Optical Observation of Angular Momentum Alignment in a Heat-Conducting Gas

R. J. van den Oord, M. C. de Lignie, J. J. M. Beenakker, and J. Korving
Huygens Laboratory, University of Leiden, 2300 RA Leiden, The Netherlands

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We have for the first time directly observed the flow of angular momentum alignment in a heat-conducting gas of rotating molecules (Kagan polarization). The sign has been determined. It is found that the polarization is proportional to the square of the angular momentum.

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In a gas of rotating molecules, a thermodynamic force such as a temperature gradient or a velocity gradient will cause the distribution of molecular angular momenta to be anisotropic. These anisotropies, that give rise to an influence of a magnetic field on the transport properties [Senftleben-Beenakker (SB) effect[1]], are an important source of information for our knowledge of the nonspherical part of the molecular interaction.[2,3] From studies of the SB effect it is found that in the presence of a velocity gradient one has a nonequilibrium alignment which is directly observable through flow birefringence.[4,5] For a temperature gradient there is a correlation between the direction of the molecular velocity and the orientation of the angular momentum, known as the Kagan polarization.[6,7] So far the Kagan polarization has eluded direct observation: All information came from studies of the SB effect. These give information on the tensorial structure of the Kagan polarization and its magnitude, which is expressed in effective cross sections. However, as the nonequilibrium polarization affects the transport properties only in second order, the sign of the Kagan polarization cannot be obtained from the SB effect. Furthermore, the actual dependence of the Kagan polarization on the magnitude of the angular momentum **J** remains unknown.[8] Knowledge of both aspects is essential for testing the validity of models for the nonspherical part of the molecular interaction, through a comparison of calculated and measured cross sections. As to the precise form of the angular momentum tensor polarization with respect to the magnitude of **J**, two choices can be considered.[9] Starting from considerations involving the intermolecular potential one is tempted to try an analysis on the basis of the angular momentum in terms of its direction only, i.e., $\mathbf{J}/|\mathbf{J}|$. On the other hand, when a Chapman-Enskog procedure is followed, **J** and the molecular velocity are treated in a similar way and the magnitude as well as the direction of **J** have to be taken into account. The Kagan polarization is then proportional to $\mathbf{J}^2$ whereas in the first choice it is independent of $|\mathbf{J}|$. In order to settle this problem unambiguously, we measured the Kagan polarization directly with an optical method as a function of J. This method has the additional advantage that now also the sign of the Kagan polarization can be determined.

In a gas of rotating molecules in the presence of a temperature gradient, ∇T, the molecular distribution function $f^{(0)}$ of reduced velocity $\mathbf{W}$ and angular momentum $\mathbf{J}$ will be deformed. One has $f=f^{(0)}(1+\phi)$ with $\phi=\boldsymbol{\phi}^E\cdot\nabla T+\boldsymbol{\phi}^K\cdot\nabla T$, where $\boldsymbol{\phi}^E$ gives rise to the microscopic energy flux and $\boldsymbol{\phi}^K$ is the Kagan vector $A\mathbf{W}\cdot[\mathbf{J}]^{(2)}$; here $[\mathbf{J}]^{(2)}$ denotes a symmetric traceless second-rank tensor. This form is dictated by the condition that $\boldsymbol{\phi}^K\cdot\nabla T$ is a true scalar. An expression for A can be obtained from the Waldmann-Snider equation.[7] One finds $A=C(\lambda/P)\mathfrak{S}(E,K)/\mathfrak{S}(K)$, with λ the heat conductivity, p the pressure, $\mathfrak{S}(E,K)$ the production cross section for Kagan polarization from the heat flux, and $\mathfrak{S}(K)$ its decay cross section[10]; C is positive and a function of molecular constants and the temperature. Hence a temperature gradient will result not only in energy transport but also in a flux of tensor polarization. To see this consider the situation for molecules moving along the direction of the temperature gradient, taken in the z direction: $\boldsymbol{\phi}^K\cdot\nabla T=AW_z[J]^{(2)}_{zz}\nabla_z T$. When A is positive these molecules will be preferably aligned with $\mathbf{J}$ along the z direction whereas for molecules moving in the opposite direction this alignment will be less probable. Those will be preferably aligned perpendicular to ∇T. So a net flux of $[J]^{(2)}_{zz}$ results without a resulting tensor polarization density. While several techniques are available to detect alignment of molecules optically, the situation is more complicated for a microscopic flux of this quantity. To be able to observe it one has to distinguish between molecules moving in opposite directions. We have solved this problem in the following way. When a molecule is excited in a laser beam it will travel during a finite time before emitting a photon. As a consequence, part of the emission takes place outside the exciting laser field. Thus by observing an appropriate spatial region of the fluorescence one can, in principle, select molecules moving in a specific direction.

The apparatus (see Fig. 1) consists of two plates at different temperatures, separated by a gap of 10 mm. Through the center of the gap a laser beam (0.5-mm full width at half intensity) runs in the x direction, with the electric vector **e** of the laser light along the y direction. Fluorescence emitted in the region between the laser beam and the hot plate (Fig. 2) comes from molecules

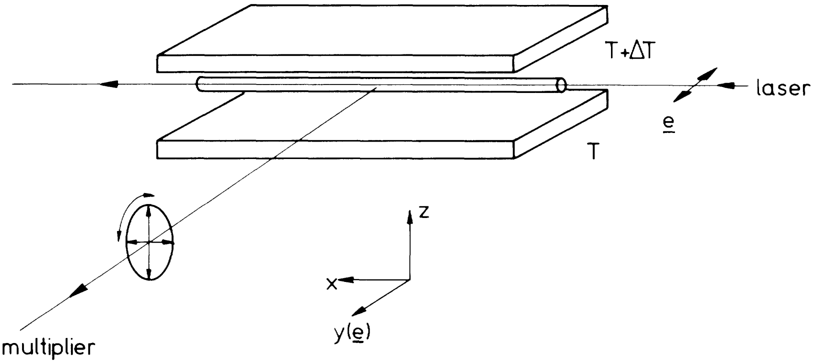

FIG. 1. Schematic diagram of the experimental setup. The ellipsoid represents the rotatable polarizer in the detection line.

that have passed the laser beam and hence have a velocity component parallel to the temperature gradient. Similarly, light emitted from below the laser beam is emitted by molecules with a velocity component antiparallel to the temperature gradient. To avoid the influence of collisions after the excitation has taken place, it is important that the mean free path of the molecules is much larger than the average distance traveled during the excited state lifetime. On the other hand, to minimize the influence of wall effects the mean free path has to be much smaller than the gap between the plates.

Iodine (I_2) was chosen as a gas because the average lifetime[11] of the excited state is approximately 1 μs, which in our experiment corresponds to an average distance traveled in the excited state of about 0.2 mm. Furthermore, iodine is well suited for this experiment because of its good fluorescence yield and the many transitions available in the visible region of the spectrum.

Once the two fluxes are separately observable, molecular alignment can be investigated with the help of polarization measurements of the fluorescent light.[12] Here use is made of the fact that for a diatomic molecule the excitation probability depends on the orientation of **J** with respect to the polarization of the laser light, because the transition dipole moment $\boldsymbol{\mu}$ is coupled with **J**. Similarly, the intensity of the fluorescence with polarization $\hat{\mathbf{i}}$, I_i, will depend on the orientation of **J** relative to $\hat{\mathbf{i}}$. Because the detection is in the same direction as the electric vector of the exciting laser beam, $I_x = I_z$ when no flux of alignment is present in the gas, as has been confirmed by experiments with $\Delta T = 0$. Hence, for a configuration as shown in Fig. 1, a nonisotropic distribution of **J** in the z direction will show up as the degree of polarization of the fluorescence, $\epsilon = (I_x - I_z)/(I_x + I_z)$.

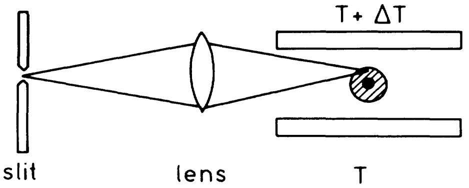

FIG. 2. Part of the fluorescence is selected by use of a lens and a slit. The black dot represents the laser beam and the hatched area indicates the fluorescence region.

By this technique, the angular momentum polarization in one of the two fluxes has been determined for a number of rovibrational states. A tunable cw dye laser pumped by an argon-ion laser was used to induce the transitions

$$B\,^3\Pi_u(v',J') \leftarrow X\,^1\Sigma_g^+((v'',J''), \quad J'-J''=\pm 1,$$

in the iodine. For a homonuclear diatomic molecule, μ is then perpendicular[13] to **J**. Because an optical polarization technique is employed, only deviations from the equilibrium distribution function depending on the orientation of the angular momenta are of interest. The nonequilibrium distribution function in one of the fluxes can then in our geometry be written as

$$f = f^{(0)}[1 + A\mathbf{J}^2\{(J_z^2 - \tfrac{1}{3}\mathbf{J}^2)/\mathbf{J}^2\}W_z\nabla_z T].$$

The factor $(J_z^2 - \frac{1}{3}\mathbf{J}^2)/\mathbf{J}^2$ contains only the orientation of **J**. Note the presence of the factor $\mathbf{J}^2$ indicating that the Chapman-Enskog procedure is followed here.

Since the fluorescence intensity is given by the product of the single-particle emission probability and the nonequilibrium function, summed over all orientations of **J**, one obtains in first order[14,15] $\epsilon = \frac{1}{7} sAJ(J+1)\nabla_z T$. The quantity s is a measure of the separation of the two fluxes. It is clear that the separation cannot be complete because of the laser beam profile.

To distinguish the effect from spurious polarizations, the plates were rotated over an angle of π around the laser beam between subsequent measurements. In this way the Kagan polarization changes sign because of the reversed temperature gradient, whereas the spurious polarizations remain constant. These effects, which are of the same order of magnitude as the Kagan polarization, can now be eliminated.

The degree of polarization of the fluorescence of one

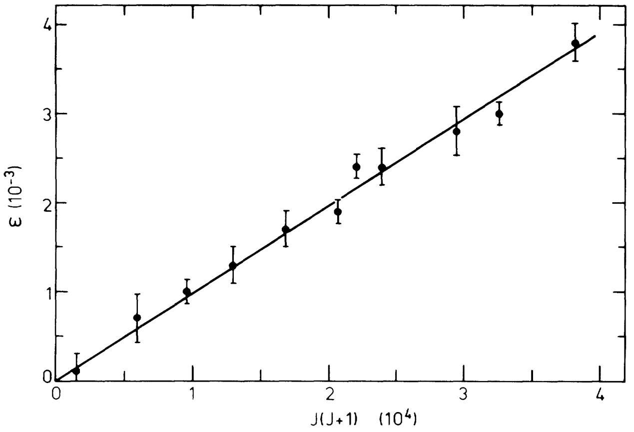

FIG. 3. ϵ as a function of $J(J+1)$. $T=533$ K, $\nabla_z T=11$ K/mm, $p=2.3$ Pa.

of the fluxes has been measured for several values of the angular momentum. To select molecules with a certain J, use has been made of calculated I_2 spectra.[16,17] As a check on the reliability of the measurements we studied the influence of the temperature gradient and the pressure by varying the temperature gradient between 0 and 11 K/mm and the pressure between 0.7 and 13 Pa. The measurements show that the polarization is proportional to the temperature gradient in the gas and inversely proportional to the pressure as is to be expected.

In Fig. 3 results are shown for an iodine pressure of 2.3 Pa, which corresponds to a mean free path of 1.8 mm. The temperature in the center of the gap was 533 K with a temperature gradient of 11 K/mm. The measurements show unambiguously that the Kagan polarization is proportional to $J(J+1)$. The sign of the polarization is also determined and it is found that the factor A is positive, i.e., molecules moving in the direction of the temperature gradient are preferably aligned with their angular momentum vector along that direction. From the expression for A one finds now also that the production cross section $\mathfrak{S}(E,K)$ has a positive sign since decay cross sections like $\mathfrak{S}(K)$ are always positive. We investigated also a possible dependence of the Kagan polarization on the vibrational level by measuring different vibrational transitions. No such dependence was found.

Although it is not the aim of this work, a value for A can be calculated from the slope of the effect versus $J(J+1)$ if s is known. A rough estimate of s can be obtained by our taking into account the intensity profile of the laser beam; we find $s=0.4$. With this value $\mathfrak{S}(E,K)/\mathfrak{S}(K)=6.3\times10^{-2}$ for I_2. Using measured[18] cross sections of N_2 one finds 5.6×10^{-2} which compares quite reasonably.

In conclusion, we can say that with the measuring technique described here, questions concerning the Kagan polarization, unsolved by experiments on the SB effects, are now satisfactorily answered. Moreover, this technique provides a useful tool to study nonequilibrium phenomena qualitatively in situations where separation of fluxes is required.

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