Experimental study of the gas-kinetic magnetic resonance in some nonparamagnetic polyatomic gases

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(Submitted 11 March 1987)
Zh. Eksp. Teor. Fiz. **94**, 88–92 (February 1988)

The gas-kinetic magnetic resonance (GMR) has been investigated experimentally for polyatomic gases with different molecular configurations, namely, CO_2, CH_4, SF_6, and NF_3. The results are in qualitative agreement with theoretical predictions. They suggest that GMR could be used to investigate the properties of many gases. The molecular g-factors determined in these experiments agree with existing data to within experimental error.

It is well-known that the gas thermal conductivity $R(H)$ undergoes a resonance reduction in mutually perpendicular ("crossed") constant and alternating magnetic fields H and $H_\sim$. This is the so-called gas-kinetic magnetic resonance (GMR).[1–6] Theory shows[2,3] that the maximum reduction in thermal conductivity, $R = R_0$, occurs when the frequency f of the field $H_\sim$ is equal to the precession frequency of the magnetic moments of the nonspherical molecules: $f = \gamma^* H_{\text{res}}$, where γ^* is the gyromagnetic ratio of the molecules under investigation and H_{res} is the resonance value of the field H. Consequently, if we know f and H_{res}, we can determine γ^*, which is related to the molecular Landé g-factor. For nonparamagnetic molecules, $g = \gamma^* h/\mu_n$, where h is Planck's constant and μ_n the nuclear magneton. It follows that GMR can be used to determine g. However, since GMR is an even effect, the sign of g cannot be determined.[1)] Theory shows[2] that the function $R(H)$ depends significantly on the chosen model of molecular scattering. Under certain special conditions, $R(H)$ can have fine structure[2,3,5] and nonmonotonic singularities in the form of GMR harmonics.[3,4] Studies of these singularities can be used to judge the anisotropy of the nonequilibrium distribution of the molecules over their vibrational states and, hence, the orientational dependence of nonspherical scattering by the molecules. Previous experimental studies of GMR in nonparamagnetic gases were confined to diatomic molecules.[1,4–6] It was shown that the function $R(H)$ was, on the whole, in good agreement with theory, but there were also some significant discrepancies, especially in the fine structure of GMR.[1] In this paper, we report an experimental study of GMR in polyatomic gases with different molecular configurations, namely, CO_2, CH_4, SF_6, and NF_3. These molecules are either slightly nonspherical or have a small value of g. This complicates studies of GMR fine structure, which was not, therefore, investigated in these experiments.

The experimental method is described in detail in Ref. 1. It is based on a dc bridge in which adjacent arms contain thermistors heated to about 100 °C in two communicating and identical measuring chambers, filled with the gas being investigated. The two chambers are placed in the gap of an electromagnet whose magnetic field H is parallel to the temperature gradient. One of the chambers (the "active chamber") is, in addition, located inside a solenoid that produces the alternating field $H_\sim$. The bridge off-balance signal is proportional to the difference δQ between the heat fluxes ΔQ and ΔQ_c in the active and comparison chambers due to the changes $\Delta\varepsilon$ and $\Delta\varepsilon_c$ in the thermal conductivities produced by the magnetic field $H + H_\sim$ in the first and H in the second chamber. It follows from Refs. 1–3 that, when $H \gg H_\sim$ and H/p is large enough (p is the pressure), $\Delta\varepsilon$ is approximately equal to the sum of the change in thermal conductivity produced in the active chamber by the field H, i.e., the even Senftleben-Beenaker effect (SBE) $\Delta\varepsilon_S$, and by GMR itself, namely, $\Delta\varepsilon_R = R(H)$. Hence, $\Delta Q = \Delta Q_S + \Delta Q_R$. In the comparison chamber (in which the heat flux is entirely due to SBE, we have $\Delta\varepsilon_c = \Delta\varepsilon_{cS}$, so that $\Delta Q_c = \Delta Q_{cS}$. The signal due to ΔQ_S produces an unwanted background, which can be biassed off by adjusting the sensitivity of the comparison chamber relative to the active chamber. When the two chambers are completely identical, $\Delta Q_S = \Delta Q_{cS}$, so that $|\delta Q| \simeq |\Delta Q_R|$. As a rule, the experimental setup could be adjusted with a precision sufficient to ensure that the off-balance signal was practically proportional to $R(H)$. The method used to extract the signal from $R(H)$ is illustrated in Fig. 1.

Measurements were performed in the following ranges of values of f, p, and H: 83–211 kHz, 10–30 mtorr, and 0–8 kOe. In all cases, the amplitude of the field $H_\sim$ was about 360 Oe (the amplitude of the rotating field was about 180 Oe). Figures 2–4 show typical $\varepsilon(H)$ curves, obtained for GMR in CO_2 (line molecule), CH_4, and SF_6 (spherical spinning tops). It was found that, for all these gases, the resonance value of the field H_{res} was proportional to the frequency (see, for example, the GMR curves for SF_6, shown in Fig.

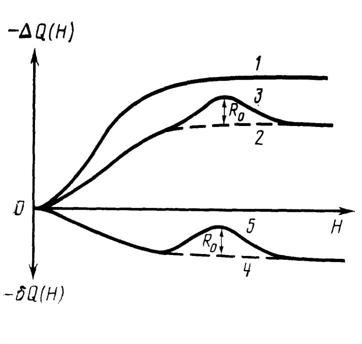

FIG. 1. Schematic illustration of the functions $\Delta Q(H)$ and $\delta Q(H)$: 1—SBE in the comparison chamber; 2,3—SBE and SBE + GMR in the active chamber; 4—difference SBE effect; 5—difference SBE + GMR effect. In contrast to the subsequent figures, these graphs do not show the nonmonotonic singularities that are unrelated to GMR at low H, but are due to the influence of the resultant field $H + H_\sim$

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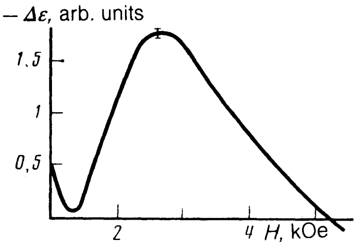

FIG. 2. The function $\Delta\varepsilon(H)$ for CO_2 at $p = 30$ mtorr and $f = 208$ kHz.

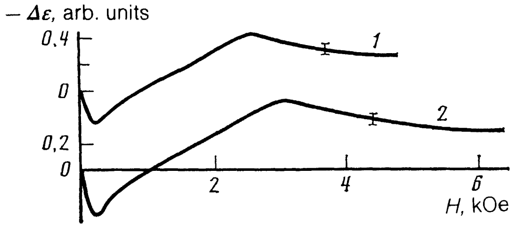

FIG. 4. The function $\Delta\varepsilon(H)$ for SF_6 at $p = 20$ mtorr, f: 1—83.5 kHz, 2—97 kHz.

4). The gyromagnetic ratios ($\gamma^* = f/H_{res}$) were found to be: $\gamma^*_{CO_2} = (37.5 \pm 3)$ Hz/Oe, $\gamma^*_{CH_4} = (220 \pm 10)$ Hz/Oe, and $\gamma^*_{CF_6} = (27 \pm 1.5)$ Hz/Oe. The corresponding values of g are listed in the table. It is clear from these data that the absolute values of g, obtained for CO_2, CH_4, and SF_6 by the GMR technique, agree to within experimental error with molecular beam data.[8-10]

The GMR experiments with NF_3 turned out to be more difficult than the others. The SBE signal could not be accurately compensated, which was probably due to SBE and GMR properties determined by the structure of this molecule. These properties require further experimental and theoretical investigation. The resonance effect was isolated as follows. We first analyzed the $\delta Q(H)$ curves, recorded for different degrees of compensation of SBE (different sensitivities of comparison chamber). If GMR occurs, then for $f =$ const it should appear on all the curves with the same value of H_{res} as a singular increase in the absolute value of the change ΔQ in the heat flux in the active chamber. The experimental identification of this singularity is preceded by the determination of the connection between the sign of the change in the heat flux in this chamber and the direction of the off-balance produced by it. When GMR occurs, the change in the frequency should produce a proportional change in H_{res}. The required effect can be detected by analyzing the $\delta Q(H)$ curves obtained in this way. Figure 5 shows the experimental results. It is clear that, despite the considerable difference between the curves, they do have common resonance features at $H = 1.8$ kOe for $f = 97$ kHz and $H = 4$ kOe for $f = 211$ kHz, which correspond to minima of the modulus of the derivative $d\delta Q/dH$ on portions of these curves that lie between the broken vertical lines at $f/H \simeq 50$ Hz/Oe. Hence, we find that $\gamma^* = (47 \pm 3)$ Hz/Oe, which corresponds to $g = 0.068 \pm 0.007$. It is important to note, in this connection, that the molecule NF_3 (symmetric top) has a magnetic moment that is not parallel to the angular momentum, and the g-factor of this molecule, determined from the Zeeman effect, is a tensor with components $g_\perp = -(0.060 \pm 0.001)$ (Refs. 11 and 12) and $g_\parallel = -0.081$ (Ref. 12). The magnetic moment, averaged over the fast rotation, is determined by the mean absolute value $|\bar{g}| \approx 0.07$, which agrees, to within experimental error, with the results obtained from our experiments. However, the precision of the experiments was not sufficient to enable us to determine the anisotropy of the g-factor.

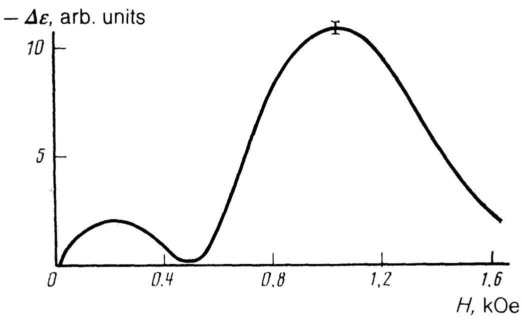

FIG. 3. The function $\Delta\varepsilon(H)$ for CH_4 at $p = 30$ mtorr and $f = 208$ kHz.

The ratio of the resonance amplitude to the SBE value at saturation, $R_0/S_\parallel$, lies in the range 0.02–0.1 for the above gases, depending on the molecular species. These values, and the overall shape of the experimental function $R(H)$, are in qualitative agreement with the theory. For CH_4 (Fig. 3), the second GMR harmonic was observed at $H \simeq 0.5$ kOe, i.e., there was a resonance increase in thermal conductivity at $H \simeq 0.5 H_{res}$. The position and form of this harmonic are in qualitative agreement with the theoretical model of P_2 scattering.[3,4] More detailed investigations are necessary to refine our information on the scattering process.

Thus, all the data obtained as a result of our experiments are in agreement, at least qualitatively, both with the theory and with existing experimental data obtained by other methods.

We note that the above value of $g_\parallel$ for NF_3 was obtained in Ref. 12 by an indirect estimate: the molecule was assigned the same value of $g_\parallel$ as that found for the molecule PF_3, which has a very similar configuration. It is noted in Ref. 13, which reports similar indirect estimates of $g_\parallel$ for the H_3CCN and H_3CNC molecules, that the relative uncertainty in these estimates may be as much as $\pm$ 10%. The authors of Refs. 11–13 were unable to determine $g_\parallel$ directly for these molecules because the nuclear quadrupole moment of the N^{14} atom introduced considerable complexity into the resonance spectrum. For the same reason, and in contrast to the GMR method, the resonance could not be observed for the N_2^{14} molecules in the molecular beam method.[6,14]

TABLE I. Absolute values of g for different gases.

Gas	GMR	Molecular beam method
CO_2	$(5.1 \pm 0.5) \cdot 10^{-2}$	$(5.508 \pm 0.005) \cdot 10^{-2}$ (Ref. 8)
CH_4	$(3 \pm 0.15) \cdot 10^{-1}$	$(3.133 \pm 0.002) \cdot 10^{-1}$ (Ref. 9)
SF_6	$(3.6 \pm 0.2) \cdot 10^{-2}$	$3.732 \cdot 10^{-2}$ (Ref. 10)

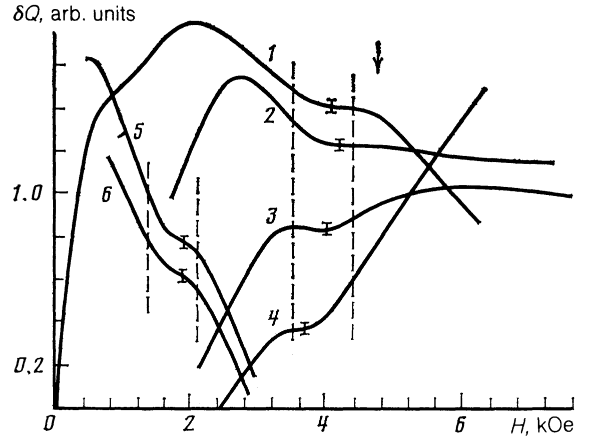

FIG. 5. The function $\Delta Q(H)$ for NF_3 at $p = 10$ mtorr. The arrow shows the direction of the resonance change ΔQ. The frequency f was: 1–4—211 kHz, 5–6—97 kHz.

It is clear from the above data that the relative uncertainty in the g-factor, determined by the GMR method ($\pm 10\%$), is higher by two orders of magnitude than the uncertainty in the molecular beam method, and up to an order of magnitude higher than that in the case of data based on the Zeeman effect. However, the GMR method has the following advantages (at least, in comparison with the above two methods, judging by the characteristics reported in Refs. 8–14): (1) relative simplicity (both in experimental respects and in the sense that the molecular g-factor can be measured directly without resorting to an analysis of the spectrum); (2) a small amount of gas is necessary for measurement (in our experiments, the threshold sensitivity was about 10^{13}–10^{14} molecules); (3) nonspherical scattering by the molecules can be investigated, and (4) in principle, the technique can be used to investigate very different molecules (for example, in our experiments, we were able to obviate the difficulties encountered in Refs. 11–13 because of the influence of the nuclear quadrupole moment on the resonance effect). The precision of the GMR method could be increased, for example, by producing and varying the field H as described in Ref. 5.

In conclusion, the authors wish to thank A. A. Sazykin and L. A. Maksimov for useful discussions.

[1)] The sign can, in fact, be found relatively simply by using the odd Senftleben-Beenaker effect.[7]

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[1] L. L. Gorelik and V. S. Laz'ko, Zh. Eksp. Teor. Fiz. **84**, 931 (1983) [Sov. Phys. JETP **57**, 541 (1983)].
[2] V. D. Borman, L. A. Maksimov, and Yu. V. Mikhailova, Zh. Eksp. Teor. Fiz. **53**, 2143 (1967) [Sov. Phys. JETP **26**, 1210 (1968)].
[3] L. A. Maksimov, Kinetic Theory of Gases with Rotational Degrees of Freedom. Doctoral Thesis [in Russian], Moscow, 1971.
[4] V. S. Laz'ko, Zh. Eksp. Teor. Fiz. **87**, 805 (1984) [Sov. Phys. JETP **60**, 458 (1984)].
[5] V. D. Borman, L. L. Gorelik, V. S. Laz'ko, B. I. Nikolaev, and A. V. Khmelev, Preprint IAE No. 2623 [in Russian], Moscow, 1976.
[6] L. L. Gorelik, Pis'ma Zh. Eksp. Teor. Fiz. **42**, 179 (1985) [Sov. Phys. JETP Lett. **42**, 221 (1985)].
[7] L. L. Gorelik, V. G. Nikolaevskiĭ, and V. V. Sinitsyn, Pis'ma Zh. Eksp. Teor. Fiz. **4**, 456 (1966) [JETP Lett. **4**, 307 (1966)].
[8] J. W. Gederberg, C. H. Anderson, and N. F. Ramsey, Phys. Rev. A **136**, 960 (1964).
[9] C. H. Anderson and N. F. Ramsey, Phys. Rev. **149**, 14 (1966).
[10] I. Ozier, R. N. Yi, and N. F. Ramsey, J. Chem. Phys. **66**, 143 (1977).
[11] R. G. Stone, J. M. Pochan, and W. H. Fligare, Inorg. Chem. **8**, 2647 (1969).
[12] W. H. Fligare and B. C. Benson, Mol. Phys. **20**, 225 (1971).
[13] J. M. Pochan, R. L. Shoemaker, R. G. Stone, and W. H. Fligare, J. Chem. Phys. **52**, 2478 (1970).
[14] S. J. Chan, M. R. Baker, and N. F. Ramsey, Phys. Rev. A **136**, 1224 (1964).

Translated by S. Chomet