Study of collisional relaxation as a function of velocity using the photon-echo method

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The photon-echo method is used to determine the rate of relaxation of the dipole moment Γ as a function of the relaxational velocity v_z in SF_6 gas and in the mixture SF_6-Kr. Comparison of these dependences with the theoretical dependences lead to the conclusion that in pure SF_6 gas the interaction is close to $V \sim 1/r^3$, which is related to the exchange mechanism of rotational relaxation in SF_6; in the mixture SF_6-Kr, short-range forces play a large role.

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The most complete information on the interaction potential of colliding particles is obtained by studying the scattering characteristics with the help of atomic or molecular beams. The use of this procedure is limited to investigations primarily of collisions of particles in the ground state. Spectroscopic methods permit studying collisions of excited particles. Information on the interaction potential can be obtained by studying the temperature dependence of collision broadening (see, for example, Ref. 1). For many objects, it is impossible to use this method due to the small range of variation of the temperature that is possible in the experiment. A more convenient method is the method of investigating the dependence of the collisional broadening on the detuning of the emission frequency.[2] The change in the homogeneous width as a function of frequency and, therefore, as a function of velocity, can be found both from an analysis of the Doppler contour of the absorption line,[2] and with the help of the methods of saturated absorption nonlinear laser spectroscopy.[3]

Application of the saturated-absorption method places stringent requirements on the line width and stability of the frequency of the laser radiation. In addition, the field-induced broadening of the line investigated must also be included.

Application of coherent transient processes, in particular, the photon echo (PE) for these purposes opens up new possibilities. The photon-echo method requires only short-time stability of the laser frequency. The PE signal appears in the absence of external fields and, for this reason, permits obtaining the dependence $\Gamma(v)$ directly from the experiment. In this case, the following conditions must be satisfied: the spectral width of the excited pulses $1/\tau$ must be much less than the Doppler width ku and the Rabbi frequency must satisfy the requirement $dE/\hbar \ll ku$. Under these conditions of excitation, primarily resonance molecules, for which the detuning Ω of the laser frequency from the center of the transition is canceled by the Doppler shift $\Omega = kv_z$, participate in the formation of the echo.

The velocity of v_z can be changed either by retuning the frequency of the laser radiation or by changing the transition frequency under the action of external fields. In Ref. 4, informatin on the intermolecular interaction potential of $^{13}CH_3F$ was obtained with the help of PE with Stark switching of the levels. This method is applicable only to molecules that have a dipole moment.

In the present work, the change in v_z was achieved by changing the frequency of the exciting laser radiation. This method of selecting the velocities of atoms interacting with the field is more universal and is applicable to any molecule.

The experiments were performed in SF_6 gas and its mixtures with Kr. A frequency-stable CO_2 laser operated on the P(18) line of the 00^01-10^00 band, which coincides with the center of the absorption band of SF_6, A_2^1 P(33) of the ν_3 band. The experimental setup is described in Ref. 5. The radiation frequency of the exciting CO_2 laser was fixed to the frequency of a stable laser with controllable detuning in the range 0–20 MHz. The frequency of the stable laser was fixed to the center of SF_6, and the frequency of the exciting laser to the frequency of the stable laser to within 100 kHz.

The relaxation rate $\Gamma(v_z = \Omega/k)$ was determined for each value of the frequency detuning Ω using the usual dependence of the PE intensity on the delay time T between the exciting pulses: $U_{PE} = U_0 \exp(-4\Gamma T)$. The measurements were performed for a series of pressures of SF_6 and of the buffer gas Kr in the range 1–5 mTorr and for delays varying from 2 to 8 μs. The results are shown in Fig. 1 in the form of the dependences of the relative magnitudes of the relaxation rate of the dipole moment $\Gamma(v_z)/\Gamma(0)$ on the quantity v_z/u, where $u \equiv \sqrt{2kT^0M_1}$ is the average thermal velocity of the excited particles along the z axis.

A theoretical analysis of the dependence $\Gamma(v)$ on the modulus of the relative velocity of the particles[6,7] for a potential $V \sim 1/r^3$ leads to the equation

$$\Gamma \sim |\mathbf{v} - \mathbf{w}|^{(n-3)/(n-1)}, \tag{1}$$

where $\mathbf{v}$ is the velocity of the excited particles, and $\mathbf{w}$ is the velocity of the buffer gas particles. It is shown in Ref. 8 that when $dE/\hbar \ll ku$ (the Rabbi frequency is less than the width of the Doppler contour), the change in the damping rate Γ of the photon-echo signals as a function of the frequency detuning Ω permits finding the dependence $\Gamma(v)$, where $v = \Omega/k$ must be taken as the argument.[8] For this reason, in order to compare with experiment, it is sufficient to average Eq. (1) over the velocities of the buffer gas particles. Such averaging was performed in Ref. 9 and gives the following dependence:

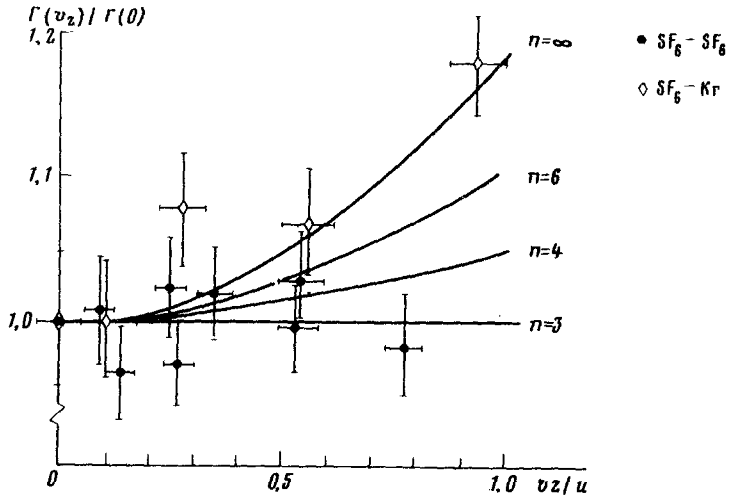

FIG. 1. Dependence of the rate of collisional relaxation of the dipole moment on the translational velocity in SF_6 and SF_6-Kr.

$$\Gamma(v_z)/\Gamma(0) = \exp(-\alpha^2x^2)\,\Phi\left(\frac{\gamma+3}{2}, \frac{3}{2}, \alpha^2x^2\right), \tag{2}$$

where $\alpha = \sqrt{2kT^0/M_1}$, M_2 is the mass of the buffer gas particles, M_1 is the mass of the excited particles, $x = v_z/u, u = \sqrt{2kT^0/M_1}$, $\gamma = (n-3)/(n-1)$, and $\Phi(a,c,z)$ is the confluent hypergeometric function.

The theoretical dependence (2) is illustrated in Fig. 1 by the solid lines for several values of n.

In pure SF_6, $\Gamma(v_z)$ is essentially independent of v_z/u in the range of values of v_z/u studied. This result indicates a dipole-dipole-type interaction $V \sim 1/r^3$. A potential of this type occurs as a result of quasiresonant exchange of a vibrational quantum, leading to rotational relaxation. In the mixture SF_6–Kr, $\Gamma(v_z)$ depends strongly on v_z (see Fig. 1), indicating a contribution from higher multipole interactions.

The photon-echo technique with frequency detuning is useful for determining the slope of the section of the interaction potential which describes a given relaxation process.

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