PARAMETRIC RESONANCE OF THE THERMAL CONDUCTIVITY OF MOLECULAR GASES IN MAGNETIC AND ELECTRIC FIELDS

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Experimental data showing a resonant change in the thermal conductivity of a paramagnetic gas (NO_2) and a polar gas (NF_3) in parallel constant and alternating magnetic and electric fields are presented.

The transfer coefficients of molecular gases and, in particular, the thermal conductivity vary in constant magnetic or electric fields. This is known as the Senftleben effect (see, for example, the review [1]). This effect is due to the fact that the interaction cross section of nonspherical molecules depends on their orientation (on the angle between the direction of the relative velocity of the colliding molecules and their angular momenta). An external magnetic or electric field causes precession of the magnetic or dipole moments of the molecules as a result of which there is an effective increase in the interaction cross section and, consequently, a reduction in the transfer coefficients. The effect obviously depends on what angle the angular momentum can turn through during the time of free flight, i.e., on the ratio of the precession frequency Ω to the collision frequency of the molecules ν or, in other words, on the ratio of the value of the field B to the gas pressure p (since $\Omega \infty B$ and $\nu \infty p$). In an intense external field, when $\Omega/\nu \gg 1$, the effect reaches saturation.

It was found [2, 3] that in an alternating field $B_1 \sin\omega t$ the value of the relative change in the transfer coefficients for a fixed ratio B_1/p decreases monotonically as the parameter ω/p increases (the dispersion of the Senftleben effect).

An interesting case is when an alternating field is superimposed on the constant field and parallel to it, i.e., the external field has the form

$$\mathbf{B}(t) = \mathbf{B}_0 (1 + b \sin \omega t), \tag{1}$$

where $b = B_1/B_0$, and B_0 and B_1 are the values and amplitude of the constant and alternating fields. As theoretical investigations have shown [4, 5], the action of the external field (1) on the kinetic coefficients of molecular gases leads to the appearance of resonance in their frequency relations (in which the number of maxima is related to the characteristic distribution of the molecules with respect to the directions of the angular momenta). Hence, investigations of the transfer coefficients in parallel constant and alternating external fields give direct information on this nonequilibrium polarization of nonspherical molecules.

The resonance variation of the thermal conductivity of oxygen in parallel constant and alternating magnetic fields was investigated in [6]. The fine structure of the resonance maxima in O_2 was investigated in [7]. Four maxima were found in the curve of the thermal conductivity (ε) of O_2 as a function of the ratio H_0/p, two of which correspond to resonance in O_2 molecules with projections of the electron spin onto the direction of the angular momentum, equal to $\sigma = \pm 1$, and the two others with $\sigma = 0$.

In the present paper we present the results of an experimental investigation of the resonance of the thermal conductivity of a paramagnetic gas (NO_2) in parallel magnetic fields. The ground state of the NO_2 molecule is $^2\Sigma$ and the projection of the uncompensated electron spin onto the direction of the angular momentum can take the value $\sigma = \pm 1/2$. Hence, unlike

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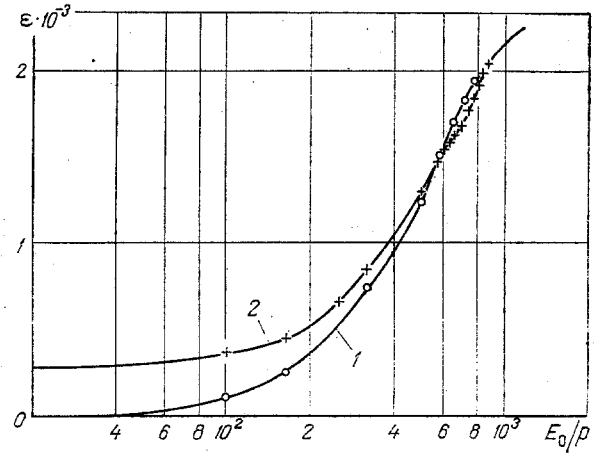

Fig. 1. The quantity $\varepsilon = [\varkappa(E) - \varkappa(0)]/\varkappa(0)$ as a function of E_0/p (V/cm•torr) in NF_3 when $E = E_0$ (1) and $E = E_0(1 + e \cdot \sin\omega t)$ (2).

oxygen on the $\varepsilon(H_0/p)$ curve for NO_2, one should observe two maxima corresponding to the quadrupole polarization of the NO_2 molecules in the presence of a temperature gradient.

According to [4, 5] a similar effect should be observed in polar gases in parallel constant and alternating electric fields. In this paper we describe the results of experiments in the course of which we observed resonance of the thermal conductivity of a polar gas (NF_3) with d = 0.240 D in parallel constant and alternating electric fields.

We used a method of measurement similar to that described in [7]. The essence of the method is the change in the resistance of a heat-sensitive probe due to a change in the thermal conductivity of the gas when the field is switched on.

In the present experiments we used two probes (the construction of the probes is described in [8]), one of which is placed in the field $B(t) = B_0(1 + b\sin\omega t)$, while the other is used as a comparison probe. Both probes are connected in adjacent arms of a dc bridge, in the diagonal of which an F116/1 photooptical amplifier is connected. In the experiments we measured the unbalance of the bridge when the alternating field was switched on, due to the change in the thermal conductivity when the constant field was switched on. The measurements were made using the "triple readout" method [9], which enabled us to get rid of the effect of uniform thermal zero drift of the measuring circuit. Random errors due to nonuniform zero drift were eliminated by averaging the results of a series of triple readouts. In the measurements of the bridge unbalance using this method we achieved a threshold sensitivity of 0.05 μV. The absolute values of the relative change in thermal conductivity (ε) in the field $B(t) = B_0(1 + b\sin\omega t)$ were found by calibrating the probes with respect to the Senftleben effect, i.e., by comparing the value of the bridge unbalance in the field B_0 measured in the experiments with the data given in [10, 11]. In this case the threshold sensitivity of the probe when measuring ε in the worst case, namely, at the lowest working pressure of 0.2 torr, when the temperature jump is a maximum, and for a temperature of the heat-sensitive element of the probe of 130°C, was approximately 10^{-6}. A similar threshold sensitivity was achieved previously [12] in measurements of the Senftleben effect. The relative calibration error due to errors in determining the pressure and the value of the field did not exceed 10%.

In experiments carried out in an electric field $E(t) = E_0(1 + e\sin\omega t)$, we measured the quantity $\varepsilon = [\varkappa(E) - \varkappa(0)]/\varkappa(0)$ [$\varkappa(E)$ and $\varkappa(0)$ are the values of the thermal conductivities in a field (E) and when E = 0, respectively, since the comparison probe was placed outside the field]. In the experiments on measuring the thermal conductivity of gases in a magnetic field $H(t) = H_0(1 + h\sin\omega t)$ the comparison probe was placed in a constant magnetic field H_0. In this case, since both probes are in a constant field, the measured quantity was $\varepsilon_H = [\varkappa(H) - \varkappa(H_0)]/\varkappa(0)$.

Figure 1 shows the results of an experimental investigation of the thermal conductivity of NF_3 in the presence of a constant electric field (curve 1) and an electric field which is a combination of parallel constant and alternating electric fields (curve 2). The measurements were made at a gas pressure p = 0.2 torr, an angular frequency ω = 5.3 MHz, and an amplitude

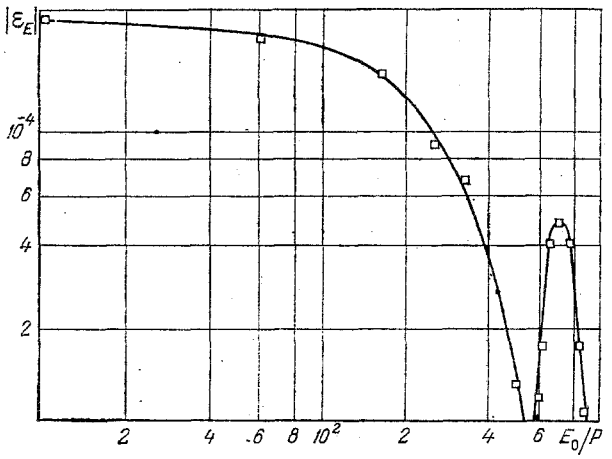

Fig. 2. Curve of $|\varepsilon_E| + |[\varkappa(E) - \varkappa(E_0)]/\varkappa(0)|$ versus E_0/p (V/cm•torr) in NF_3 for $\omega = 5.3$ MHz and $E_1 = 75$ V/cm.

of the alternating field $E_1 = 75$ V/cm over a range of values of the constant field $E_0 = (30\text{-}200)$ V/cm. The measured quantity in this experimental geometry is a combination of the components of the thermal conductivity tensor $\varepsilon = {}^1/_5(3\varepsilon_\parallel + 2\varepsilon_\perp)$ ($\varepsilon_\parallel$ and $\varepsilon_\perp$ are the values corresponding to the conditions when the field is parallel and perpendicular to the temperature gradient).

It is seen from the figure that in a constant electric field E_0 the thermal conductivity of NF_3 decreases and the curve $\varepsilon(E_0/p)$ has a monotonic form, while in the region of large values of E_0/p the value of ε reaches saturation. When an alternating electric field is switched on parallel to the constant field it is found that in the region of values of $E_0/p = (600\text{-}800)$ V/cm•torr, a characteristic resonant deviation from the similar curve in the field E_0 appears in the curve of $\varepsilon(E_0/p)$ (see Fig. 1). When the ratio E_0/p is increased further the change in the thermal conductivity approaches its limiting value ε_{sat} on $\varepsilon(E_0/p)$. It should be noted that in a field $E(t) = E_0(1 + e\sin\omega t)$, on $\varepsilon(E_0/p)$, when $E_0/p = 0$ the value of $\varepsilon(0)$ differs from zero and has the value $\varepsilon = -2.6\cdot10^{-4}$ (see Fig. 1). This is due to the change in thermal conductivity in the field E_1.

To analyze the experimental data it is convenient to use the expression for the relative change in thermal conductivity in an external magnetic or electric field $B(t) = B_0(1 + b\sin\omega t)$, which, according to [4], can be written in the form

$$\varepsilon = \frac{\varkappa(B) - \varkappa(0)}{\varkappa(0)} = -\sum_{m=1}^{l} \Lambda_{lm} \left\langle \left(\frac{m\Omega_0}{\nu}\right)^2 \left[1 + \left(\frac{m\Omega_0}{\nu}\right)^2\right]^{-1} + \right.$$
$$+ \left(\frac{m\Omega_1}{\nu}\right)^2 \left[1 + \left(\frac{\omega}{\nu}\right)^2 + \frac{1}{2}\left(\frac{m\Omega_1}{\nu}\right)^2 - 3\left(\frac{m\Omega_0}{\nu}\right)^2\right] \times$$
$$\times \left\{\left[1 + \left(\frac{\omega}{\nu}\right)^2 + \frac{1}{2}\left(\frac{m\Omega_1}{\nu}\right)^2 - 3\left(\frac{m\Omega_0}{\nu}\right)^2\right]^2 + \right.$$
$$\left. \left. + \left(\frac{m\Omega_0}{\nu}\right)^2 \left[3 + \left(\frac{\omega}{\nu}\right)^2 + \frac{1}{2}\left(\frac{m\Omega_1}{\nu}\right)^2 - \left(\frac{m\Omega_0}{\nu}\right)^2\right]^2\right\}^{-1} \right\rangle, \qquad (2)$$

where $\Omega_{0,1} = \gamma B_{0,1}$ are the precession frequencies of the molecules in fields B_0 and B_1, $\gamma = d\bar{\alpha}/\bar{M}$, $\bar{M}$ and $\bar{\alpha}$ are the statistical averages of the values of the angular momentum of the molecules, $\alpha = \cos(\mathbf{dM})$ for polar molecules, $\gamma = 2\mu_0\sigma/\bar{M}$ for paramagnetic molecules, and ν is the relaxation frequency, which has the same order of magnitude as the collision frequency of the molecules. The value of Λ_{lm} is determined by the characteristic intermolecular interaction and within the framework of the theory considered should be derived from the experiment. The number l is equal to the rank of the tensor describing the nonequilibrium polarization of nonspherical molecules in angular momentum space. In the case of quadrupolarization of the molecules $l = 2$.

The first term in Eq. (2) is identical with the expression for the relative change in the thermal conductivity in a constant external field B_0 (the Senftleben effect). Analysis

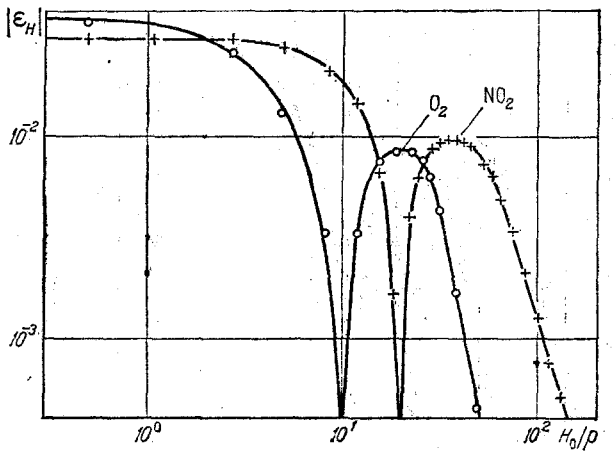

Fig. 3. The quantity $|\varepsilon_H| = |[\varkappa(H) - \varkappa(H_0)]/\varkappa(0)|$ as a function of H_0/p (Oe/torr) in O_2 and NO_2 for $\omega = 3.6$ MHz and $H_1 = 12$ Oe.

of the second term in Eq. (2) shows that the dependence of this term on the parameter Ω_0/ν has a resonant form. The position of the resonance is given by

$$\left(\frac{m\Omega_0}{\nu}\right)^2 = 3 + \left(\frac{\omega}{\nu}\right)^2 + \frac{1}{2}\left(\frac{m\Omega_1}{\nu}\right)^2, \tag{3}$$

and its value equals

$$\frac{1}{2}\Lambda_{lm}\left(\frac{m\Omega_1}{\nu}\right)^2\left[4 + \left(\frac{\omega}{\nu}\right)^2 + \frac{1}{2}\left(\frac{m\Omega_1}{\nu}\right)^2\right]^{-1}. \tag{4}$$

According to Eq. (3), for quadrupolarization of the molecules (m = 1, 2) two maxima should be observed on the $\varepsilon(\Omega_0/\nu)$ curve (the fine structure of the resonance).

In order to compare the measurement results shown in Fig. 1 (curve 2) with the theoretical expression (2) it is best to represent the experimental data in the form of a curve which is the difference between curves 2 and 1. The resulting curve represents the change in the thermal conductivity $\varepsilon_E = [\varkappa(E) - \varkappa(E_0)]/\varkappa(0)$ as a function of E_0/p and should be described by the second term in Eq. (2). The result of this graphical subtraction is shown in Fig. 2.

A qualitative comparison of the experimental curve (Fig. 2) with the theoretical curve shows that they behave in the same way. For small values of E_0/p the effect is negative, and as E_0/p increases, the effect increases monotonically. When $E_0/p = 730$ V/cm•torr, ε_E reaches a maximum value. Estimates of the values of E_0/p at which two maxima should be observed on the $\varepsilon_E(E_0/p)$ curve in NF_3 gave values of 720 V/cm•torr (for m = 2) and 1430 V/cm•torr (for m = 1) ($\gamma = 0.03$ MHz/V/cm and $\nu = 1.4 \cdot 10^{10}$ Hz/atm). A comparison with the experimental value 730 V/cm•torr shows agreement between the values of E_0/p for the position of the maximum corresponding to m = 2 in Eq. (3).

Unfortunately, it was not possible to detect the second maximum depicted by theory in an electric field because of the discharge which occurred in the probe chamber at high values of E_0/p.

It should be noted that measurements made at other frequencies of the alternating field showed that the position of the maximum is displaced along the E_0/p scale and its value changes in accordance with the theoretical expressions for these quantities obtained from Eq. (2). Thus, the experimentally obtained value $(E_0/p)_{res} = 640$ V/cm•torr under the experimental conditions p = 0.2 torr, $\omega = 1.66$ MHz, and $E_1 = 75$ V/cm agreed satisfactorily with the theoretical value $(E_0/p)_{res} = 685$ V/cm•torr for m = 2, calculated from Eq. (3) for these conditions.

The appearance of resonant behavior in the transfer coefficients in an external field (1) can be understood if we take into account the fact that the parameter Ω/ν changes with time according to the expression $\Omega/\nu = (\Omega_0/\nu)(1 + b\sin\omega t)$. It is easy to see that when $\Omega_0/\nu \gg 1$ this time dependence of Ω/ν leads to the appearance of smaller cross sections (compared with the case of a constant field) due to disturbance of the condition $\Omega/\nu \gg 1$ and leads

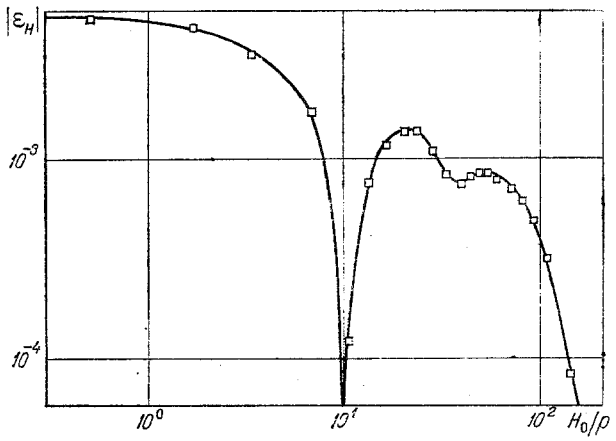

Fig. 4. Curve of $|\varepsilon_H| = |[\varkappa(H) - \varkappa(H_0)]/\varkappa(0)|$ as a function of H_0/p (Oe/torr) in NO_2 for ω = 10 MHz and H_1 = 6 Oe.

to an increase in the transfer coefficients, where obviously the value of the effect will depend on the parameter $b = B_1/B_0$. It is also clear that the "detuning" of the precession frequency Ω_0 when the frequency of the alternating field ω changes will have a resonant effect on the change in the transfer coefficients. Thus, when $\Omega_0/\nu \gg 1$ and $b \ll 1$, resonance in the transfer coefficients should be observed when $\omega = m\Omega_0$.

It should be noted that resonance of the transfer coefficients in parallel constant and alternating external fields differs considerably from gas-kinetic resonance in crossed fields, one of which is constant and the other rotating [13, 14]. In crossed fields, due to the complex precessional motion of the molecules, there is an additional increase in the collision cross section and, consequently, a reduction in the transfer coefficients. We note also that in crossed fields the parameter Ω/ν is independent of the time, and for resonance of the transfer coefficients in parallel fields it is this dependence of Ω/ν on the time which is important. Hence, resonance in parallel constant and alternating external fields should be called parametric resonance by analogy with [15].

Figure 3 shows a curve of $\varepsilon_H(H_0/p)$ for NO_2 in parallel constant and alternating magnetic fields [a curve of $\varepsilon_H(H_0/p)$ for O_2 is shown for comparison]. The measurements were made at a gas pressure p = 0.4 torr,* an angular frequency of the alternating field ω = 3.6 MHz, and an amplitude of the alternating field H_1 = 12 Oe. In all the experiments described below ε_H was measured under conditions when $\mathbf{H} \perp \nabla T$. It is seen from the figure that the value of ε_H changes sign when H_0/p = 20 Oe/torr. When H_0/p = 36 Oe/torr, ε_H reaches a maximum value.

The graphs of $\varepsilon_H(H_0/p)$ for NO_2 and O_2 shown in Fig. 3 are similar to the graphs of the change in thermal conductivity of NF_3 in an electric field $E(t) = E_0(1 + e\sin\omega t)$ (see Fig. 2).

The behavior of the thermal conductivity of O_2 and NO_2 in a magnetic field $H(t) = H_0(1 + h\sin\omega t)$, like the behavior of the thermal conductivity of NF_3 in an electric field $E(t) = E_0(1 + e\sin\omega t)$, is qualitatively described by the theoretical equation (2). Table 1 shows values of $(H_0/p)_{res}$ for O_2 and NO_2 calculated from Eq. (3) and obtained from the experimental curves for ω = 3.6 MHz, H_1 = 12 Oe, and p = 0.4 torr. The values of γ for O_2 and NO_2 were taken equal to 1.4 and 0.7 MHz/Oe ($\bar{M} \simeq \bar{J}$, $\bar{J}$ = 14 for O_2 and NO_2), and the collision frequencies of the O_2 and NO_2 molecules were taken as $0.8 \cdot 10^{10}$ and $1 \cdot 10^{10}$ Hz/atm, respectively.

According to Eq. (3), the distance between the maxima of the fine structure increases as ω/p increases or as H_1/p decreases. The existence of a fine structure in the resonance of the thermal conductivity of NO_2 in a magnetic field $H(t) = H_0(1 + h\sin\omega t)$ is confirmed by the experimental curve of $\varepsilon_H(H_0/p)$ shown in Fig. 4. The measurements were made for p = 0.4 torr, ω = 10 MHz, and H_1 = 6 Oe. The values of H_0/p for which two maxima of the resonance line are observed (22 and 50 Oe/torr) agree satisfactorily with the values H_0/p (26.5 and 49.5 Oe/torr) calculated from Eq. (3).

*It should be noted that under the experimental conditions existing here ($p \leq 0.4$ torr), according to the data given in [16], there are practically no dimer molecules of NO_2 present.

TABLE 1. Theoretical and Experimental Values of $(H_0/p)_{res}$, Oe/torr

Gas	m	$(H_0/p)_{res}$	
		material	experimental
O_2	1	27	20
	2	23	
NO_2	1	46,5	
	2	35	36

From this it follows that in NO_2, when there is a temperature gradient present, quadrupolarization of the molecules occurs.

The above investigations show that resonance of the thermal conductivity of molecular gases in external fields can be used to study nonequilibrium polarization of molecules due to a macroscopic gradient and the nonspherical nature of molecular scattering.

NOTATION

ν, collision frequency of the molecules; Ω, precession frequency of the molecules; p, gas pressure; B_0, B_1, value and amplitude of the constant and alternating external (magnetic or electric) field, respectively; E, electric field; H, magnetic field; $b = B_1/B_0$; $e = E_1/E_0$; $h = H_1/H_0$; ω, angular frequency of the alternating field; ε, relative change in thermal conductivity; d, dipole moment of the molecule; $\varkappa(0)$, thermal conductivity when there is no external field; M, angular momentum of the molecule; σ, projection of the spin on the angular momentum of the molecule; $\alpha = \cos(\mathbf{dM})$; $\varepsilon_\parallel$, $\varepsilon_\perp$, values of ε for $B \parallel \nabla T$ and $B \perp \nabla T$, respectively; ∇T, temperature gradient; J, rotational quantum number; $(E_0/p)_{res}$, value of E_0/p for which $\varepsilon = \varepsilon_{res}$; μ_0, Bohr magneton.

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