Faraday Rotation for the Hydrogen Molecule

By Yasumasa I'HAYA

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Quantum mechanical theories of the magneto-optical rotation in polyatomic molecules have been developed by Kronig,[1] Serber,[2] Carroll,[3] and Groenewege.[4] Recently we included the contribution of the induced magnetic moment and of the perturbed Boltzmann factors and, using a time-dependent second-order perturbation theory, derived a general formula for the Faraday effect of diamagnetic molecules.[5] The Verdet constant, which is the rotation per gauss per cm., is shown to be temperature-dependent for polyatomic molecules of any symmetry, but temperature-independent for diamagnetic diatomic molecules (no paramagnetic rotation).

If we consider states of up to 3d, the molecular wave function in the hydrogen molecule is $(1s\sigma)^2$ for the ground state and $(1s\sigma)(2p\pi)$, $(1s\sigma)(3p\pi)$, $(1s\sigma)(4p\sigma)$ for the excited state. These are:

$$(1s\sigma)^2:\ N=N_1[s_a(1)+s_b(1)]\ [s_a(2)+s_b(2)]$$

$$(1s\sigma)(2p\pi):\ \Pi=N_2[s_a(1)+s_b(1)]\ [\pi_a(2)+\pi_b(2)]$$

$$(1s\sigma)(3p\pi):\ \Pi'=N_3[s_a(1)+s_b(1)]\ [\pi'_a(2)+\pi'_b(2)]$$

$$(1s\sigma)(4p\sigma):\ \Sigma=N_4[s_a(1)+s_b(1)]\ [\sigma_a(2)+\sigma_b(2)]$$

where N_i is the normalization constant and where s_i, σ_i, π_i, and π'_i are the complex normalized hydrogenic atomic orbitals of 1s, $2p_0$, $2p_+$, and $3p_+$ respectively. The other elements do not contribute to the theoretical expression for the Verdet constant because of their symmetry.

With these molecular orbitals, the Verdet constant may be expressed as:

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[1] R. de L. Kronig, *Z. Physik*, **45**, 458, 508 (1927).
[2] R. Serber, *Phys. Rev.*, **41**, 489 (1932).
[3] T. Carroll, ibid., **52**, 822 (1937).
[4] M. P. Groenewege, *Mol. Phys.*, **5**, 541 (1962).
[5] Y. I'Haya, to be published.

$$V=\frac{4\pi e^3N\nu^2}{3hmc^2i}\Big[\frac{1}{\nu_4}\Big(\frac{1}{\nu_1{}^2-\nu^2}-\frac{1}{\nu_3{}^2-\nu^2}\Big)\times i\langle N|x|\Pi\rangle\langle\Pi\Big|z\frac{\partial}{\partial x}-x\frac{\partial}{\partial z}\Big|\Sigma\rangle\langle\Sigma|z|N\rangle+\frac{\nu_1{}^2}{(\nu_1{}^2-\nu^2)^2}\langle\Pi\Big|x\frac{\partial}{\partial y}-y\frac{\partial}{\partial x}\Big|\Pi\rangle\Big|\langle N|x|\Pi\rangle\Big|^2+\frac{2\nu_2{}^2}{(\nu_2{}^2-\nu^2)^2}\langle\Pi'\Big|x\frac{\partial}{\partial y}-y\frac{\partial}{\partial x}\Big|\Pi'\rangle\Big|\langle N|x|\Pi'\rangle\Big|^2\Big] \qquad (1)$$

e, m, h, and c being the usual notations and N, the number of molecules per unit volume ($N=0.2686\times10^{20}\,\mathrm{cm}^{-3}$ at 0°C, 1 atm.). Here ν_i is the energy difference between the states measured in units of reciprocal seconds, as is shown in Fig. 1. Their observed values are[6]: $\nu_1=2.999249$, $\nu_2=3.414317$, $\nu_3=3.447654$ (estimated), and $\nu_4=0.448405$, all expressed in units of $10^{15}\,\mathrm{sec}^{-1}$. The matrix elements which appear in Eq. 1 are calculated using elliptical coordinates, the internuclear distance in H_2 being assumed to be 1.40 a.u. When the frequency of the incident light, ν, is $0.519027\times10^{15}\,\mathrm{sec}^{-1}$ (5780A), the Verdet constant is calculated to be 3.140 μmin. (microminutes) per oe.-cm.-atm.

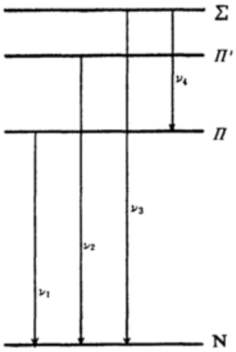

Fig. 1. Molecular electronic states in H_2, which contribute to the Faraday rotation.

The corresponding experimental value reported by Ingersoll and Liebenberg is 6.269 μmin. per oe.-cm.-atm.[7] We cannot judge at this stage whether the many other excited states, 4pπ, 5pπ, and so on, contribute strongly. Further studies are, therefore, now in progress with more elaborate excited-state wave functions; the results will be published elsewhere.

Department of Materials Science
The University of Electro-Communications
Chofu-shi, Tokyo

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[6] G. Herzberg, "Spectra of Diatomic Molecules," Van Nostrand, New York (1950), p. 531.

[7] L. R. Ingersoll and D. H. Libenberg, *J. Opt. Soc. Am.*, **46**, 538 (1956).