calculations of $\Delta(^{13}C)/I_0$ [7] have been used here [19].

A quantitative agreement with liquid-phase experiments typically requires considering both intramolecular dynamics and solvation, whereas the present calculations only treat static, isolated molecules. Hence, CCSD is the primary point of comparison for the other (DFT) levels of theory, and the CCSD performance in relation to experiment carries information about the significance of the further effects. Experimental Verdet constants for $H_2O(l)$ are well reproduced at the CCSD/co-1 level, with $V(\omega)$ only 5%–8% below the measured values (Table I). Analysis of the DFT performance is given in Ref. [24]. As before [18], the admixture of the exact HF exchange in hybrid DFT affects the hyperfine property significantly. Based on the experimental and present *ab initio* data, the functionals with 25% (PBE0 [25]) or 50% (BHandHLYP [26,27]) exact HF exchange provide reliable Verdet constants. Among the other molecules (in Ref. [24]), the DFT data agree well with the experiment for $C_2H_5OH(l)$ and $CH_3NO_2(l)$. No experimental results exist for urea.

Table II and material in Ref. [24] reveal a parallel performance of the methods for NSOR as for $V(\omega)$. This behavior is expected, as the two observables are determined by similar physics, Eq. (4). The experimental ^1H NSOR of 0.4 and 0.2×10^{-6} rad/(M cm) in $H_2O(l)$ were obtained in Ref. [8] for the wavelengths of 532 and 770 nm, respectively. These data are quantitatively reproduced at the CCSD level. Based on the available experimental and *ab initio* results, the BHandHLYP functional was chosen for further calculations. The same choice was made in Ref. [7] for laser-induced ^{13}C NMR frequency shifts. Medium effects may be roughly estimated based on the gas-to-liquid shifts in a related property, the nuclear shielding constant σ. For water, $\sigma(^1H/^{17}O)$ decrease by

TABLE I. Calculated Verdet constants V [in rad/(T m)] for liquid water using different methods and basis sets [a].

		HF	BHandHLYP		B3LYP	BLYP	PBE0	PBE	CC2	CCSD		Literature[b]	
ω (a.u.)	λ (nm)	co-2	co-1	co-2	co-2	co-2	co-2	co-2	co-2	co-1	co-2	Exp.	DFT
0.0932147	488.8	3.72	5.02	4.95	6.53	8.30	5.93	7.91	6.61	5.41	5.52	5.85 [20]	
0.0885585	514.5	3.33	4.48	4.42	5.82	7.38	5.29	7.03	5.89	4.83	4.93	5.24 [20]	7.38 [21]
0.0773571	589.0	2.49	3.34	3.30	4.32	5.44	3.93	5.19	4.38	3.60	3.67	3.79 [22], 3.81 [23]	
0.0656249	694.3	1.76	2.36	2.32	3.03	3.80	2.76	3.63	3.08	2.54	2.58	2.66 [20]	
0.0428226	1064.0	0.73	0.98	0.96	1.25	1.55	1.14	1.49	1.27	1.05	1.07		
0.0345439	1319.0	0.47	0.63	0.62	0.80	1.00	0.73	0.96	0.82	0.68	0.69		

[a] The exponent range of the co-1 basis is wider than that of co-2, indicating higher quality of co-1. With experimental $\mathcal{N}$ based on mass density 998.2 kg m^{-3} and $\boldsymbol{R}_0$ placed at the center of mass.

[b] Liquid-state measurements at room temperature [20], 20 °C [22], and 17 °C [23].

TABLE II. Calculated $\Phi_{\mathrm{NSOR}}/([\;]l)$ [in 10^{-6} rad/(M cm)] for ^{1}H in liquid water using different methods and basis sets [a].

		HF	BHandHLYP		B3LYP	BLYP	PBE0	PBE	CC2	CCSD		
ω (a.u.)	λ (nm)	co-2	co-1	co-2	co-2	co-2	co-2	co-2	co-2	co-1	co-2	Exp.
0.0932147	488.8	0.30	0.42	0.41	0.55	0.74	0.51	0.71	0.58	0.48	0.48	
0.0885585	514.5	0.27	0.37	0.36	0.49	0.66	0.45	0.63	0.52	0.43	0.42	
0.0856454	532.0	0.25	0.35	0.33	0.46	0.61	0.42	0.59	0.48	0.40	0.39	0.4[b]
0.0773571	589.0	0.20	0.28	0.27	0.37	0.49	0.33	0.47	0.39	0.32	0.32	
0.0591732	770.0	0.12	0.16	0.16	0.21	0.27	0.26	0.26	0.22	0.19	0.18	0.2[b]
0.0428226	1064.0	0.06	0.08	0.08	0.11	0.14	0.10	0.13	0.11	0.10	0.09	

[a] Normalized to 1 M = 1 mol dm^{-3} concentration and full polarization of spins, i.e., $\langle I_Z \rangle = 1/2$ for ^{1}H.

[b] Ref. [8]. Liquid-state measurement.

approximately 10% from gas to liquid phase [28]. Solvent effects of this magnitude would not affect our methodological conclusions for NSOR.

Figure 1 reveals very different NSOR angles for similar nuclei in different molecules and nonequivalent groups in the same molecule. Hence, NSOR encodes information on the chemical environment of nuclei, providing a kind of optically detected chemical shift. In particular, a signal 100 times that of ^{1}H is obtained for ^{17}O in $H_2O(l)$, rendering the latter an attractive target for further experiments. ^{17}O NSOR in $C_2H_5OH(l)$ is also considerable. ^{15}N in urea exhibits bigger NSOR than ^{13}C or ^{1}H. In ethanol, distinct NSORs prevail for ^{13}C in the methyl (CH_3) and methylene (CH_2) groups, as well as for ^{1}H in the alcohol (OH) and the CH_3/CH_2 groups.

Efficient chemical distinction by NSOR entails selection of nuclear spins, instead of recording the average rotation resulting from all of them. The nature of the quantum mechanical operators involved, Eq. (4), suggests that selectivity either in nuclear magnetization or optical excitation could be employed. Elaborating the latter, with ω approaching optical resonance, $\boldsymbol{\alpha}^{l(I_K)}(\omega)$ is expected to undergo massive amplification [4,6,7]. Thus, optical excitation of a chromophore could be used to select the NSOR signal from that group. Figure 2 presents a proof of the concept. In ethanol, excitation around 174 nm incites the NSOR signals from both nuclei in the OH group, whereas around 149 nm the protons of the OH and CH_3 moieties but not CH_2 are activated [29]. In the same vein, at 141 and 139 nm, ^{1}H NSOR by the CH_2 group greatly exceeds that due to the CH_3 and OH groups. Experimentally, however, the availability of such ultraviolet beams and their absorption in ethanol are likely to be prohibitive. A larger photoactive compound, PSB11, could be more amenable. For PSB11 at the optimized ground-state geometry [30], the results in Ref. [24] show that the chain protons are more active around resonances than those of the ring structure, and distinct behavior is witnessed for the CH_n ($n = 1, 2, 3$) and NH_2 (amino) groups. Table III indicates chemical distinction at standard laser frequencies in PSB11. Magnitudes

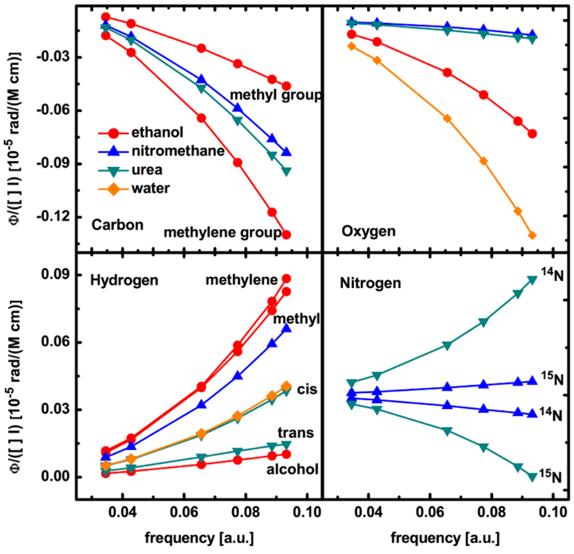

FIG. 1 (color online). Calculated $\Phi_{\mathrm{NSOR}}/([\;]l)$ [in 10^{-5} rad/(M cm)] as a function of laser frequency in liquid ethanol, nitromethane, and water, as well as solid urea at the BHandHLYP/co-2 level. Experimentally equivalent nuclei are averaged.

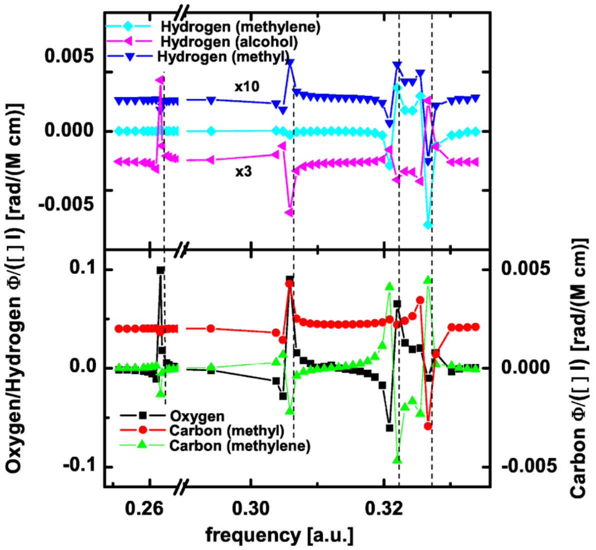

FIG. 2 (color online). $\Phi_{\mathrm{NSOR}}/([\;]l)$ [in rad/(M cm)] in liquid ethanol close to optical resonances (173.59, 148.72, 141.38, and 139.25 nm, dashed vertical lines) at the BHandHLYP/co-2 level of theory. Offsets of 0.002 rad/(M cm) are used to improve visibility.

TABLE III. Calculated $\Phi_{\mathrm{NSOR}}/([\ ]l)$ [in 10^{-7} rad/(M cm)] for ^{1}H in PSB11 at the BHandHLYP/co-2 level. The numbering refers to groups of equivalent nuclei as indicated in Ref. [24].

ω (a.u.)	λ (nm)	47 + 48	46	37…39	40	49 + 50	32…34	26…31	24 + 25	22 + 23
0.0932147	488.8	153.45	−386.83	693.41	85.18	−174.00	265.29	−126.55	26.98	148.15
0.0885585	514.5	−18.44	68.65	−73.24	−11.95	30.42	−27.66	25.45	6.94	−7.20
0.0773571	589.0	−2.75	18.07	−11.63	2.72	10.59	−2.25	9.28	5.21	2.75
0.0656249	694.3	−0.66	9.15	−3.39	2.97	6.16	0.50	5.53	3.73	2.86
0.0428226	1064.0	0.05	2.94	−0.25	1.43	2.25	0.72	2.07	1.58	1.40
0.0345439	1319.0	0.07	1.82	−0.05	0.94	1.43	0.52	1.32	1.02	0.96

of ^{1}H NSOR greatly exceeding those of water are seen due to the proximity of the lowest excitation energy.

Summarizing, NSOR may provide a sensitive NMR modality, provided that signals encoding different chemical surroundings of the nuclei can be distinguished. We have shown by first-principles calculations the existence of such a chemical distinction between different molecules and inequivalent sites in the same molecule. We obtain quantitative agreement with the experimental ^{1}H NSOR in liquid water [8] and predict larger signals for ^{17}O, as well as ^{1}H in PSB11. NSOR around optical resonance facilitates enhanced distinction between chromophores. These findings should encourage further investigation into spectroscopic applications of NSOR. Studies of intermolecular interaction and relativistic effects on the NSOR in $H_2O(l)$ and Xe(l), respectively, are in progress.

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