

"Gaslike character" of rotational motion of SF₆ molecules in a liquid

O.P. Revokatov, M.G. Gangardt, and S.V. Parfenov

Moscow State University

(Submitted May 12, 1974)

ZhETF Pis. Red. 19, 761-764 (June 20, 1974)

It is shown by analysis of NMR relaxation data that in liquid SF₆ the molecular angular momentum is effectively transferred via pair collisions.

The determination of the character of thermal motion of polyatomic molecules in liquids and in compressed gases is of great interest for the physics of condensed media. In the analysis of thermal motion of such molecules it is necessary to take into account not only the translational degrees of freedom, but also the molecule rotation.

An effective method of investigating molecular rotational motion is the NMR relaxation method, which, if the object is successfully chosen, makes it possible to determine the correlation times that characterize this motion.

Convenient objects for such investigations are molecules containing ¹⁹F nuclei. The nuclei of the fluorine atoms have a large spin-rotational interaction constant, making its contribution to the rate of the spin-lattice relaxation appreciable and making it possible to determine an important characteristic of the thermal motion, namely the correlation time τ_J of the angular momentum of the molecules.^[1] Many experimental investigations have by now been made of the dependence of the spin-lattice relaxation time and of the self-diffusion coefficient on the temperature and on the density for molecules of this type. In particular, the temperature dependence of T_1 and D has been thoroughly investigated for sulfur hexafluoride SF₆ along the coexistence curve and along a number of isochors from the melting temperature to $1.3T_{cr}$.^[1-3] The dependence of T_1 on the pressure and on the temperature was also investigated for gaseous SF₆ of low density. It follows from the experimental results that T_1 of SF₆ in vapor and in compressed gas is proportional at constant temperature to the density in the interval from 0.04 to 175 Amagat units.

The dominant mechanism of NMR relaxation in the indicated density interval for SF₆ is the spin-rotational interaction.^[3,4] The spin-lattice relaxation time for this mechanism is determined by the relation

$$\frac{1}{T_1} = \frac{2\pi I kT}{h^2} C_{\text{eff}}^2 \tau_J, \quad (1)$$

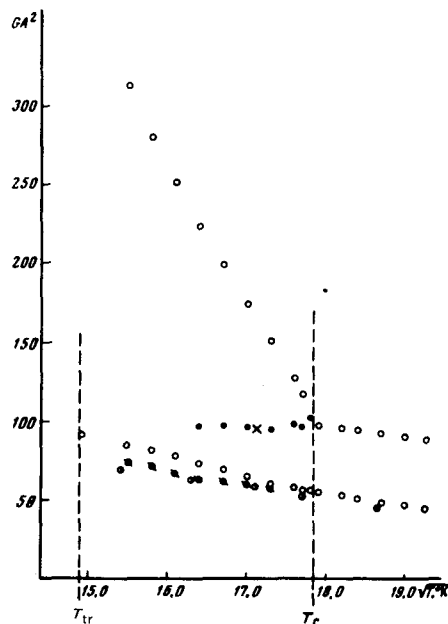
where I is the moment of inertia of the molecule, C_{eff} is the effective constant of the spin-rotational interaction, τ_J is the correlation time of the angular momentum

of the molecule, T is the absolute temperature, k is Boltzmann's constant, and h is Planck's constant.

Therefore τ_J^{-1} is proportional to the density, and it can be assumed that the collisions that lead to changes in the angular momentum of the molecule are binary. This gives grounds for using for the calculation of σ_J the relation

$$\frac{1}{\tau_J} = n \sigma_J \bar{v}, \quad (2)$$

where n is the density, σ_J is the cross section of the collisions leading to a change in the angular momentum of the molecules, and $\bar{v} = \sqrt{8kT/\pi m}$ is the average thermal velocity of the molecule. The result is shown in the figure. Similar calculations for the liquid phase of SF₆ along the coexistence curve have shown that σ_J in the liquid differs from the analogous quantity for vapor by



Upper curve—temperature dependence of σ_J on the temperature: \circ —gas and liquid, \bullet —vapor, \times —gas-kinetic cross section of the molecule. Lower curve—temperature dependence of σ_J : \circ —gas and liquid, \odot —vapor, \emptyset —rarefied gas.

only 15%, although the densities of the liquid and of the vapor differ in this case by a factor of almost 60. If it is assumed, as is usually done, that the constants of the spin-rotational interaction in the liquid and in the gas differ little, and that the contribution of the mechanism of the spin-rotational interaction to the NMR relaxation is dominant also in liquid SF₆,^[1,3] then it can be assumed that the angular momentum of the molecules in the liquid SF₆ is transferred effectively in the same manner as in gas, via pair collisions, i. e., the rotational motion of the SF₆ molecules in the liquid is "gaslike."

The figure shows also the results of the calculation of the cross section of the molecular collisions that lead to change of the momentum. The correlation time was determined from the measured value of the self-diffusion coefficient D :

$$\tau_{\rho} = \frac{mD}{kT}, \quad (3)$$

and σ_{ρ} was determined from a formula analogous to (2). In vapor and gas, this cross section coincides with the gas-kinetic value, and in liquid it turns out to be larger by several times.

The results of investigations of the rotational motion of molecules of lower symmetry (C_{3v}) than SF₆ (O_h), are now being readied for publication.

The authors are grateful to Prof. A. I. Burshtein for a discussion of the results.

¹W.R. Hackelman and P. S. Hubbard, J. Chem. Phys. **39**, 2688 (1963).

²O. P. Revokatov and S. V. Parfenov, ZhETF Pis. Red. **15**, 151 (1972) [JETP Lett. **15**, 103 (1972)].

³J. Tison and E. Hunt, J. Chem. Phys. **54**, 1526 (1971).

⁴J. A. Courtney and R. L. Armstrong, Can. J. Phys. **50**, 1252 (1972).