

## Magneto-Optical Rotation in Molecules\*

### II. The Verdet Constant for the Hydrogen Molecule

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The Verdet constant for the hydrogen molecule is calculated using the general formula derived in the previous paper. The excited states up to and including  $n = 4$  are considered. The result well compares with the experiments. It is found that the magnetic rotation in the hydrogen molecule is due almost entirely to the excited  $(1\sigma)(2p\pi)$  and  $(1\sigma)(4p\pi)$  states.

Die Verdet-Konstante wird mit Hilfe einer allgemeinen Formel (Teil I) für Wasserstoff berechnet. Das Ergebnis stimmt mit den Experimenten gut überein. Es ergibt sich, daß die magnetische Drehung in Wasserstoff fast vollständig den angeregten Zuständen  $(1\sigma)(2p\pi)$  und  $(1\sigma)(4p\pi)$  zugeschrieben werden muß.

La constante de Verdet de la molécule d'hydrogène est calculée à l'aide de la formule générale établie dans l'article précédent. Les états excités sont considérés jusqu'à  $n = 4$  inclus. Les résultats sont en bon accord avec les données expérimentales. La rotation magnétique de la molécule d'hydrogène est due presque totalement aux états excités  $(1\sigma)(2p\pi)$  et  $(1\sigma)(4p\pi)$ .

#### 1. Introduction

In a previous paper [4] (hereafter called Part I), we have derived a general formula for the magneto-optical rotation of diamagnetic molecules, including the contribution of the induced magnetic moments and of the perturbed Boltzmann factors. The Verdet constant, which is the rotation of the plane of polarization per gauss per cm, was shown to be temperature dependent for general polyatomic molecules of all symmetry classes.

In spite of the large number of theoretical investigations, there have been few quantitative calculations of the angle of rotation, namely of the Verdet constant. STEPHEN [11] and STONE [12] have computed purely theoretically the magnetic rotatory dispersions in molecules of tetrahedral symmetry. They obtained the agreement with the measured dispersion in the accuracy of about 2 min in a region well removed from resonance with any absorption line but poor results in the neighbourhood of absorption lines. This may be due to the use of the same dispersion equation in both regions. As mentioned in the opening paragraph of

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the previous paper, it is quite clear that the phenomena in these two regions are rather different and should be treated separately.

Magneto-optical rotation experiment on gases and vapours requires a special technique to measure very small angle of rotation. An excellent series of experimental works has been published by INGERSOLL and LIEBENBERG [6], who eliminated most of the experimental errors and measured the Verdet constant of many common gases with considerable accuracy. TOBIAS and KAUZMANN [14] examined the relationship between the theoretical expression for the Verdet constant obtained by SERBER [10] and some of the observed values given by INGERSOLL and LIEBENBERG. For diamagnetic diatomic and linear triatomic molecules, they obtained the approximate proportionality between  $\nu V^{-1/2}$  and  $\nu^2$ , which yields an empirical expression of the form

$$V = A_0 \nu^2 / (\nu_0^2 - \nu^2)^2 \quad (1)$$

where  $A_0$  and  $\nu_0$  are constants. This means that INGERSOLL and LIEBENBERG's measurements of the rotation in above mentioned molecules are representable almost exactly by the so-called "normal" Verdet constant. HOUGEN [3] explained the anomalous magnetic rotation of oxygen by including the interaction of the spin magnetic moment with the magnetic field of the light wave and obtained an empirical expression which can be fitted to the experimental data.

The purpose of the present paper is to demonstrate the purely theoretical calculation of the Verdet constant using the general formula obtained in Part I. Since in general our knowledge of molecules, specifically of their excited state wave functions, is not sufficient to permit explicit calculation of every terms required by Eq. (64) of Part I, and at the same time the existing measurements of the rotation is not considered to be completely reliable, comparison of the theoretical and observed Verdet constants might be meaningless. Nevertheless, it is believed that a numerical check of the general formula given in Part I for a simple molecule will throw light on further applications to more complicated molecules. In this paper, the hydrogen molecule is taken up as a pilot. A preliminary report has been published previously [5].

## 2. Method of Calculation

If a molecule is diamagnetic in its ground state, the diagonal elements of the angular momentum operator, namely  $\langle n | \mathfrak{M} | n \rangle$  in Eq. (64) of Part I, vanish so that the Verdet constant comes out to be temperature-independent. Moreover, the scalar triple product of the magnetic dipole moment,

$$\langle n | \mathfrak{M} | n' \rangle \langle n' | \mathfrak{M} | n'' \rangle \langle n'' | \mathfrak{M} | n \rangle,$$

is very small for diamagnetic molecules (this quantity actually vanishes in case of the hydrogen molecule). The Verdet constant of such molecules, therefore, can be expressed in a more concise form:

$$\begin{aligned} V = & (4\pi^2 N\nu^2/3 h^2 c) \sum_n B_n \mathcal{I} m \sum_{n'} [-2\nu(n'n)\tau(n'n)\langle n' | \mathfrak{M} | n' \rangle \times \\ & \times \langle n | \mathfrak{R} | n' \rangle \langle n' | \mathfrak{R} | n \rangle - \nu^{-2}\nu(n'n)\tau(n'n)\langle n | \mathfrak{R} | n \rangle \langle n | \mathfrak{R} | n' \rangle \langle n' | \mathfrak{M} | n \rangle + \\ & + \sum_{\substack{n'' \neq n' \\ n'' \neq n}} \nu^{-1}(n''n') \{ \tau(n'n) - \tau(n''n) \} \langle n | \mathfrak{R} | n' \rangle \langle n' | \mathfrak{M} | n'' \rangle \langle n'' | \mathfrak{R} | n \rangle - \\ & - 2 \sum_{\substack{n'' \neq n' \\ n'' \neq n}} \nu^{-1}(n''n)\tau(n'n)\langle n | \mathfrak{R} | n' \rangle \langle n' | \mathfrak{R} | n'' \rangle \langle n'' | \mathfrak{M} | n \rangle] \quad (2) \end{aligned}$$

where  $\nu(n' n)$  is the energy difference between states  $n'$  and  $n$  measured in units of reciprocal seconds and

$$\tau(n' n) = 1 / \{\nu^2(n' n) - \nu^2\}. \quad (3)$$

If the excited vibrational and electronic states are sufficiently greater in energy than the ground state, the statistical weight of the ground state  $B_n$  could be replaced by unity and the summation over  $n$  could not be required. For homonuclear diatomic molecules, there exists no nonvanishing diagonal element of the electric dipole moment operator,  $\langle n | \mathfrak{R} | n \rangle$ , so that Eq. (2) further reduces to

$$\begin{aligned} V = & (4\pi^2 N\nu^2/3 h^2 c) \mathcal{I} m \sum_{n'} [-2\nu(n' n) \tau^2(n' n) \langle n' | \mathfrak{M} | n' \rangle \langle n | \mathfrak{R} | n' \rangle \times \\ & \times \langle n' | \mathfrak{R} | n \rangle + \sum_{n'' \neq n'} \nu^{-1}(n'' n') \{\tau(n' n) - \\ & - \tau(n'' n)\} \langle n | \mathfrak{R} | n' \rangle \langle n' | \mathfrak{M} | n'' \rangle \langle n'' | \mathfrak{R} | n \rangle - \\ & - 2 \sum_{n'' \neq n} \nu^{-1}(n'' n) \tau(n' n) \langle n | \mathfrak{R} | n' \rangle \langle n' | \mathfrak{R} | n'' \rangle \langle n'' | \mathfrak{M} | n \rangle] \end{aligned} \quad (4)$$

which is the working formula for the Verdet constant of diamagnetic homonuclear diatomic molecules.

If atomic orbitals up to and including  $n = 4$  ( $n$  is the principal quantum number) are considered, it will be found in a later paragraph that only contributions from  $2p_0$ ,  $2p_+$ ,  $2p_-$ ,  $3p_+$ ,  $3p_-$ ,  $4p_+$  and  $4p_-$  atomic orbitals are obtained. Namely, the excited states which contribute to the magnetic rotation will be  $(1s\sigma)(2p\pi)$ ,  $(1s\sigma)(3p\pi)$ ,  $(1s\sigma)(4p\pi)$ , and  $(1s\sigma)(4p\sigma)$ , the former three being doubly degenerate (doubly excited configurations are neglected).

$$\begin{aligned} (1s\sigma)^2 & : N = N_1 \{s_a(1) + s_b(1)\} \{s_a(2) + s_b(2)\} \\ (1s\sigma)(2p\pi) & : \bar{I} = N_2 \{s_a(1) + s_b(1)\} \{\pi_a(2) + \pi_b(2)\} \\ (1s\sigma)(3p\pi) & : \bar{I}' = N_3 \{s_a(1) + s_b(1)\} \{\pi'_a(2) + \pi'_b(2)\} \\ (1s\sigma)(4p\pi) & : \bar{I}'' = N_4 \{s_a(1) + s_b(1)\} \{\pi''_a(2) + \pi''_b(2)\} \\ (1s\sigma)(4p\sigma) & : \Sigma = N_5 \{s_a(1) + s_b(1)\} \{\sigma_a(2) + \sigma_b(2)\} \end{aligned} \quad (5)$$

where the  $z$ -axis is taken on the line joining both hydrogen atoms  $a$  and  $b$ . The degenerate functions  $\bar{I}$ ,  $\bar{I}'$ , and  $\bar{I}''$  are obtained by replacing  $\pi$ ,  $\pi'$ , and  $\pi''$  by  $\bar{\pi}$ ,  $\bar{\pi}'$ , and  $\bar{\pi}''$ , respectively. Each atomic orbital in Eq. (5) is a normalized hydrogen wave function,

$$\begin{aligned} s & = (1/\pi)^{1/2} \exp(-r) \\ \sigma & = (1/2)^2 (1/2\pi)^{1/2} r \exp(-r/2) \cos \theta \\ \left. \begin{aligned} \pi \\ \bar{\pi} \end{aligned} \right\} & = (1/2)^3 (1/\pi)^{1/2} r \exp(-r/2) \sin \theta \exp(\pm i\phi) \\ \left. \begin{aligned} \pi' \\ \bar{\pi}' \end{aligned} \right\} & = (1/3)^4 (1/\pi)^{1/2} (6r - r^2) \exp(-r/3) \sin \theta \exp(\pm i\phi) \\ \left. \begin{aligned} \pi'' \\ \bar{\pi}'' \end{aligned} \right\} & = (1/2)^9 (1/10\pi)^{1/2} (80r - 20r^2 + r^3) \exp(-r/4) \sin \theta \exp(\pm i\phi) \end{aligned} \quad (6)$$

and  $N_i$  is the normalization constant,

$$\begin{aligned}
N_1 &= 1/ (2 + 2 S) \\
N_2 &= 1/ [2 (1 + S)^{1/2} (1 + S_\pi)^{1/2}] \\
N_3 &= 1/ [2 (1 + S)^{1/2} (1 + S_{\pi'})^{1/2}] \\
N_4 &= 1/ [2 (1 + S)^{1/2} (1 + S_{\pi''})^{1/2}] \\
N_5 &= 1/ [2 (1 + S)^{1/2} (1 + S_\sigma)^{1/2}]
\end{aligned} \tag{7}$$

where  $S$ ,  $S_\pi$ , and  $S_\sigma$  are the overlap integrals between the same kind of atomic orbitals shown in Eq. (6). We have used Bohr unit ( $a_0 = 0,52917 \text{ \AA}$ ) for the unit of length.

For molecules possessing cylindrical symmetry, the selection rule for the quantum number  $A$  which is the projection of the orbital angular momentum on the line joining the nuclei, say the  $z$ -axis, shows that the nonvanishing matrix elements of an arbitrary vector physical quantity  $F$  are [7]

$$\langle n, A | F_z | n', A \rangle, \langle n, A | F_x + i F_y | n', A - 1 \rangle, \langle n, A - 1 | F_x - i F_y | n', A \rangle. \tag{8}$$

Here  $n$  stands for the assembly of quantum numbers labeling the state with the exception of  $A$ . If, in addition, the molecule is homonuclear diatomic, there is also a selection rule regarding parity. The matrix elements of a polar vector such as the electric dipole moment are non-zero only for transitions between states of opposite parity. The reverse is true for an axial vector such as the magnetic dipole moment. Therefore, one can easily show that only matrix elements of the electric dipole moment  $\mathfrak{R}$  and the magnetic dipole moment  $\mathfrak{M}$ ,

$$\begin{aligned}
\langle N | R_z | \Sigma \rangle, \quad \langle \Sigma | R_z | N \rangle \\
\langle II | R_x + i R_y | N \rangle
\end{aligned}$$

also for  $II'$ ,  $II''$  and  $\bar{II}$ ,  $\bar{II}'$ , and  $\bar{II}''$  (the same in the following)

$$\begin{aligned}
\langle N | R_x - i R_y | II \rangle, \langle II | M_z | II \rangle, \langle II | M_x + i M_y | \Sigma \rangle \\
\langle \Sigma | M_x - i M_y | II \rangle
\end{aligned} \tag{9}$$

are nonvanishing.

Expanding the scalar triple product in the first term of Eq. (4) into their components and applying the selection rules mentioned above, one obtains

$$\begin{aligned}
- \mathcal{J} m \sum_{II} 2 \nu (II, N) \tau^2 (II, N) (e^3 \hbar / 2 imc) m_z (II, II) \times \\
\times \{x(N, II) y(II, N) - y(N, II) x(II, N)\}
\end{aligned} \tag{10}$$

where we have redefined

$$\mathfrak{R} = e \tau, \quad \mathfrak{M} = (e \hbar / 2 imc) m \tag{11}$$

and used abbreviations such as

$$x(N, II) \equiv \langle N | x | II \rangle. \tag{12}$$

The summation in Eq. (10) should be carried out over all  $II$ -type functions shown in Eq. (5) and their complex conjugates. A relationship obtained from the selection rule

$$y(N, II) = i x(N, II) \tag{13}$$

together with identities

$$\begin{aligned}
x(II, N) = x(N, II) = x(N, \bar{II}) = x(\bar{II}, N) \\
y(II, N) = -y(N, II) = -y(\bar{II}, N) = y(N, \bar{II})
\end{aligned} \tag{14}$$

makes both terms in the curly bracket in Eq. (10) equal, so that the first term of Eq. (4), exclusive of the coefficient before the summation symbol, turns out to be

$$\mathcal{I}m \sum'_{II} 4 \nu (II, N) \tau^2 (II, N) m_z (II, II) | x (N, II) |^2 \quad (15)$$

where it should be noted that  $x (N, II)$  is real but  $m_z (II, II)$  is a purely imaginary quantity; the prime on the summation sign indicates that the degenerate states  $\bar{II}$ ,  $\bar{II}'$ , and  $\bar{II}''$  are to be omitted.

The second terms of Eq. (4) can be expanded into

$$\begin{aligned} \mathcal{I}m \sum'_{II} (e^3 \hbar/2 imc) [\nu^{-1} (\Sigma, II) \{ \tau (II, N) - \tau (\Sigma, N) \} \{ x (N, II) m_y (II, \Sigma) - \\ - y (N, II) m_x (II, \Sigma) \} z (\Sigma, N) + \nu^{-1} (II, \Sigma) \{ \tau (\Sigma, N) - \tau (II, N) \} \\ z (N, \Sigma) \{ m_x (\Sigma, II) y (II, N) - m_y (\Sigma, II) x (II, N) \}]. \end{aligned} \quad (16)$$

Table 1. Integrals over Atomic Orbitals

integral	a.u.	integral	
$\langle s_a   x   \pi_a \rangle$	0.526749	$\langle \sigma_a   m_y   \pi_a \rangle$	0.707107
$\langle s_a   x   \pi_b \rangle$	0.479106	$\langle \sigma_a   m_y   \pi_b \rangle$	0.637396
$\langle s_a   x   \pi'_a \rangle$	0.210938	$\langle \sigma_a   m_y   \pi'_a \rangle$	0
$\langle s_a   x   \pi'_b \rangle$	0.183579	$\langle \sigma_a   m_y   \pi'_b \rangle$	-0.017344
$\langle s_a   x   \pi''_a \rangle$	0.124346	$\langle \sigma_a   m_y   \pi''_a \rangle$	0
$\langle s_a   x   \pi''_b \rangle$	0.104779	$\langle \sigma_a   m_y   \pi''_b \rangle$	-0.015152
$\langle s_a   z   \sigma_a \rangle$	0.744936	$s = \langle s_a   s_b \rangle$	0.752943
$\langle s_a   z   \sigma_b \rangle$	0.792305	$s\sigma = \langle \sigma_a   \sigma_b \rangle$	0.862201
		$s\pi = \langle \pi_a   \pi_b \rangle$	0.952881
		$s'_\pi = \langle \pi'_a   \pi'_b \rangle$	0.972581
		$s''_\pi = \langle \pi''_a   \pi''_b \rangle$	0.826924

In the same way as before, the identities Eqs. (13) and (14) together with

$$z (\Sigma, N) = z (N, \Sigma) \quad (17)$$

and

$$m_y (II, \Sigma) = -m_y (\Sigma, II) = -im_x (II, \Sigma) = im_x (\Sigma, II) = m_y (\bar{II}, \Sigma) = im_x (\bar{II}, \Sigma)$$

make each term in Eq. (16) and also a term arising from a degenerate state equal, so that one gets

$$\sum'_{II} 4 \nu^{-1} (\Sigma, II) \{ \tau (II, N) - \tau (\Sigma, N) \} x (N, II) m_y (\Sigma, II) z (N, \Sigma) \quad (18)$$

where the prime on the summation sign has the same meaning as in Eq. (15). It can be easily shown that there is no contribution from the third term in Eq. (4). Altogether, the Verdet constant for the hydrogen molecule can be expressed as

$$\begin{aligned} V = (16 \pi e^3 N \nu^2 / 3 \hbar mc^2) \sum'_{II} [\nu (N, II) \tau^2 (II, N) \mathcal{I}m \{ m_z (II, II) \} | x (N, II) |^2 + \\ + \nu^{-1} (\Sigma, II) \{ \tau (II, N) - \tau (\Sigma, N) \} x (N, II) m_y (\Sigma, II) z (N, \Sigma)]. \end{aligned} \quad (19)$$

All integrals over molecular orbitals appeared in Eq. (19) can be expressed in terms of integrals over atomic orbitals, which numerical values are obtained using prolate spheroidal coordinate and are shown in Tab. 1. The internuclear distance in the hydrogen molecule was assumed to be 1.40 a.u. The molecular electronic

states in the hydrogen molecule, which contribute to the magneto-optical rotation, are schematically shown in Fig. 1. The observed values of the transition energy for the lower two transitions measured in units of  $10^{15} \text{ sec}^{-1}$  are

$$\begin{aligned} \nu (II, N) &= 2.999189 [I] \\ \nu (II', N) &= 3.414248 [I3] \end{aligned} \quad (20)$$

but there have been no data available for  $\nu (II'', N)$  and  $\nu (\Sigma, N)$ . According to RICHARDSON'S assignment [9], it is likely that  $(1s\sigma) (4p\sigma)$  state lies in  $118,029 \text{ cm}^{-1}$  above the ground state; namely the value

$$\nu (\Sigma, N) = 3.538391 \quad (21)$$

in unit of  $10^{15} \text{ sec}^{-1}$  was adopted. On the other hand,  $(1s\sigma) (4p\pi)$  state seems to lie a little higher in energy than  $(1s\sigma) (4p\sigma)$  state, as can be seen in the molecular energy diagram [8]. Therefore, it was assumed that

$$\begin{aligned} \nu (II'', N) &= 119,000 \text{ cm}^{-1} \\ &= 3.5675 \times 10^{15} \text{ sec}^{-1}. \end{aligned} \quad (22)$$

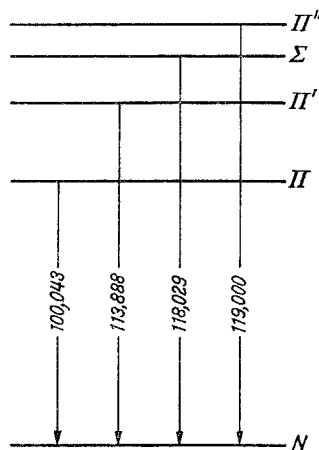


Fig. 1. Molecular Electronic States in  $H_2$ , which Contribute to the Magnetic Rotation; Energy Interval in units of  $\text{cm}^{-1}$ .

### 3. Results and Discussion

Tab. 2 shows an example of calculations of the Verdet constant when the frequency of the incident light  $\nu$  is  $0.519029 \times 10^{15} \text{ sec}^{-1}$  ( $5780 \text{ \AA}$ ). In the first column, are shown the product of the matrix elements appeared in Eq. (19). Their numerical values are given in the second column in units of  $10^{-16} \text{ cm}^2$ . The last column presents the contribution of each term to the total Verdet constant in units of  $\mu \text{ min}$  per oe-cm-atm (hereafter abbreviated as  $\mu \text{ min}$ ). Total Verdet constant  $7.861 \mu \text{ min}^*$ , shown at the bottom of Tab. 2, well compares with the corresponding experimental value  $6.269 \mu \text{ min}$  reported by INGERSOLL and LIEBENBERG. It can be seen in the last column of Tab. 2 that the contribution of  $(1s\sigma) (2p\pi)$  and  $(1s\sigma) (4p\sigma)$  amounts to  $7.518 \mu \text{ min}$  which is 96% of the total Verdet constant. This means that the uncertainty involved in estimating the

Table 2. *The Matrix Elements and the Verdet Constant*

Matrix Elements	$10^{-16} \text{ cm}^2$	Contribution to $V$ , $\mu \text{ min}$
$x(N, II) m_y(\Sigma, II) z(N, \Sigma)$	0.091324	4.747
$x(N, II') m_y(\Sigma, II') z(N, \Sigma)$	-0.000447	-0.019
$x(N, II'') m_y(\Sigma, II'') z(N, \Sigma)$	-0.000245	-0.010
$-im_z(II, II)  x(N, II) ^2$	0.082769	2.771
$-im_z(II', II')  x(N, II') ^2$	0.012604	0.282
$-im_z(II'', II'')  x(N, II'') ^2$	0.004590	0.090
(Total)		7.861

\* In the previous paper, ref. [5], a factor of two has been omitted in the general formula for the Verdet constant, so that the calculated value was about one half of the value reported here in this paper.

location of the ( $1s\sigma$ ) ( $4p\pi$ ) state may be out of the question. At the same time, it will be concluded that the magnetic rotation in the hydrogen molecule is due almost entirely to the two excited states mentioned above.

We cannot judge at this stage, however, whether the uncertainty involved in the experimental value of  $\nu$  ( $\Sigma$ ,  $N$ ) leads to rather large theoretical Verdet constant (about 25% larger than the observed one). The reason is that if one wants to reproduce the observed value  $6.269 \mu \text{ min}$  exactly, one has to assign  $\nu$  ( $\Sigma$ ,  $N$ ) to be  $4.652326 \times 10^{15} \text{ sec}^{-1}$  ( $155,186 \text{ cm}^{-1}$ ), but this value is obviously meaningless because it exceeds the observed ionization limit  $124,429 \text{ cm}^{-1}$  [2]. It may then be tentatively concluded that experimentally indefinite quantity  $\nu$  ( $\Sigma$ ,  $N$ ) is not very different from the value adopted in Eq. (21).

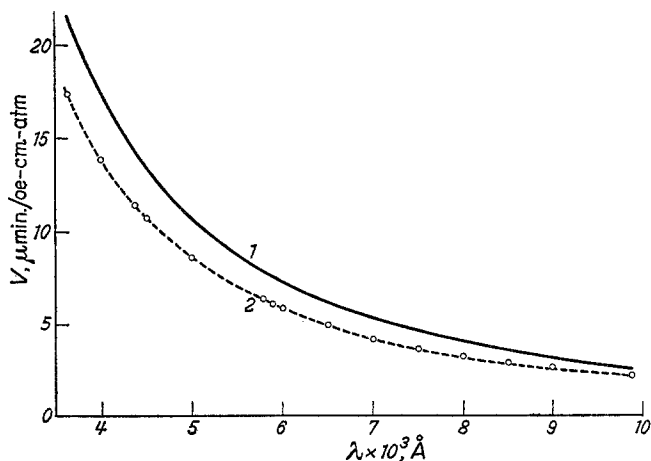


Fig. 2. Magnetic Rotatory Dispersion in  $\text{H}_2$ . 1. Calculated; 2. Observed [6].

In Fig. 2, the calculated magneto-optical rotatory dispersion is compared graphically with the experimental curve obtained by INGERSOLL and LIEBENBERG. Over-all discrepancy is about 25%, and this may indicate that if more accurate wave functions are used almost complete agreement could be obtained. As stated in sec 1, TOBIAS and KAUFMANN have shown that the same experimental dispersion curve is well represented by an expression of the so-called normal Verdet constant shown in Eq. (1) with  $A_0 = 2.72 \times 10^{33} \mu \text{ min sec}^{-2}$  and  $\nu_0 = 3.33 \times 10^{15} \text{ sec}^{-1}$ . From the theoretical viewpoint, on the other side, if  $\nu$  ( $\Sigma$ ,  $II$ ) were made small compared to  $\nu$  ( $II$ ,  $N$ )  $- \nu$ , one could approximately put

$$\nu^{-1}(\Sigma, II) \{ \tau(II, N) - \tau(\Sigma, N) \} \simeq 2 \nu(II, N) \tau^2(II, N) \quad (23)$$

so that Eq. (19) reduces to

$$V = (16 \pi e^3 N \nu^2 / 3 h m c^2) \sum'_{II} \nu(II, N) \tau^2(II, N) [\mathcal{I} m \{ m_z(II, II) \} |x(N, II)|^2 + \\ + 2 x(N, II) m_y(\Sigma, II) z(N, \Sigma)] \quad (24)$$

which contains the normal term only. Although this is actually not the case [the ratio  $\nu(\Sigma, II) : (\nu(II, N) - \nu)$  is about 1:6], there is no telling whether the rota-

tion in the hydrogen molecule is not exactly representable by the normal Verdet constant. Good excited state wave functions or more reliable measurements of the magnetic rotation will make the situation clearer.

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