

The first term is due to the Zeeman splitting of the absorption lines, the second term is due to the change in oscillator strength and the last term due is to the change in the population associated with the absorption lines. In a diamagnetic molecule the last term is zero. Hence one can represent the Verdet constant  $V$  i.e., rotation per unit length and unit magnetic field in a general form having two terms, as follows

$$V = \frac{c}{2mc^2} \frac{1}{n} \sum_i \gamma_i \left[ \frac{A_i \nu^2}{(\nu_i^2 - \nu^2)^2} - \frac{B_i \nu^2}{(\nu_i^2 - \nu^2)} \right] \quad (8)$$

where  $A_i$  and  $B_i$  are constants. This equation is same as the modified Becquerel relation and is a combination of Drude's type A and type B formulae. We shall call the first term in eq. (8) as A term and the second as B term.

### 3. DISPERSION FORMULAE FOR OPTICAL AND MAGNETO-OPTIC DISPERSION

Darwin & Watson (1927) and Serber (1932) examined the available data on Verdet constant of some crystals and gas molecules to find out which type of formula was most satisfactory experimentally. With the limited and not so accurate data that were available to them they found that the B term has little part to play in explaining rotation while the rotation is well explained by the A term alone. But at the same time, due to the lack of accurate data they could not rule out the influence of B term, as the variation with wavelength of A term is faster than that of the B term and in the ultraviolet region the A term predominates. So the ideal place to look for the B term would be away from the ultraviolet region where most of the molecules have their absorption maxima. Accurate values of magneto-optic rotation over the entire range of wavelength-right from near infrared to ultraviolet region are necessary before we can completely, rule out the existence of B term. In the case of diamagnetic cubic crystals it has been shown by Sivaramakrishnan & Ramaseshan (1956) that the B term does not contribute significantly in explaining experimental data on Faraday rotation.

Tobias & Kauzmann (1961) with the aid of quantum mechanics showed that for diamagnetics  $V$  is given by the sum of two terms similar to A term and B term where both the terms contribute to the same order of magnitude to rotation. Since accurate data of magneto-optic rotation for many diamagnetic gas molecules are now available (Ingersoll & Liebenberg 1954, 1956) over a wider range of wavelength (3650Å to 7000Å), the present authors were encouraged to take up a detailed analysis of the data for these gas molecules and see which formula fits best.

The present work has been taken up with a view to see

(1) Whether the magnetic rotation can be represented by a formula having only A term or only B term or a combination of both.

(2) Whether all the frequencies which contribute to refraction also contribute in the same proportion to magnetic gyration in these gas molecules and hence the magneto-optic anomaly factor is the same or different for different absorption frequencies.

In attempting to find which type of formula is not satisfactory experimentally it is necessary to construct an adequate formula for refractive dispersion using either observed or at least reasonable absorption frequencies and test which formula fits best.

In the case of monoatomic gas molecules refraction and Faraday rotation dispersion data are accurately known. In these gas molecules, since the first excited state is far removed from the ground state the electronic absorption frequencies will lie in the vacuum ultraviolet region. Here we do not have the experimentally observed frequencies. A single frequency (see table 1) is arrived at by fitting the refractive index data in the Drude type formula and this frequency may represent the weighted mean of all frequencies that may be present.

Table 1. Table of constants in the dispersion formulae for optical refraction and magnetic gyration

Gas	$A_1 \times 10^{-4}$	$A_2 \times 10^{-4}$	$\lambda_1 A$	$\lambda_2 A$	$\gamma$
He	0.6936	—	475	—	1
Ne	1.335	—	475	—	0.98
A	5.562	—	720	—	1.02
Kr	8.435	—	825	—	1.01
Xe	13.76	—	990	—	1.02
H <sub>2</sub>	2.718	—	860	—	0.93
N <sub>2</sub>	4.525	1.362	650	950	0.63
CO	0.227	6.2	776	1150	0.40

The refractive dispersion relation used here is of the form  $n^2 - 1 = \sum_i \frac{A_i \lambda^2}{(\lambda^2 - \lambda_i^2)}$  and the magneto-optic dispersion formula used is of the form

$$V = \frac{e}{2mc^2 n} \sum_i \left( \gamma_i \frac{A_i \lambda^2 \lambda_i^2}{(\lambda^2 - \lambda_i^2)^2} + \frac{B_i \lambda^2}{(\lambda^2 - \lambda_i^2)} \right)$$

where  $\lambda_i$  is the wavelength corresponding to the absorption frequency  $\nu_i$  and  $\lambda$  is the incident wavelength. It is found that in all these contribution of gas molecules to rotation by the second term (i.e., B term) is extremely small and

the data on magneto-optic rotation can very well be expressed by a formula having the A term only i.e.,

$$V = \frac{e}{2mc^2} \frac{1}{n} \sum_i \frac{\gamma_i A_i \lambda^2 \lambda_i^2}{(\lambda^2 - \lambda_i^2)^2}$$

This means that classically the change in oscillator strength or quantum mechanically the mixing of molecular states does not tell much on rotation and the Zeeman splitting alone is responsible for rotation. The same values of  $A$  and  $\lambda_i$  which fit refraction data also fit the magneto-optic dispersion data. It is also seen that the constants  $A$  and  $\lambda_i$  do not fit into a rotation formula having B term alone. The values of the anomaly factor  $\gamma$  for these gas molecules and the constants  $A_i$  and  $\lambda_i$  are given in table 1. The experimental and calculated value of  $V$  are given in table 2. They are found to agree well within the experimental error.

In the diatomic diamagnetic gas molecules, (CO, N<sub>2</sub>, H<sub>2</sub>), that were analysed it is seen that the use of two absorption frequencies in the formula for optical refraction was found to be necessary to have a good fit of the experimental data. Correspondingly the rotation data were also fitted with the same two frequencies. The two frequencies are the weighted mean of absorption frequencies that may exist in these molecules at these regions. The absorption frequencies used here are the observed ones (Herzberg 1950) and they belong to the important absorption band series that are

Table 2. Experimental and calculated values of Verdet constants for inert gases

$\lambda A$	He		Ne		A		Kr		Xe	
	$V_{exp}$	$V_{cal}$	$V_{exp}$	$V_{cal}$	$V_{exp}$	$V_{cal}$	$V_{exp}$	$V_{cal}$	$V_{exp}$	$V_{cal}$
4000	1.01	1.01	1.95	1.92	19.78	19.69	40.92	40.69	98.95	98.20
4360	0.85	0.85	1.65	1.63	16.49	16.4	33.88	33.79	81.07	80.97
4500	0.799	0.80	1.54	1.52	15.41	15.35	31.69	31.55	75.54	75.51
5000	0.64	0.64	1.22	1.21	12.33	12.3	25.39	25.2	60.33	60.00
5460	0.53	0.53	1.01	1.01	10.24	10.25	21.02	20.95	49.34	49.54
5780	0.47	0.47	0.90	0.90	9.13	9.13	18.6	18.58	43.59	43.88
5893	0.46	0.46	0.86	0.86	8.76	8.74	17.78	17.87	41.84	41.8
6000	0.44	0.44	0.82	0.83	8.42	8.43	17.13	17.21	40.1	40.26
6500	0.37	0.37	0.62	0.62	7.06	7.12	14.36	14.54	33.65	34.02
7000	0.325	0.325	—	—	6.02	6.10	12.24	12.4	28.59	29.00

( $V$  is given in microminutes/gauss/cm.)

observed in these gas molecules. The constants and the absorption frequencies are given in table 1.

In these molecules also we found that the B term is not necessary to account for the data on the dispersion of magnetic gyration and a formula with A term alone explains satisfactorily the data on rotation. The same two absorption frequencies and the constants  $A_1$  and  $A_2$  are used in the dispersion formula to fit both the refraction and rotation data. The experimental and calculated values of  $V$  for these molecules are given in table 3.

Table 3. Experimental and calculated values of  $V$  for diatomic molecules

$\lambda A$	$H_2$		$N_2$		$CO$	
	$V_{exp}$	$V_{cal}$	$V_{exp}$	$V_{cal}$	$V_{exp}$	$V_{cal}$
4000	13.85	13.82	13.61	13.62	24.74	25.04
4360	11.40	11.43	11.27	11.31	20.28	20.49
4500	10.67	10.68	10.54	10.58	19.00	19.06
5000	8.55	8.52	8.44	8.46	15.11	15.04
5460	7.05	7.06	7.05	7.04	12.48	12.39
5780	6.27	6.26	6.27	6.26	11.30	10.95
5893	0.03	6.02	6.05	6.01	10.52	10.5
6000	5.81	5.80	5.81	5.79	10.10	10.10
6500	4.88	4.91	4.91	4.91	8.47	8.51
7000	4.14	4.21	4.19	4.22	7.21	7.27

( $V$  is given in microminutes/gauss/cm.)

#### 4. MAGNETO-OPTIC ANOMALY FACTOR

Our expression for Verdet constant is nothing but the modified Becquerel formula (4) in which the magneto-optic anomaly factor  $\gamma$  is different for different absorption frequencies. One can calculate the  $\gamma$  factor from the experimental values of rotation and optical dispersion. If the  $\gamma$  value for different wavelengths happens to be constant then it means that the anomaly factor for the different absorption frequencies are the same. If one finds that  $\gamma$  factor varies with wavelength it signifies that the different absorption frequencies may have different  $\gamma$  factor values i.e., the Zeeman splitting may be different for the different absorption frequencies. In the case of both monatomic and diatomic molecules

analysed here it is found that the mean anomaly factor is a constant thereby indicating that the Zeeman splitting is the same for all the absorption frequencies that control the optical dispersion. The  $\gamma$  values calculated for all these molecules are given in table I. It can be seen from the table that the  $\gamma$  value for almost all the monatomic gases is almost the theoretical value of unity. A deviation from this value would mean a failure of the Larmor's theorem in the molecules. When the bonding in a molecule (diatomic or polyatomic) is strong, the electric field in the molecule deviates more and more from the central nature. In the absence of a central field the Larmor precession of the electrons in the molecules may be expected to be less than that in the presence of the central field. And hence the Zeeman splitting will not be the normal one. One could therefore expect the  $\gamma$  factor which is the ratio of the actual Zeeman splitting to the normal value to be less than unity. Except in the case of atoms and molecules possessing inert gas configuration the  $\gamma$  value will be less than the value unity, thereby giving an idea about the strength of the binding present (Ramaseshan 1950). In the case of diatomic molecules  $A_2$ ,  $N_2$ , and CO the values of the anomaly factor are found to be 0.93, 0.63 and 0.4 respectively and the corresponding force constants for these molecules calculated from Raman and infrared data are 4.22, 8.97 and  $11.82 \times 10^6$  dynes/cm respectively. This indicates a correlation between the anomaly factor and the binding; stronger the binding lower is the  $\gamma$  value.

## 5. CONCLUSION

It is seen that the magneto-optic dispersion data in diamagnetic molecules is well represented by a formula of the type A and the Zeeman splitting of the absorption frequency alone accounts for the dispersion of Faraday rotation. The change in oscillator strength or the intensity of the lines does not seem to contribute much to the magnetic rotation. All the dispersion frequencies which contribute to refraction contribute to rotation too in the same proportion. The Zeeman splitting is found to be normal in the case of noble gases and therefore the magneto-optic anomaly factor is found to be nearly unity. In the other cases the values deviate considerably, but the anomaly factor is found to be a constant for all the incident wavelengths thereby indicating that the different absorption frequencies that control refraction and rotation have the same anomaly factor.

The authors are presently analysing some of the polyatomic diamagnetic gases and these will be reported later.

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