The electron lifetime τ at low pressures is determined by the time of diffusion to the cell walls. The value of τ estimated as in[8], turns out to be $\tau = 1.5 \times 10^{-5}$ sec under our conditions. This means that $\omega\tau = 1$ corresponds to $\omega/2\pi = 11$ kHz. Consequently, when the mutual orientation (or magnitude) of the spin moments of Rb and He* varies with a frequency exceeding 11 kHz, the signals corresponding to the variation in the electron density should decrease with increasing frequency. This appears to explain the fact that signals such as those shown in Fig. 3 were not observed in strong magnetic fields.

We note in conclusion that, even a partial conservation of the resultant spin during Penning collisions between Rb and He* suffices to explain the experimental dependence of the mutual spin orientation of the Rb and He* atoms on the electron density in the plasma. To assess the extent to which the resultant spin is conserved during such collisions requires further investigation.

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Translated by S. Chomet

Gas diffusion: Its dependence on nuclear spin

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(Submitted July 2, 1975)
Zh. Eksp. Teor. Fiz. **70**, 76–80 (January 1976)

The influence of the nuclear spin on the diffusion of a molecular gas due to the precession of the angular momentum in the electric field of the nuclear quadrupole or in the magnetic field of the nuclear magnetic moment is considered. The expected effect could be detected at low pressure in gas mixtures with molecules of the type HA, where among the isomers of the nucleus A there are long lived isomers with large nuclear spins. In principle this effect could be used for the separation of nuclear isomers.

PACS numbers: 51.10.+y

1. The theory of gas diffusion allows one to predict the change in the diffusion coefficient of a molecular gas in the case when the nuclear spin of one of the atoms which make up the molecule differs from zero, as compared with the diffusion coefficient of isomers of the same molecules without nuclear spin. This effect is analogous to the well-known Senftleben effect (cf. the reviews[1]) consisting in the influence of an external magnetic field on the kinetic coefficients of molecular gases.

The gist of the effect is related to the fact that the nuclear spin violates the conservation of the angular momentum **K** of the molecule during its free flight between collisions. In the absence of nuclear spin the diffusion coefficient is proportional to the mean free path λ, averaged over the different orientations of the angular momentum of the molecule. In the presence of spin the molecule tumbles and its angular momentum is not constant along the free path. Therefore one first averages the scattering cross section σ over the directions of the angular momentum and then calculates the mean free path from this average cross section. If the cross section depends on the orientation of the angular momentum then the difference between $\bar{\lambda} \propto \overline{\sigma^{-1}}$ and $\lambda \propto (\bar{\sigma})^{-1}$ may be substantial. We consider this result of influence of the nuclear spin on diffusion using the diffusion of diatomic molecules in a monoatomic gas as an example.

2. The diffusion of molecules in an atomic gas is described by a kinetic equation which is classical in the translational degrees of freedom and quantized in the internal degrees of freedom:

$$\partial f/\partial t + (\mathbf{v}\nabla) f + i\hbar^{-1}[H, f] = -J_{\text{coll}}. \tag{1}$$

Here f is the molecular distribution function and J_{coll} is the collision integral. The operator describing the internal energy of the molecule will be written in the form[2]

$$H = B\hat{\mathbf{K}}^2 + V, \tag{2}$$

where the first term describes the rotational energy of the molecule and the second term determines the hyperfine interaction between the rotation of the molecules and the nuclear spin. For definiteness we consider a nonparamagnetic diatomic molecule in which only one of the nuclei has nonzero spin I. If $I \geqslant 1$ the main contribution to V comes from the quadrupole interaction of the nucleus with the electrons. If $I = \frac{1}{2}$ the source of hyperfine splitting is the interaction between the nuclear and rotational magnetic moments.

At normal pressures the broadening of the energy levels of the molecules owing to collisions, $\hbar\tau^{-1}$, is large compared to the distances between the hyperfine splitting ΔE of the molecular levels, one may consider the spin of the nucleus completely decoupled from the angular momentum of the molecule and the nuclear spin will not exert any influence on the diffusion. However, for sufficiently small pressures, when

$$\hbar\tau^{-1}\ll\Delta E, \tag{3}$$

the total angular momentum $\mathbf{F}=\mathbf{K}+\mathbf{I}$ is a good quantum number. This means that during the free flight time τ between collisions there occurs a complete averaging of the angular momentum **K** which precesses around **F**. It follows that if the condition (3) is satisfied the quasistationary solution of the equation (1) is almost diagonal in the wave-function representation

$$|a\rangle=|KIFM\rangle=\sum_{m\sigma}\langle m\sigma|FM\rangle|Km\rangle|I\sigma\rangle \tag{4}$$

($\langle m\sigma|FM\rangle$ is a Clebsch–Gordan coefficient).

We represent the distribution function in the form

$$f_{a'a}(\mathbf{v})=n(\mathbf{r})f_{KI}f(\mathbf{v})(\delta_{a'a}+\chi_{a'a}), \tag{5}$$

where $n(\mathbf{r})$ is the nonuniform molecular density and f_{KI} and $f(\mathbf{v})$ are the equilibrium distribution functions with respect to the internal and external degrees of freedom:

$$\begin{gathered}f_{KI}=Z^{-1}e^{-BK(K+1)/T},\quad \sum_K g_{KI}f_{KI}=1;\\ f(\mathbf{v})=\left(\frac{m}{2\pi T}\right)^{3/2}\exp\left(-\frac{mv^2}{2T}\right),\quad \int d^3v f(\mathbf{v})=1.\end{gathered} \tag{6}$$

We consider that the temperature is large compared to the hyperfine splitting and that all the $g_{KI}=(2K+1)\times(2I+1)$ states with given K are equally populated. The matrix χ characterizes the deviation from local equilibrium ($\chi\sim\nabla n$).

In the linear approximation in the density gradient the kinetic equation (1) takes the form

$$\begin{gathered}\mathbf{v}\nabla\ln n+\hat{\omega}\chi=-\hat{\Omega}\chi,\\ (\hat{\omega}\chi)_{a'a}=i/\hbar^{-1}(E_{F'}-E_F)\chi_{a'a},\\ J_{\text{coll}}=nf_{KI}f(\mathbf{v})\hat{\Omega}\chi.\end{gathered} \tag{7}$$

The collision integral has been written under the assumption that for collisions of a molecule with atoms of a gaseous medium the magnitude of the angular momentum does not change.

We shall search for the matrix χ in the form

$$\chi=-(\nabla\ln n)\boldsymbol{\chi}.$$

The vector $\boldsymbol{\chi}$ determines the diffusion coefficient:

$$\begin{gathered}D={}^1/_3\langle\mathbf{v},\boldsymbol{\chi}\rangle,\\ \langle A,B\rangle\equiv\int d^3v f(\mathbf{v})\sum_{a'a}f_K A^{*}_{a'a}B_{a'a}\end{gathered} \tag{8}$$

and satisfies the equation

$$(\hat{\Omega}+\hat{\omega})\boldsymbol{\chi}=\mathbf{v}. \tag{9}$$

The last equation is very close in form to the equation which describes the kinetics of a molecular gas in an external field.[3] The operator $\hat{\omega}$, as in the theory of the Senftleben effect, mixes states with different projections of the angular momentum. But in the Senftleben effect this mixing is caused by the precession of **K** around the external field, whereas in the case under consideration it is caused by the precession of the angular momentum around the total angular momentum of the molecule **F**.

We shall assume that the asphericity of the molecule is small. This assumption is inessential, but is in agreement with the smallness of the Senftleben effect and simplifies the calculations. Then the collision operator can be written in the form of a sum of a spherical part Ω_0 and a nonspherical part Ω_1 and represent the solution of Eq. (9) in the form of an expansion in powers of the asphericity. As a result the diffusion coefficient becomes in quadratic approximation with respect to the asphericity[3]

$$\begin{gathered}D=D_0+D_2;\quad D_0={}^1/_3\langle\mathbf{v},\hat{\Omega}_0^{-1}\mathbf{v}\rangle,\\ D_2={}^1/_3\langle\hat{\Omega}_1\hat{\Omega}_0^{-1}\mathbf{v},(\hat{\Omega}_0+\hat{\omega})^{-1}\hat{\Omega}_1\hat{\Omega}_0^{-1}\mathbf{v}\rangle.\end{gathered} \tag{10}$$

In order to make the last expression more concrete we shall assume that the functions v_α and $T_{\alpha\beta}v_\beta$, where

$$T_{\alpha\beta}\infty\hat{K}_\alpha\hat{K}_\beta+\hat{K}_\beta\hat{K}_\alpha-{}^2/_3\delta_{\alpha\beta}K(K+1).$$

are eigenfunctions of the operator $\hat{\Omega}_0$, while the operator $\hat{\Omega}_1$ transforms these functions into one another. This is in fact a solution of Eq. (9) in the two-moment approximation. The first function is the usual initial moment in the diffusion problem and the equation

$$\hat{\Omega}_1 v_\alpha=\Omega_1 T_{\alpha\beta}v_\beta \tag{11}$$

describes phenomenologically the appearance of a correlation between the direction of motion of the molecule and the quadrupolarization of the angular momentum owing to the scattering of nonspherical molecules on the atoms of the gaseous medium. The independence of the expression (11) of the nuclear spin reflects the assumed spin-independence of the cross section.

In the framework of the two-moment approximation the expressions (10) are equal to

$$D_0=T/m_0\Omega_0 \tag{12}$$

(m_0 is the mass of the molecule);

$$D_2=\frac{T}{3m_0}\left\langle T_{\alpha\beta},\left(\frac{\Omega_1}{\Omega_0}\right)^2(\Omega_K+\hat{\omega})^{-1}T_{\alpha\beta}\right\rangle. \tag{13}$$

Here it has been taken into account that the eigenvalue Ω_K of the function $T_{\alpha\beta}v_\beta$ and the matrix element Ω_1 generally depend on the quantity K.

It is convenient to rewrite the last expression in spherical coordinates:

$$D_2=\frac{T}{3m_0}\sum_K f_{KI}\left(\frac{\Omega_1}{\Omega_0}\right)^2\sum_{qF'M'FM}|(T_{2q})_{F'M',FM}|^2\left[\Omega_K+\frac{i}{\hbar}(E_{F'}-E_F)\right]^{-1}. \tag{14}$$

Rewriting the spherical tensor T_{2q} in the representation (4) and making use of the standard technique of angular-momentum addition[2] we obtain

$$D_2=\frac{T}{3m_0}\sum_K f_{KI}\left(\frac{\Omega_1}{\Omega_0}\right)^2\sum_{F'F}(2F'+1)(2F+1)$$
$$\times\begin{Bmatrix} I & K & F' \\ 2 & F & K\end{Bmatrix}^2\Omega_K\left[\Omega_K^2+\frac{1}{\hbar^2}(E_{F'}-E_F)^2\right]^{-1}. \qquad (15)$$

The reduced matrix element $\langle K||T_2||K\rangle=1$ if the tensor is normalized by the condition $T^2=1$. If $\hbar\Omega_K\gg\Delta E$ one may neglect in (15) the hyperfine spitting. We then obtain directly from (14)

$$D_2=(T/3m_0)\sum_K f_{K0}(\Omega_1/\Omega_0)^2\Omega_K^{-1}. \qquad (16)$$

In the opposite case, when $\hbar\Omega_K\gg\Delta E$ the terms which are off-diagonal in F become small under the sum in (15). Omitting these terms we obtain

$$D_2=(T/3m_0)\sum_K f_{K0}(\Omega_1/\Omega_0)^2\Omega_K^{-1}\xi_{KI};$$
$$\xi_{KI}=\frac{1}{2I+1}\sum_F(2F+1)^2\begin{Bmatrix} I & K & F \\ 2 & F & K\end{Bmatrix}^2. \qquad (17)$$

The coefficients ξ_{KI} characterize the decrease of the partial contributions of states with given K owing to precession. These coefficients decrease monotonically as I increases, and $\xi_{K0}=1$, $\xi_{K\infty}=1/5$.

A correction of the form (13) to the diffusion coefficient is typical for the cases when the cross section for collisions is an even function of the angular momentum. If odd terms in K play the leading role in the nonspherical part of the cross section, then in place of the vector $T_{\alpha\beta}v_\beta$ one has to choose as second moment, e.g., the vector $\mathbf{v}\times\mathbf{K}$. The operator Ω_1 is antihermitian with respect to the transitions $\mathbf{v}\to\mathbf{v}\times\mathbf{K}$ and in place of Eqs. (15)–(17) one obtains expressions with the opposite sign; in addition in the 6*j*-symbols 2 is replaced by 1.

Thus the diffusion coefficient either decreases (17), or increases when the hyperfine interaction is switched on. A similar situation arises in the Senftleben effect. For the majority of molecular gases the kinetic coefficients decrease in a magnetic field (normal Senftleben effect), i.e., the case leading to (17) is realized.

In order to get an intuitive feeling for the influence of the nuclear spin on diffusion of the molecules we shall assume that the separations between the rotational levels are large and that the states with $K\geqslant 2$ are totally frozen. Then for two kinds of molecules which interact identically with the atoms of the gas and differ only in the magnitude of the nuclear spin we shall have

$$D=D_0+\frac{T}{3m_0}\left(\frac{\Omega_1}{\Omega_0}\right)^2\frac{1}{\Omega_{K=1}}\frac{e^{-2B/T}}{1+3e^{-2B/T}}\xi_{1I},$$
$$\xi_{10}=1,\quad \xi_{11}={}^5/_{18},\quad \xi_{1\infty}={}^1/_5. \qquad (18)$$

3. In conclusion we discuss the conditions for which it is possible to observe the phenomenon under discussion. The main condition is (3). The hyperfine splitting of the molecular levels is characterized by frequencies of the order of 10^7 s^{-1}. Comparing this with the frequency of collisions under normal pressure: $\Omega=\tau^{-1}=10^{10}$ s^{-1} we see that in order that condition (3) be satisfied one must lower the pressure to values of $P<10^{-3}$ atm.

Another condition for effective mixing of states with different projections of the angular momentum on the direction of motion is the requirement that the nuclear spin not be small compared to the average angular momentum $\bar{K}$. Usually for normal temperature B/T is of the order 0.01 and $\bar{K}$ is of the order 10. Then $\bar{K}\gg I$ and in the course of precession only a small fraction $(2I+1)/(2\bar{K}+1)$ of states gets mixed. The separation between the rotational levels is maximal for the molecules H_2, HD and D_2, but these are not interesting for us: the differences in their diffusion coefficients are due to other coarser causes. From the point of view of the detection of the effect under consideration the best hope is for hydrogen-containing molecules of the type HA, where A is a heavy atom for which B is of the order 10 K and for a normal temperature $\bar{K}\simeq 5$. Favorable to the detection of a dependence of the diffusion on the nuclear moment is also the presence among the isomers of the atom A of long-lived isomers with larger nuclear angular momentum ($I=4-5$).

A third condition for the existence of a dependence of D on I is the asphericity of the molecules, i.e., the dependence of the collision cross section on the projection of the angular momentum on the direction of motion. From the experiments on the Senftleben effect it is known that this asphericity is small. This implies that the maximal magnitude of the expected effect as well as that of the Senftleben effect is of the order of one percent.

The enumerated conditions make it difficult to detect the effect under consideration. Nevertheless, it presents physical interest as one of the few macroscopic phenomena which is sensitive to nuclear *s* structure. Moreover, it becomes possible in principle to make use of the dependence of diffusion on the nuclear spin for a spatial separation of longlived isomers by means of a mass-diffusion method, as well as for the determination of isomer concentrations.

A last remark. The effect considered above, which is due to molecule–atom collisions, can be directly transposed to other kinetic coefficients in purely molecular gases (molecule–molecule collisions), and can be extended to transport phenomena in a molecular Knudsen gas (molecule-wall collisions[4]).

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Translated by M. E. Mayer