

# Kinetically isolated subsystems of rotational levels of heavy water molecule in atom-molecule collisions

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The experimental observation of an anomaly in the behavior of the rotational relaxation time  $T_1$  of the  $D_2O$  molecule as a function of the density of atomic particles in the gas mixture is reported. The anomaly is related to the existence of kinetically isolated groups of rotational levels of molecules, which manifest themselves in atom-molecule collisions.

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Collisional selection rules for rotational transitions of polyatomic molecules, which are based on the three-dimensional form of the interacting particles, are well known. The symmetry of the distribution of atoms making up the molecule is manifested in the properties of the intermolecular interaction potential, which must remain

unchanged under symmetry operations that transform the atomic configuration into itself. In symmetric top molecules, the nonspherical part of the interaction potential, which is determined by the type of the molecule, establishes some selection rules and relaxation channels for nonspherical scattering.<sup>1</sup> In asymmetric top molecules, the symmetry of the spatial type of the molecules gives rise to selection rules that separate the set of rotational levels of the molecule into subsystems, transitions between which are not allowed in collisions of the molecule with an atom.<sup>2,3</sup>

In this paper, we report the results of experiments intended to reveal the kinetically isolated subsystems of the  $D_2O$  molecule in the gas phase.

According to Refs. 2 and 3, the system of rotational levels of the molecule with point symmetry group  $C_{2v}$  (the molecules  $H_2O$  and  $D_2O$ ) separates into four subsystems ( $A^+$ ,  $B_1^+$ ), ( $A^-$ ,  $B_1^-$ ), ( $B_2^+$ ,  $B_3^+$ ), ( $B_2^-$ ,  $B_3^-$ ), where  $A$ ,  $B_1$ ,  $B_2$ , and  $B_3$  is the classification used for the energy levels of the asymmetric top, and the signs  $+$  and  $-$  indicate the type of symmetry of the wave functions with respect to reflection in the plane passing through the  $Oz'$  axis of the moving system of coordinates.<sup>4</sup> The first two subsystems belong to the paramodification of  $D_2O$  molecules (even nuclear spin), and the two other subsystems belong to orthomodifications (odd nuclear spin). Collision-induced transitions between nuclear-spin modifications are forbidden. In the experiments the subsystems ( $A^+$ ,  $B_1^+$ ), ( $A^-$ ,  $B_1^-$ ) of the paramodification of the  $D_2O$  molecule were studied.

Kinetic isolation of the subsystem occurs if  $D_2O$ -Ar collisions, which give rise to transitions only between levels of each of the subsystems, predominate in the gas, while  $D_2O$ - $D_2O$  collisions, which give rise to transitions between levels without any regard as to their belonging to subsystems, occur quite rarely. The selection rule for  $D_2O$ - $D_2O$  collisions is determined by the type of the potential, for example, dipole-dipole, dipole-quadrupole, etc. Away from thermal equilibrium,  $D_2O$ -Ar collisions restore the equilibrium distribution within subsystems, while  $D_2O$ - $D_2O$  collisions establish equilibrium both within the subsystems and between them. Under the condition,  $\nu(D_2O-Ar) \gg \nu(D_2O-D_2O)$ , where  $\nu$  is the frequency of the corresponding inelastic collisions, in the time interval  $\ll 1/\nu(D_2O-D_2O)$ , the subsystems behave like thermodynamically equilibrium, weakly interacting systems. A subsystem can be observed by determining the rotational relaxation time of the population for transitions within and between subsystems.

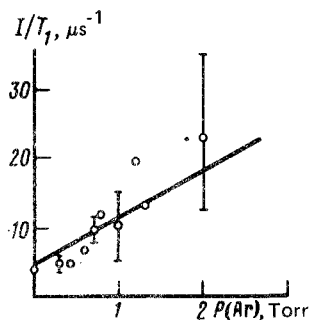


FIG. 1.

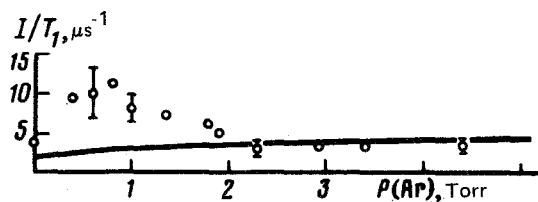


FIG. 2.

The coefficient of saturated absorption was measured with an automatic submillimeter spectrometer<sup>5</sup> in the spectral transitions  $2_{11} - 2_{20}$ ,  $2_{02} - 2_{11}$ ,  $1_{11} - 2_{02}$  with wavelengths 0.402, 0.735, and 0.653 mm at a constant pressure of 0.04 Torr of  $D_2O$  vapor and with the argon pressure varying in the range 0.3–4.5 Torr. The gas mixture was at room temperature. In accordance with the identification of the levels  $1_{11} - B_1^+$ ,  $2_{02} - A^+$ ,  $2_{11} - B_1^-$ ,  $2_{20} - A^+$ , the first two transitions couple levels of different subsystems, and the last transition occurs within the subsystem. The relaxation time of the population  $T_1$  was determined from the coefficient of absorption with different power level and spectral line width (time  $T_2$ ) using the standard procedure.<sup>6</sup> It should be noted that in the experiments on stationary saturation the lower limit of the frequency in the spectrum of relaxation frequencies of the multilevel systems is measured.

The dependence of  $T_1$  on the argon concentration in the mixture behaves in the usual way (see Fig. 1) for a transition within the subsystem ( $A^+B_1^+$ ) and it decreases with increasing pressure of the relaxant gas. Because of the short relaxation time within the subsystem, it is impossible to saturate the transition  $1_{11} - 2_{02}$  at argon pressures exceeding 2 Torr. For transitions between subsystems (see Figs. 2 and 3), the time  $T_1$  does not depend on the pressure of the atomic gas and at high argon pressures it remains at the level of relaxation time in pure  $D_2O$  vapor.

The system of kinetic equations with parameters which best described the non-equilibrium rotational distribution of the paramodification of  $D_2O$  molecules in an argon jet in the temperature range 300–60 K was used to model numerically the conditions of the present experiments and for the calculation. In this system of equations, the temperature dependence of the transition probabilities is given by the Polyani–Woodall equation. The results of calculations of  $T_1^{-1}$  as a function of the argon content in the mixture are illustrated in Figs. 1–3 in the form of solid curves. Surprisingly good agreement was obtained with experiment, if we take into account the fact

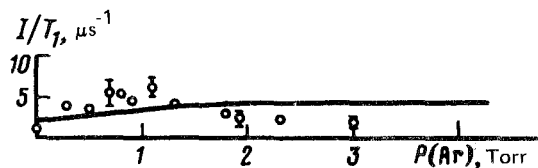


FIG. 3.

that the parameters in the system of kinetic equations were determined for the temperature range 60–120 K.

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