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Thermomagnetic-Torque Measurements in Dilute Polyatomic Gases

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Measurements of the thermomagnetic torque for a large number of gases indicate that the field and pressure dependences of the torque can be represented by a single curve for most gases. The pressure (P) dependence of H_0, the field for maximum torque, is given by $H_0 = b(P+a)$, where b and a are constants. The molecular rotational g values for the gases can be estimated from the relation $g_J = 1.27\times10^{16}\sigma\bar{v}/(QbT)$, where σ is the molecular cross section, $\bar{v}$ the average molecular velocity, T the absolute temperature, and Q a constant (taken to be 4π). The sign of g_J is given by the torque direction. Values of g_J calculated from the torque are in reasonable agreement with other determinations for all gases except Cl_2. Previously undetermined g_J values are estimated for a number of gases. The existence of multiple torque maxima in O_2, NO, NO_2, and HD is discussed.

I. INTRODUCTION

In 1967, Scott, Sturner, and Williamson reported measurements on a thermomagnetic-torque effect in polyatomic gases.[1] In this effect, a cylinder which is exchanging thermal energy with a dilute gas rotates when an axial magnetic field H is applied. The torque direction depends on whether the energy transfer is into or out of the surface. It also depends on the direction of the magnetic field and on the sign of the molecular rotational g factor of the particular gas molecules involved.[2] The magnitude of this torque N is a function of the magnetic field intensity and exhibits a maximum $N_{\max}$ which occurs at a field H_0. Both $N_{\max}$ and H_0 depend on the gas pressure and on the nature of the gas.

The original paper on this effect generated considerable theoretical interest[3-7] because the effect seems to offer a means of studying some of the aspherical properties of molecules. We have, therefore, conducted additional experiments on a large number of gases and report the results in this paper.

II. GENERAL TORQUE CHARACTERISTICS

In the thermomagnetic gas torque effect, the normalized torque–versus–magnetic-field curves at a given pressure have a characteristic shape shown in Fig. 1. A change in the gas pressure changes the magnitude of the torque peak and its field position, but normalization produces the characteristic curve. Figure 2 illustrates this fact by giving normalized semilogarithmic plots for various pressures of nitrogen. This same curve shape is also characteristic of most of the gases investigated. Figure 3 compares normalized plots for N_2, CO, and O_2.

The magnetic field H_0 at which the maximum

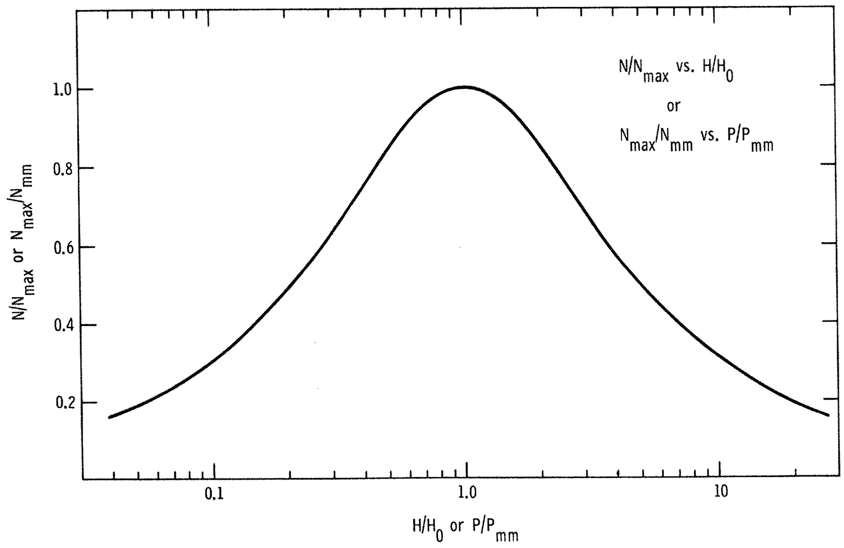

FIG. 1. Normalized plots of torque versus magnetic field at constant pressure and peak value of torque versus pressure.

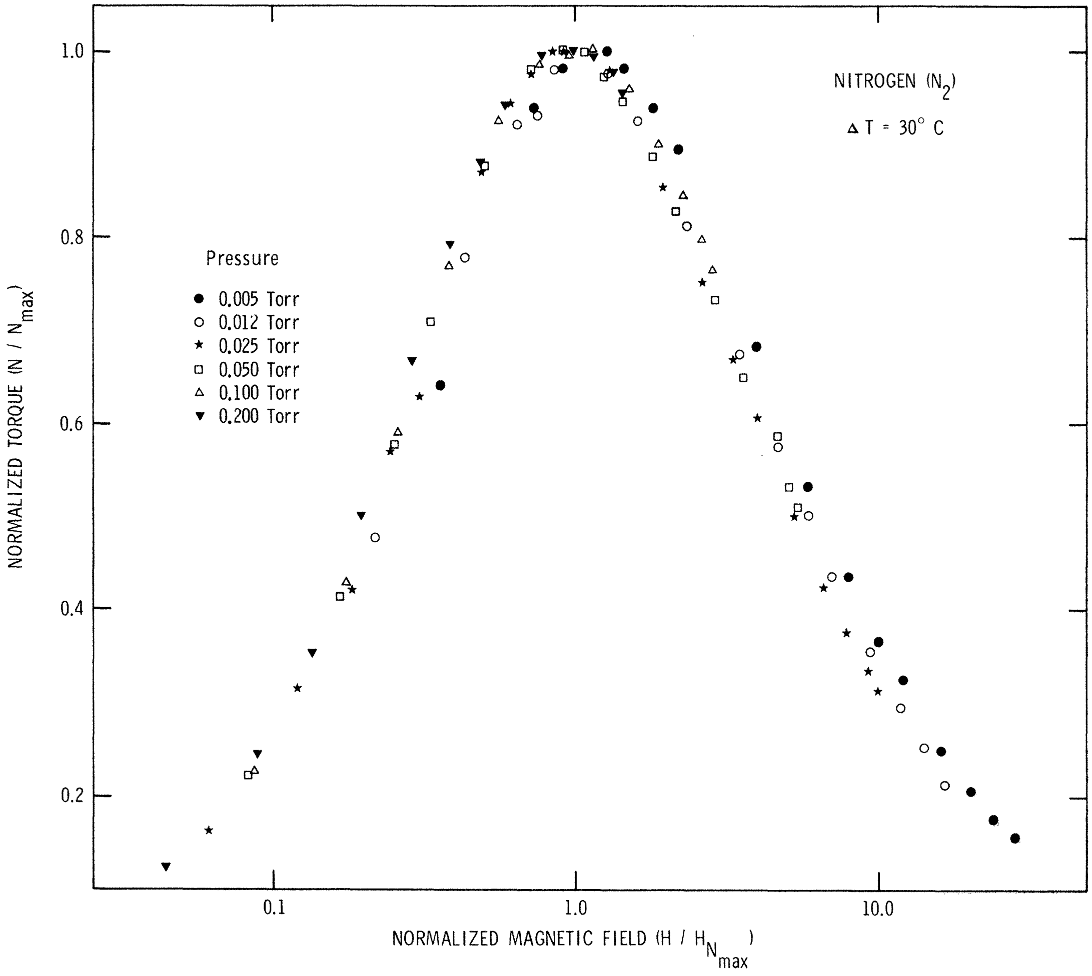

FIG. 2. Normalized plots of torque versus magnetic field for six different pressures of N_2.

torque for each pressure P occurs is linearly related to P but with a nonzero intercept for $P = 0$. This nonzero intercept is undoubtedly due to Knudsen effects which depend on the dimensions of the apparatus in which the measurements are made. A schematic drawing giving apparatus dimensions is shown in Fig. 4. The relationship between H_0 and P can be expressed reasonably well as

$$H_0 = b(P + a), \tag{1}$$

where b and a are constants. The value of b is characteristic of the particular gas and is equal to the high-pressure value of H/P (i.e., for the absence of Knudsen effects). The value of a depends both on the gas and on the dimensions of the measuring apparatus.

N_{max}, the value of the torque at $H = H_0$, is pressure dependent. At a certain gas pressure P_{mm}, N_{max} attains its highest possible value, N_{mm}. This pressure is only slightly dependent on the particular gas involved, being in the neighborhood of 0.035 Torr. A normalized curve of the pressure dependence of the torque maximum is identical (within experimental error) to the normalized curve of torque versus field. This common shape is shown in Fig. 1. Since the pressure dependence of H_0 is given by Eq. (1), the magnitude of N can be determined for any field and pressure from the values of a, b, N_{mm}, and P_{mm} and the two superimposed curves of Fig. 1.

Table I gives these values for the various gases investigated. Values of N_{mm}, although usually measured for a temperature difference ΔT between inner and outer cylinders of about 30°C, are quoted for $\Delta T = 1°$C. (The torque has been shown to be proportional to the temperature difference for ΔT values which are small compared to the absolute temperature of the measurement.) All of our measurements have been made for field values below 10^3 Oe and in the pressure range 0.001–2.0 Torr. Uncertainties in the table values are caused by nonuniformity in the magnetic field, and difficulty in determining surface temperatures and gas pressures rather than in the measurements of torque. Pres-

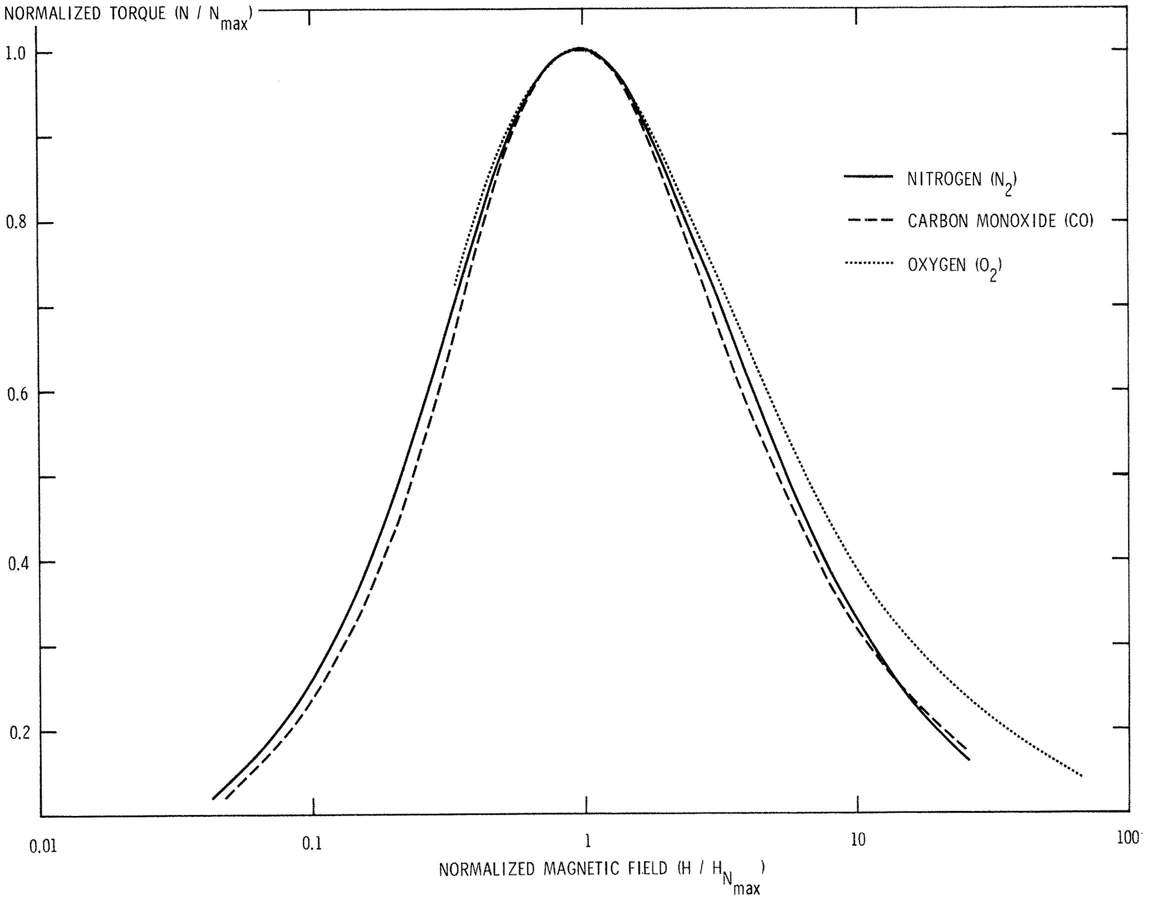

FIG. 3. Normalized curves for N_2, CO, and O_2.

sure uncertainties are estimated to be ± 100% at the lowest pressure and ± 10% for pressures above 0.020 Torr. Uncertainties in ΔT should be on the order of 20%, which would affect only the values for N_{mm}. The field is uniform to within ± 5%. The sign of N_{mm} is taken to be the same as the sign of g_J as verified for N_2 (and hence is opposite to that arbitrarily taken in Ref. 1).

III. GASES HAVING UNIQUE CHARACTERISTICS

Most gases have characteristics which can be summarized quite well by the constants given in Table I. With these constants and Fig. 1 we can construct curves representing our measured data to within the accuracy limits of the experiments. Some gases, however, appear to have more than one peak in their torque-versus-magnetic-field curves. Examples of gases with more than one peak are nitric oxide, nitrogen dioxide, oxygen, and hydrogen deuteride. Figure 5 gives a semilogrithmic plot of torque versus field for various pressures of nitrogen dioxide. Although this gas has two molecular forms (NO_2 and N_2O_4) at sufficiently high pressures, the pressures of our experiments were so low that only NO_2 should be present in the bulk gas.[8] Hence, the explanation of the double peak cannot be a straightforward assignment to two forms of nitrogen dioxide. We shall discuss this problem more fully in Sec. IV.

FIG. 4. Schematic drawing of apparatus used to measure the thermomagnetic gas torque. *C*: glass chamber, inside diam = 7.6 cm, length = 61 cm; *M*: mirror; *L*: lens; *H*: Helmholtz coil used for fields up to 120 Oe, diam ≈ 30 cm; *S*: solenoid used for fields above 120 Oe, inside diam = 9.5 cm, outside diam = 19 cm, length = 30 cm; *R*: heated cylindrical torque detector, diam = 1.9 cm, length = 20 cm.

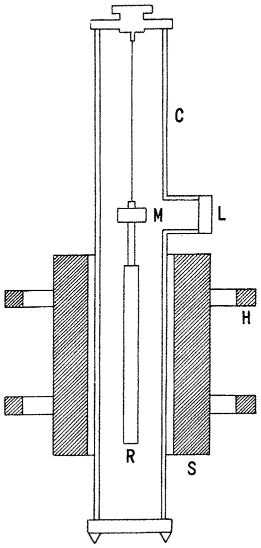

TABLE I. Thermomagnetic gas torque constants for heated cylinder 1.9 cm diam and 20 cm long in 7.6-cm-diam glass chamber. Torques for the following gases were either too small to be observed, or were made uncertain by contamination by gases displaying much larger effect: He, Ar, Xe, H_2O, D_2O, HDO, NH_3, C_6H_6, H_2S, CH_3Br, CH_3I.

Gas	$b\left(\frac{\text{Oe}}{\text{Torr}}\right)$	a(Torr)	P_{mm}(Torr)	$\frac{N_{mm}}{\Delta T}\left(\frac{\text{dyn cm}}{°\text{C}}\right)$
NO_2(low-field peak)	10.2	0.030	0.030	-0.06×10^{-3}
NO (low-field peak)	12.	0.007	0.030	−0.38
HD(low-field peak)	55.	0.08	0.050	+0.15
HD(high-field peak)	135.	0.8	0.350	+0.15
D_2	87.	0.10	0.04[a]	+0.012
H_2	100.[a]	0.005[a]	0.04[a]	+0.003
O_2	62.	0.008	0.035	−0.25
NO_2 (high-field peak)	1450.	0.015	0.038	−0.33
N_2	1750.	0.005	0.032	−0.83
Cl_2	2000.	0.004	0.050	−0.57
CO	2100.	0.004	0.032	−1.0
CH_4	2130.	0.008	0.040	+0.09
CH_3D	2340.	0.019	0.040	+0.08
CD_4	3340.	0.006	0.038	+0.14
SO_2	9100.	0.003	0.018	−0.13
SF_6	11000.	0.022	0.03[a]	−0.27[a]
N_2O	12000.	0.005	0.035	−0.53
CF_4	12000.	0.026	0.035	−0.31
CO_2	13000.	0.005	0.024	−0.83
SIF_4	14000.	0.012	0.025	−0.26
C_2H_4	17000.	0.001	0.032	−0.22
OCS	25000.	0.006	0.024	−0.50
C_2H_6	62000.	0.005	[b]	+ [b]
CF_2Cl_2	66000.[a]	0.002[a]	[b]	− [b]
$CHCl_3$	86000.[a]	0.001[a]	[b]	− [b]
CCl_4	135000.	[b]	[b]	− [b]
CH_3Cl	$>10^5$	[b]	[b]	− [b]
CH_2Cl_2	$>10^5$	[b]	[b]	− [b]
$CHClF_2$	$>10^5$	[b]	[b]	− [b]
C_3H_8	$>10^5$	[b]	[b]	+ [b]
C_4H_{10}	$>10^5$	[b]	[b]	+ [b]

[a] Values very approximate.

[b] Available field intensities too low for this determination.

Figure 6 shows a torque-field plot for nitric oxide. NO does not dimerize but it does combine readily with oxygen to form NO_2. In our experiments, attempts were made to freeze out with dry ice any NO_2 impurity before introducing the gas into the apparatus. However, the possibility still exists that O_2 was desorbed from the apparatus, so that NO_2 was actually present during the experiments and accounts for the second (high-field) peak. The low-field NO peak is also peculiar in that it is considerably sharper than the standard shape of Fig. 1. This is shown in Fig. 7, where normalized plots for N_2 and NO are compared. We discuss NO more fully in Sec. IV.

Williamson[9] has conducted extensive experiments on O_2. He has found that the original peak reported[1] for O_2 can be resolved into two peaks having the standard shape, with the second peak occurring at a field some 20 times smaller than the original peak for a pressure of 0.2 Torr.

The field dependence of the torque for HD is complex – at least two peaks were originally observed.[10] The high-field HD peak appeared to be unique in that its field position was independent of pressure up to about 0.35 Torr.[10] We have extended this work on HD to considerably higher pressures and the results are shown in Fig. 8. It appears that the position of this high-field peak is linearly dependent on the pressure at these higher-pressure values.

IV. DISCUSSION

Since, as has been shown theoretically[3,4] and experimentally,[11,12] the competition of collision and precession processes produces the gas torque, it is evident that there are two causes for the existence of multiple peaks in the torque: (a) more than one molecular precession frequency; or (b) more than one molecular collision process with different frequencies. Let us discuss these two cases in some detail.

A. Multiple Precession Frequencies

The existence of more than one molecular precession frequency can result from the presence of more than one molecular species as in a mixture or in a paramagnetic gas such as O_2, NO, or NO_2 with a distribution of rotational moments corresponding to the populations of its rotational energy levels.

1. *Oxygen*

As mentioned in Ref. 12, the distribution of moments of O_2 accounts quite nicely for the two peaks found by Williamson. It is possible to estimate g_J values for oxygen from Hund's rule *b*.[13,14] Since the gas torque is an odd function of magnetic field, the contributions of molecules with $M_s = \pm 1$ will roughly cancel,[14] although a net excess of $M_s = +1$ molecules will produce a small effect.[15] Hence those molecules with $M_s = 0$ will dominate the torque. We expect only "rapidly rotating" molecules to contribute to the torque[16] (i.e., molecules which rotate more than once in the time taken to move a molecular diameter). Approximate considerations lead to the conclusion that a rapidly rotating molecule is one for which the rotational quantum number J (K for oxygen) is somewhat greater than the most probable value of J (or K). Recalling that for $^{16}O_2$ only K = odd states are allowed,[17,18] we have calculated g_J values for the $M_s = 0, \pm 1$ states. From these calculations we conclude that the effective g_J distribution (i.e., for rapid rotators) for the $M_s = 0$ molecules will peak at about -10 to -20. The effective distribution corresponding to the excess of $M_s = +1$ molecules over $M_s = -1$ molecules will peak at $g_J \approx -250$.

2. *Nitric Oxide*

The rotational magnetic moment of NO in the $^2\Pi_{1/2}$ ground state has been measured by Ramsey[19] using molecular-beam techniques. His results correspond to a g_J value of 48.2 with the sign undetermined. Mizushima *et al*,[20] from their microwave work, found $g_J = -42.2$ for the $J = 3/2$ level in the $^2\Pi_{1/2}$ state; they also calculated $g_J = -42$ for this same state. In our dynamic studies of the gas torque,[11] we have found $g_J = -49.3$, in good agreement with the result of Ramsey. The negative sign of g_J has also been verified by measurements of

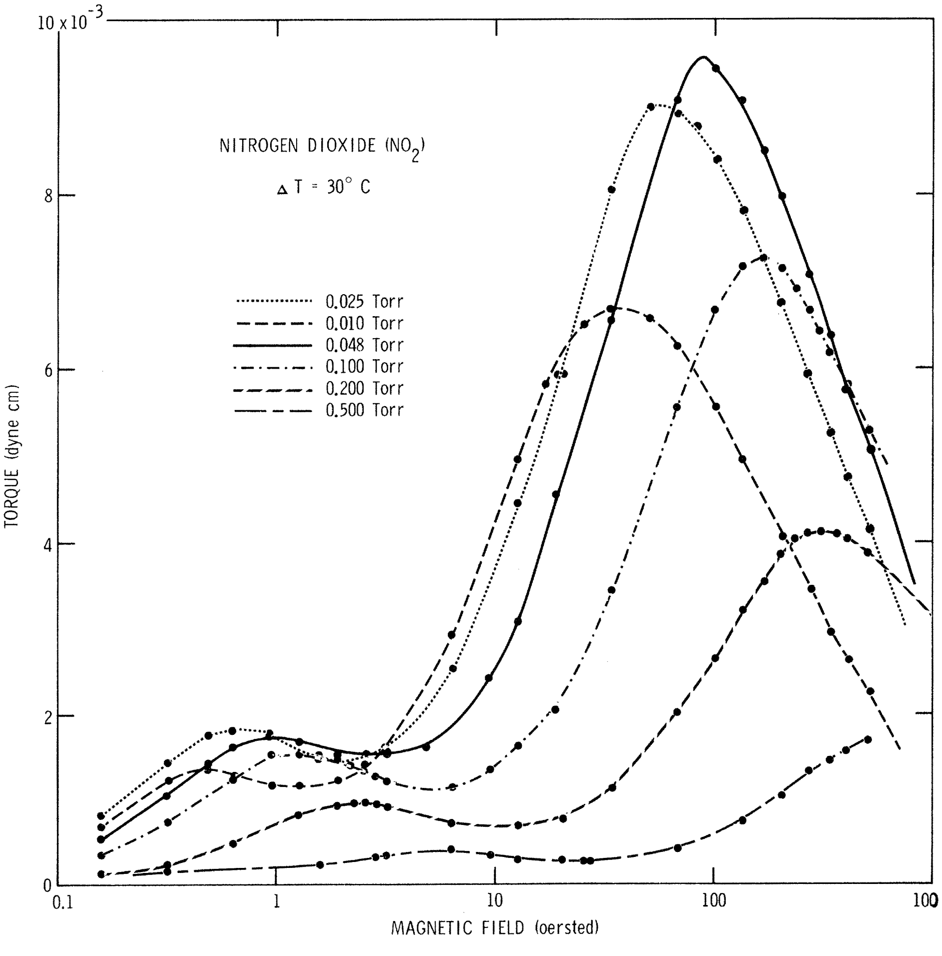

FIG. 5. Torque-versus-field curves for nitrogen dioxide (NO_2).

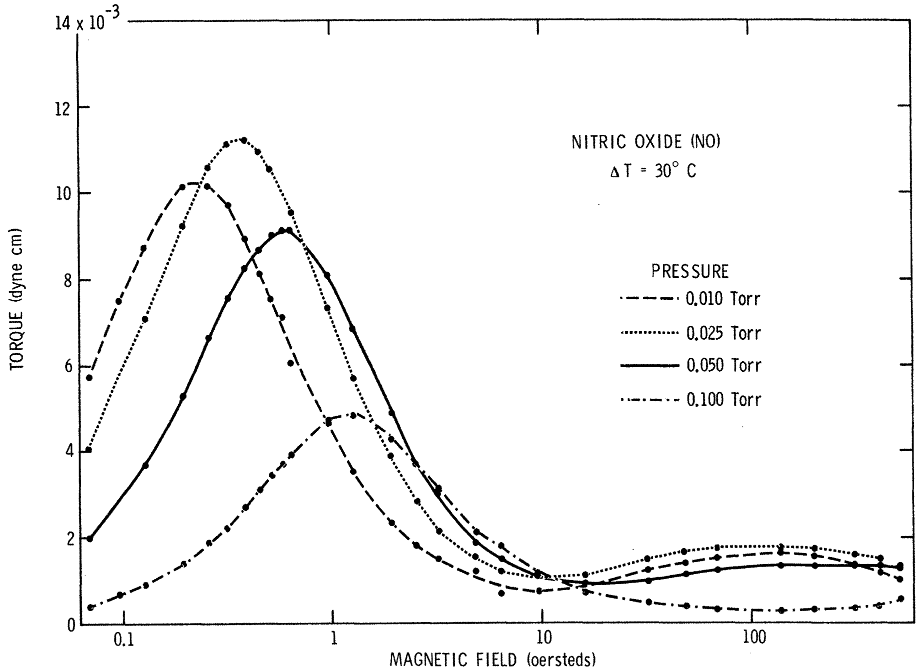

FIG. 6. Torque-versus-field curves for nitric oxide (NO).

transverse heat transport in the presence of a magnetic field.[21]

Dousmanis *et al.*[22] have developed a theory for intermediate coupling in $^2\Pi$ states, and Robinson[23] has applied it to calculate g_J for NO in the $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ states. Because the systematics of Ref. 22 correspond to ESR notation in which g for an electron is positive, we must multiply the results of Robinson by -1. The resulting calculated g factors for the $^2\Pi_{1/2}$ state agree well with experiment – ranging from -42.6 for $J=\frac{3}{2}$ to a maximum magnitude of -51.5 ($J=\frac{13}{2}$) and gently decreasing in magnitude to -42.8 at $J=\frac{51}{2}$. Thus the theoretical g_J for NO in the $^2\Pi_{1/2}$ state is fairly independent of J, as suggested by the work of Ramsey[19] and the dynamic experiments.[12]

As mentioned above, the low-field peak for NO is sharper than the standard shape. This fact can be qualitatively explained by considering the contribution of molecules in the $^2\Pi_{3/2}$ state. By taking g_J to

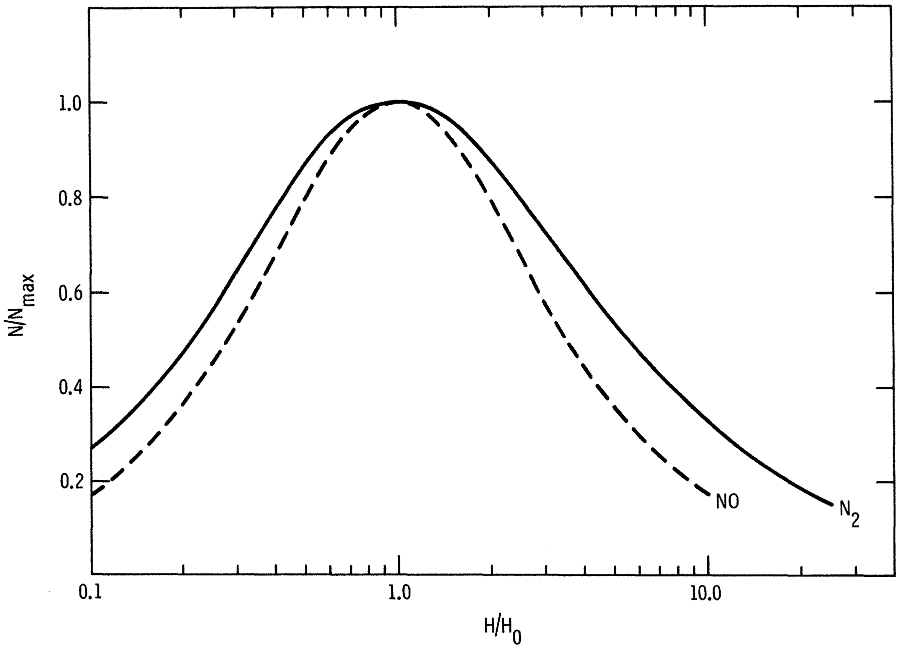

FIG. 7. Normalized plots of torque versus magnetic field for N_2 and NO showing deviation of NO from standard shape.

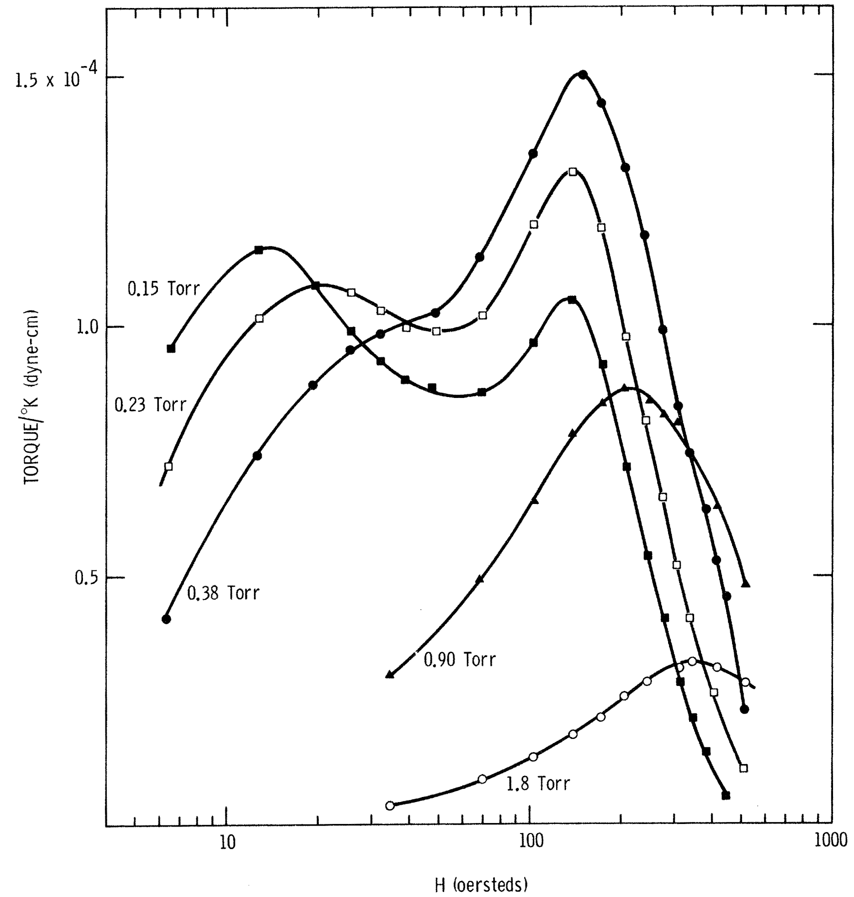

FIG. 8. Semilogarithmic plot of torque versus field for HD.

be given by the negative of the values calculated by Robinson, we estimate the effective distribution of g_J as a function of J for the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ levels. The populations of the J levels are calculated in the manner of Beringer and Castle.[24] Since the g factors for the rapidly rotating $^2\Pi_{3/2}$ molecules are smaller than and opposite in sign to those for molecules in the $^2\Pi_{1/2}$ state,[23] the net effect is a narrowing of the torque curve – predominately on the high-field side.

The high-field peak in the gas torque for NO is felt to be due to nitrogen dioxide contaminant – perhaps due to reaction of NO with adsorbed O_2.

3. *Nitrogen Dioxide*

Although NO_2 is triatomic, its ground state is analogous to a $^2\Sigma$ state with its magnetic moment arising from the spin of the odd electron.[25] Nitrogen dioxide forms a dimer N_2O_4; however, at the low pressures of this experiment the gas should be effectively[8] 100% NO_2 (unless some surface interaction prevents equilibration). This fact makes the explanation of the high-field peak difficult.

The weak low-field peak we attribute to paramagnetic NO_2. We have calculated a distribution function of g_J for molecules in the $M_s = +\frac{1}{2}$ and $-\frac{1}{2}$ states. The excess of molecules in the $M_s = +\frac{1}{2}$ level yields an effective distribution of negative g_J values, which, for rapidly rotating molecules, peaks in the neighborhood of -100.

The explanation of the strong high-field peak is difficult if we assume complete absence of N_2O_4 – which, if present, would be expected to yield a peak near that observed. It seems unreasonable to ascribe the high-field peak to an impurity unless some reaction occurs in the apparatus since the gas used was 99.9% pure. Therefore, for lack of a better explanation, we speculate that, owing to some surface interaction, N_2O_4 may be present near the pendulum surface – producing the high-field torque. This proposal is somewhat substantiated by experiments designed to measure bulk circumferential flow in the gas.[26] In these experiments the low-field peak in nitrogen dioxide predominates.

In an attempt to determine whether a change in temperature would shift the relative concentrations of the species producing the two peaks we performed two experiments at an ambient temperature of about 82° C, an increase of 60° C above the usual temperature. Both peaks decreased to about 0.7 times their room-temperature value, but their relative amplitudes remained essentially unchanged.

TABLE II. Calculation of g_J from gas torque.

Gas	σ(cm^2)	$\bar{v}$ (cm/sec)	g_J [a]	
			From torque [Eq. (2)]	Other
NO_2	(6) $\times 10^{-15}$	3.7×10^4	−72	−40 to −150[b]
$NO(^2\pi_{1/2})$	4.1	4.6	−55	−48.2 ± 1[b–f]
O_2	3.8	4.4	− 9	−10 to −20[b,e,g]
N_2O_4(?)	(~9)	2.6	− 0.54	
N_2	4.3	4.7	− 0.39	−0.2593[g–i]
Cl_2	(5)	3.0	− 0.25	0.0290[j,k]
CO	4.2	4.7	− 0.32	−0.2691[l]
CH_4	5.0	6.3	+ 0.50	+0.3133[m]
CH_3D	(5)	6.1	+ 0.44	+[m]
CD_4	4.7	5.6	+ 0.26	
SO_2	(4)	3.1	− 0.046	0.084[j,n]
SF_6	(6.5)	2.1	− 0.042	
N_2O	6.5	3.8	− 0.069	0.086[j,n]
CF_4	(5.5)	2.7	− 0.042	−0.03126[o]
CO_2	5.2	3.8	− 0.051	−0.05508[i,p]
SiF_4	(6)	2.5	− 0.036	−0.03191[o]
C_2H_4	(6)	4.8	− 0.057	
OCS	(6)	3.2	− 0.026	−0.02889[p]
C_2H_6	(6.5)	4.7	+ 0.017	
CF_2Cl_2	(6.5)	2.3	− 0.0076	
$CHCl_3$	(6.5)	2.3	− 0.0059	
CCl_4	(7)	2.0	− 0.0035	

CH_3Cl, CH_2Cl_2, and $CHClF_2$ have negative g_j values; C_3H_8 and C_4H_{10} have positive g_J values.

[a] Where rotational magnetic moment is measured in nuclear magnetons.

[b] See Sec. IV A.

[c] N. F. Ramsey (Ref. 19) (magnitude only).

[d] M. Mizushima *et al.* (Ref. 20).

[e] Negative sign confirmed by L. J. F. Hermans *et al.* (Ref. 21).

[f] G. W. Smith and G. G. Scott (Ref. 12).

[g] Sign determined by L. J. F. Hermans *et al.* (Ref. 21), and by J. Korving, H. Hulsman, H. F. P. Knaap, and J. J. M. Beenakker, Phys. Letters 21, 5 (1966).

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[i] Sign determined by J. Korving, L. J. F. Hermans, J. J. de Groot, H. F. P. Knaap, and J. J. M. Beenakker, J. Mol. Spectry. 20, 294 (1966).

[j] Sign not determined. (Values of 6 in parentheses are rough estimates.)

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The negative result of this experiment leaves the nature of the high-field peak essentially unexplained. (See note added in proof.)

B. Multiple Collision Frequencies

At present, HD appears to be the only gas falling into this category.[10,12] The low-field peak has been shown to occur at fields too low for elastic collisions, and dynamic experiments[12] have supported the view that inelastic collisions are important for this peak. This result is in agreement with the conclusion of Korving *et al.*[27] that inelastic collisions must be invoked to explain anomalous viscosity effects in the hydrogen isotopes. It seems unlikely that inelastic collisions should be important for any of the other gases reported here.

C. Calculation of g_J from Simple Model

A simple model of the gas torque was presented in Ref. 12. It was shown that the molecular g factor can be calculated roughly from the relation

$$g_J = 1.27 \times 10^{16} \sigma\, \bar{v}/QbT, \tag{2}$$

where σ is the collision cross section (cm^2), $\bar{v}$ the average molecular velocity (cm/sec), b the parameter of Eq. (1) (Oe/Torr), T the temperature (°K), and Q a constant. The sign of g_J is given by the direction of the torque, taking that of N_2 to correspond to a negative g value. In Ref. 12, Q was taken to be 10; however, a recent derivation[28] of Eq. (2) indicates that is is better to take $Q = 4\pi$, which value we use in the present paper.

In a number of instances σ was calculable from viscosity (η) data in the International Critical Tables using the relation[29] $\sigma = m\bar{v}/(3\eta)$. Values of σ are given in Table II. It was necessary to estimate σ for molecules for which η was not known; the values are indicated by parentheses in Table II. Since σ is not a highly variable parameter, this procedure was felt to be adequate for the degree of approximation in the simple model. Values of σ for the hydrogen molecules are not included in Table II — because of the inelastic collision difficulty. Values of $\bar{v}$, calculated from kinetic theory,[29] are also given in Table II.

In the last two columns of Table II are given g_J as calculated from Eq. (2) and as determined by other methods. We see that reasonable agreement is obtained for all gases but Cl_2. The disagreement for this gas is not understood, but the reactivity of Cl_2 makes it suspect. It is worth noting that the model predicts $g_J = -0.54$ for N_2O_4, assuming the high-field peak of nitrogen dioxide to be due to that gas.

In conclusion, we remark that the general features of the gas torque seem to be understandable. However, there are several aspects of the phenomenon which remain unexplained. It appears that the gas torque may prove useful in determining the sign of molecular g values and in estimating their magnitude.

D. Comment on Dynamic Experiment in NO

In Ref. 12 we pointed out that in the precession effect of NO the width $\Delta\nu_2$ of the double Larmor frequency line is $0.4\nu_2$, where ν_2 is the frequency of the line. Thus $\Delta\nu_2$, like ν_2, is proportional to the field strength. In that earlier work we suggested no explanation for the linear dependence of $\Delta\nu_2$ upon H. However, at present this behavior does seem explainable in terms of the distribution of g_J values calculated by Robinson.[23] If the linewidth were solely a result of the distribution of moments, $\Delta\nu_2$ would indeed be proportional to H. In addition, the fact that absolute values of g_J for rapidly rotating molecules ($J > \frac{21}{2}$) range from 12 to 50 (for both $^2\Pi_{1/2}$ and $^3\Pi_{3/2}$ molecules in suitably populated levels) is in reasonable agreement with $\Delta\nu \approx 0.4\nu_2$.

Note added in proof. We have recently conducted experiments on HNO_3 which also gave two peaks at field values close to those observed for NO_2. HNO_3 is a highly reactive molecule and could be expected to form in our original apparatus by the combination of NO_2 with trace amounts of water. Therefore these NO_2 peaks might be due to any of the numerous reaction products of NO_2, HNO_3, and H_2O.

ACKNOWLEDGMENTS

The authors thank Professor N. F. Ramsey, Professor D. W. Robinson, Professor R. M. Williamson, and Dr. L. T. Klauder for valuable comments on aspects of the work.

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[1] G. G. Scott, H. W. Sturner, and R. M. Williamson, Phys. Rev. 158, 117 (1967).

[2] The torque direction is that of the product $g_J(\hat{H}\times\hat{\Phi})\times\hat{n}$, where g_J is the molecular g factor, $\hat{H}$ is a unit vector in the field direction, $\hat{\Phi}$ is a unit vector in the direction of the radial temperature gradient, and $\hat{n}$ is a unit vector normal to the pendulum surface.

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