Direct measurement of thermalization rate of the ground state of K_2 molecules

M. P. Auzin'sh, I. Ya. Pirags, R. S. Ferber, and O. A. Shmit
P. Stuchki State University

(Submitted 2 April 1980)
Pis'ma Zh. Eksp. Teor. Fiz. **31**, No. 10, 589–592 (20 May 1980)

A method of direct measurement of thermalization rate of the population γ of a vibrational-rotational electronic ground state level of diatomic molecules from the kinetics of laser-excited fluorescence was proposed. The values of γ for the K_2 molecules in a potassium vapor and the effective cross section of thermalizing K_2–K collisions were determined experimentally.

PACS numbers: 33.50.Dq, 34.90. + q, 33.10.Jx

It is very difficult to investigate the collisional relaxation processes from the internal degrees of freedom because of the absence of radiative transitions in the electronic ground state of homonuclear diatomic molecules.[1-3] The use of optical pumping method (alignment) was reported in Refs. 4 and 5, while use of the Hanle effect of the v'', J'' electronic ground-state level for the Na_2 and K_2 molecules in alkali vapor, was reported in Ref. 6. However these require additional data (absorption probability, Lande factors, etc.) for conversion to the relaxation rates.

The direct measurement method proposed here involves the following procedure. Suppose a laser radiation induces optical transitions from the v'', J'' ground-state level to the v', J' level of the electronic excited state. Because of a large number of allowed spontaneous transitions to the ground state, the probability that they populate the initial level is small, and it turns out to be depopulated when the absorption rate $B\rho$ is comparable to the total rate of radiationless relaxation processes γ. If the exciting radiation is attenuated sufficiently rapidly (during the time $\Delta t \ll \gamma^{-1}$) (Fig. 1a), it can be converted from a destructive to a test radiation; therefore, the restoration of population of the v'', J'' level can be monitored from the kinetics of the fluorescence induced by it (Fig. 1b).

This method was used for K_2 molecules (see also Refs. 4 and 5) in thermodynamic equilibrium in potassium vapor, where $[K_2]/[K] \sim 0.002$. The 632.8-nm He-Ne laser radiation effectively excites the Q transition ($v'' = 1$, $J'' = 72$) $X\,^1\Sigma_g^+ \rightarrow (v' = 8,$

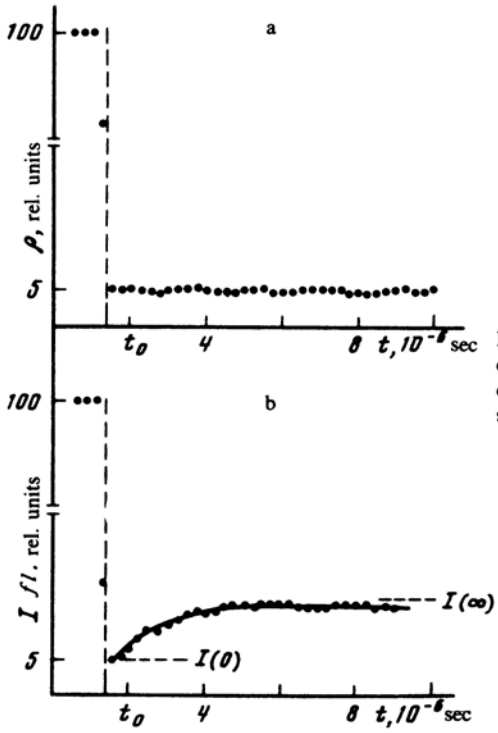

FIG. 1. Shape of the trailing edge of the pulse: (a) excitations, (b) K_2 fluorescence; $T = 488$ K; the solid curve was calculated from Eq. (1), $\gamma = 0.96 \times 10^6$ sec^{-1}.

$J' = 72$) $B\,{}^1\Pi_u$ to K_2. According to Ref. 6, the rate of spontaneous decay (8.72) $B\,{}^1\Pi_u$ is 0.93×10^8 sec^{-1} and the absorption rate under the experimental condition is $B\rho \sim 10^6$ sec^{-1}, which makes it possible to disregard the induced transitions in the radiation and to solve the simplified kinetic equation.[5] Thus, the predicted time dependence of the intensity I_{fl} for any line of progression of the fluorescence excited by a laser beam attenuated during the time $t = t_0$ has the form

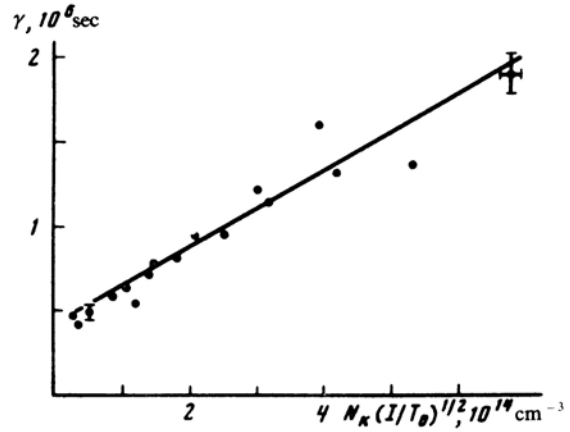

FIG. 2. Dependence of thermalization rate on concentration of the K atoms.

$$I_{fl}(t - t_0) = I(\infty) - [I(\infty) - I(0)]e^{-\gamma(t - t_0)}, \quad (1)$$

where $I(0)$ and $I(\infty)$ are the $I_{fl}(t - t_0)$ values for $t = t_0$ and $t = \infty$ (Fig. 1b). Therefore, the restoration of thermally balanced concentration of the v'', J'' level in this model and an increase in the fluorescence intensity associated with it occur exponentially with a characteristic time $\tau = \gamma^{-1}$.

The experimental measurements were performed in the following manner. The radiation of the LG-36A He-Ne laser of power density $\rho \sim \text{W}\cdot\text{cm}^{-2}$ was modulated by using an electro-optical ML-3 modulator. The time dependence of ρ had the shape of square pulses of duration $T = 30\,\mu$sec [it was necessary that $T \gg 1(\gamma + B\rho)$], repetition frequency of 9 kHz, and the rise and drop edges of the order of $0.05\,\mu$sec; the modulation depth was about 0.95 (Fig. 1a)., The fluorescence emitted at 90° was focused on the entrance of the DFS-12 monochromator (0.5 nm/mm), which isolated the Q 16 line, and was recorded by a cooled FEU-79 photomultiplier with use of single-photon, statistical kinetics analysis[7] with a subsequent time-amplitude conversion and storage in a AI-256-6 pulse analyzer. By selecting a storage time (up to 6 hours for extremely weak light fluxes), we were able to achieve the required measurement accuracy.

The characteristic measured time dependence of I_{fl} is shown in Fig. 1b. Using Eq. (1) we can determine γ directly. The depth of the "trough" $[I(\infty) - I(0)]/I(\infty)$ is associated with the parameter $B\rho/\gamma$ characterizing the depopulation efficiency. The relaxation rates γ determined in this manner are plotted in Fig. 2 as a function of concentration N_K of the potassium atoms which play the role of a thermostat for the K_2 molecules. The temperature range was from $T_0 = 443$ K to $T = 514$ K and the corresponding concentration of K atoms ranges fro 0.3×10^{14} to 5.5×10^{14} cm^{-3}; the total concentration range of the K_2 molecules was 0.13×10^{11} to 11×10^{11} cm^{-3}. The slope of the line on the plot in Fig. 2 enabled us to determine the effective total cross section of the thermalizing collisions $\langle\sigma(K_2 - K)\rangle$ of the K_2 molecules (1.72) $X\,^1\Sigma_g^+$ with the K atoms, assuming that

$$\gamma = \gamma_0 + \langle\sigma(K_2 - K)\rangle \bar{u} N_K. \quad (2)$$

The $(T/T_0)^{1/2}$ factor on the plot in Fig. 2 was introduced because the relative rate of the colliding partners, averaged over the Maxwellian distribution, was $\bar{u} = \sim T^{1/2}$. The cross section, averaged over a number of experiments, was $\langle\sigma(K_2 - K)\rangle = (3.3 \pm 0.5)\times10^{-14}$ cm^2 with a confidence coefficient of 0.9. The value of γ_0, which is assumed to be independent of N_K, has the meaning of the reciprocal free time of flight of the molecules through the laser beam.

The elementary processes contributing to the measured total cross section for relaxation of population to a thermally balanced one (thermalization) are difficult to describe in detail at this stage of investigation. The most probable processes are the induced $K_2 - K$ collisions and inelastic transitions from the rotational (and, to a lesser extent, vibrational) levels that are located within the limits of the energy $\Delta E \sim kT$ from the depopulated level; this is the T-R and T-V exchange. One of the mechanisms might be a relaxation during a chemical reaction of an exchange between a K atom and one

of the atoms in K_2 whose cross section, according to the data of Ref. 8, is 1.6×10^{-14} cm^2.

It is remarkable that the cross section obtained in this work coincides in magnitude with that for the alignment relaxation ($v'' = 1$, $J'' = 72$) $X\,^1\Sigma_g^+$ in the $K_2 - K$ pairs, which was measured earlier by using two methods: the optical pumping method[5] gave $(2 \pm 1)\times10^{-14}$ cm^2 and the method of Hanle effect of the ground state[6] gave $(2.5 \pm 0.5)\times10^{-14}$ cm^2. This fact confirms experimentally the assumption[5,6] that the alignment relaxation of the v'', J'' level of the $X\,^1\Sigma_g^+$ state of the alkali dimers in a vapor occurs primarily as a result of a population exchange between different vibrational-rotational levels.

[1]R. E. Drullinger and T. N. Zare, J. Chem. Phys. **51**, 5532 (1969); **59**, 4225 (1973).
[2]R. Feinberg, R. E. Teets, J. Rubbmer, and A. L. Schawlow, J. Chem. Phys. **66**, 4330 (1977).
[3]K. Bergmann, R. Engelhardt, U. Hefter, P. Hering, and J. Witt, Phys. Rev. Lett. **40**, 1446 (1978).
[4]V. B. Grushevskiĭ, M. Ya. Tamanis, R. S. Ferber, and O. A. Schmit, Optika i Spektroskopiya **42**, 993 (1977).
[5]R. S. Ferber, Izv. Akad. Nauk SSSR, physical series, **43**, 419 (1979).
[6]R. S. Ferber, O. A. Schmit, and M. Ya. Tamanis, Chem. Phys. Lett. **61**, 441 (1979).
[7]L. M. Bolinger and G. E. Thomas, Scientific Instruments **9**, 39 (1961).
[8]W. Kamke, Phys. Lett. **55A**, 15 (1975).

Hybridization of collective oscillations in ^{3}He–A near the transition to the A_1 phase

G. E. Gurgenishvili and G. A. Kharadze
Institute of Physics, Academy of Sciences of the Georgian SSR

(Submitted 2 April 1980)
Pis'ma Zh. Eksp. Teor. Fiz. **31**, No. 10, 593–595 (20 May 1980)

Hydrodynamic oscillations of longitudinal magnetization and entropy in a superfluid ^{3}He–A in a magnetic field are analyzed. It is shown that in the neighborhood of a transition to the A_1 phase there is a strong mixing of the entropy (and temperature) oscillations with the spin wave.

PACS numbers: 67.50.Fi, 64.70.Ja, 65.50. + m

Liquid ^{3}He-A is a mixture of two, weakly interacting superfluid components characterized by Cooper pairing in the spin states $\uparrow\uparrow$ and $\downarrow\downarrow$. In the presence of a strong magnetic field and in the immediate vicinity of the transition to a normal phase, the quasi-particle pairing amplitudes with a projection of the total spin $S_z = \pm 1$ are not equal to each other ($\Delta_\uparrow \neq \Delta_\downarrow$). Taking into account this fact, the order parameter describing the superfield ^{3}He-A can be represented in the form

$$A_{\mu i} = \Delta(T) d_\mu u_i = \Delta(T)(a_+ \mathbf{d}_1 + i a_- \mathbf{d}_2)_\mu (\mathbf{u}_1 + i\mathbf{u}_2)_i , \quad (1)$$

where $(\mathbf{d}_1,\mathbf{d}_2)$ and $(\mathbf{u}_1,\mathbf{u}_2)$ are unit vectors in the spin orbital spaces, respectively, $a_\pm = (\Delta_\uparrow \pm \Delta_\downarrow)/2\Delta$, and $\Delta^2 = \frac{1}{2}(\Delta_\uparrow^2 + \Delta_\downarrow^2)$.