

Rotationally selective condensation of heavy water in a supersonic carbon dioxide jet

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D_2O molecules condense only from the rotational ground state. A deviation from equilibrium in terms of the para- and ortho- D_2O molecules has been achieved in the gas phase.

The initial stage of the vapor-liquid phase transition involves the formation of dimer molecules of the condensing gas. The formation of molecules from atoms or of complex molecular formations from simpler formations is usually controlled by the internal state of the particles that are combining. Illustrative cases are the particular

ways in which excimer molecules form and spin-controlled chemical reactions. It may be that the probability for the formation of dimer molecules and small clusters also depends on the internal state of the molecules in the group, so that the vapor-liquid phase transition may turn out to be selective in terms of internal degrees of freedom of the molecules.

In the present letter we offer proof of the first assertion in the abstract, found by a method of quantitative spectroscopy of rotational transitions of water molecules. All parts of the proof lean heavily on knowledge of the qualitative and quantitative behavior of the rotational relaxation of D_2O molecules in the gas phase.¹⁻³ A decrease in the number of molecules in the vapor phase and an increase in the temperature of the gas (because of the evolution of the latent heat of the phase transition) are adopted as the basic indicators of a condensation process. For these experiments we selected the heterogeneous condensation of D_2O molecules on carbon dioxide molecules.⁴

The experiments are carried out in a free supersonic jet of carbon dioxide or nitrogen with a small admixture of heavy-water vapor. The gas mixture, with a fixed initial pressure of 0.35 torr D_2O and with a carrier-gas pressure varied over the range $P_0 = 5-30$ torr, with an initial temperature of 290 K, expands into a low-pressure vacuum chamber (10^{-2} torr) through a plane sonic nozzle (slit) with a throat height of 3 mm. We measure the interval absorption coefficient α at a point 20 mm from the slit, at the axis of the jet in a zone on the order of 1 mm in size of the supersonic flow ($M \approx 4$). For these measurements we use a submillimeter spectrometer and the procedure described in Refs. 1 and 2.

As the gas in a supersonic jet cools, the value of α may differ from the equilibrium value α_e for isentropic flow, for two reasons: the slowness of the relaxation at low

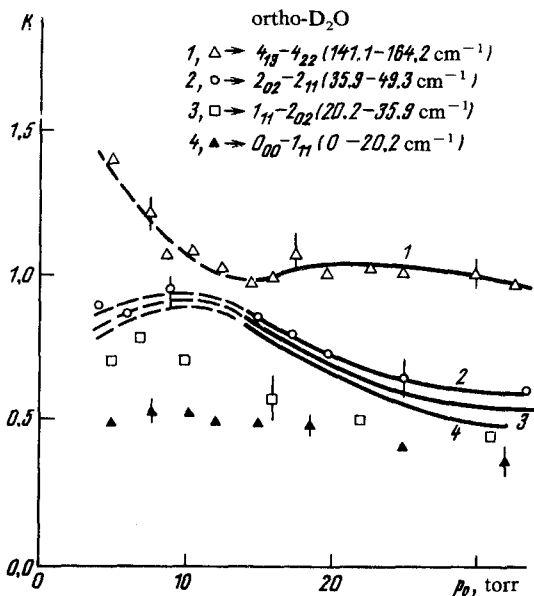


FIG. 1.

pressure of the carrier gas and condensation. Control experiments with nitrogen revealed that the absorption for all the transitions studied at $P_0 \geq 25$ torr is close to the equilibrium value α_e . In a nitrogen jet, water vapor does not condense under our experimental conditions.

Figure 1 shows experimental results on the coefficient $K = \alpha/\alpha_e$, which shows the deviation from equilibrium, as a function of P_0 in a $\text{CO}_2\text{-D}_2\text{O}$ mixture for the $4_{13}\text{-}4_{22}$ and $2_{02}\text{-}2_{11}$ transitions of ortho- D_2O molecules. The reason for the values $K \neq 1$ for these transitions at low pressures of the carrier gas is the slowness of the rotational relaxation. As P_0 is increased, this deviation from equilibrium should disappear ($K = 1$), as in the case with nitrogen, beginning at some point on the pressure scale. Carbon dioxide, which is more effective in promoting relaxation,³ makes this event possible at pressures of only $P_0 \geq 15$ torr. The behavior of K as a function of P_0 , however, is different, because of the condensation, which raises the gas temperature and causes a departure of D_2O molecules from the gas phase.

Knowing the absorption coefficient α for the two rotational transitions, and equating it to the calculated value $\tilde{\alpha}(T, N)$ for a Boltzmann distribution among levels, we can unambiguously determine the properties of the flow: the temperature T and the density (N) of the molecules in the observation zone.⁵ Figure 2 shows values found by this method for $\Delta T = T - T_e$ and $\Delta N = (N - N_e)/N_e$ as a function of P_0 over the pressure interval 15–30 torr for the $4_{13}\text{-}4_{22}$ and $2_{02}\text{-}2_{11}$ transitions. Here T_e and N_e are the gas temperature and the density of D_2O molecules without condensation. As expected, the gas temperature increases, while the density of ortho-molecules decreases, with increasing P_0 .

Condensation can also distort the Boltzmann distribution among rotational lev-

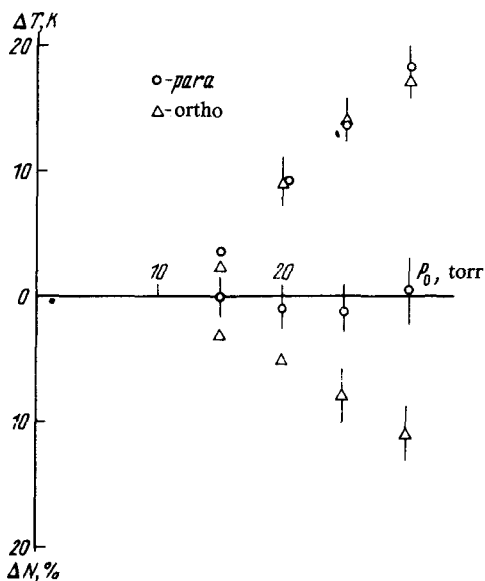


FIG. 2.

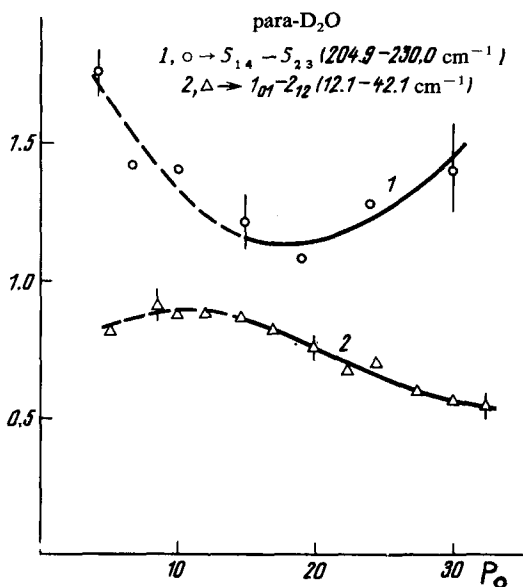


FIG. 3.

els.⁶ Comparison of the calculated values of $\tilde{\alpha}(T, N)$ (curves 1-4 in Fig. 1) with values of α measured for other transitions of the ortho-molecules shows that there is a difference for only the lowest-lying transitions, $0_{00}-1_{11}$ and $1_{11}-2_{02}$, where the absorption is much weaker than the calculated value. This result means that the D_2O molecules enter into the condensate from only the lower-lying rotational levels. A calculation for the rotational relaxation of D_2O molecules on the basis of the kinetic model^{3,2} shows that the water molecules condense from only the ground state with a probability of 10^{-1} per collision with a CO_2 molecule; the deficiency of molecules in other levels of the ortho-modification is attributed to collisional relaxation.

There is another possibility for confirming this conclusion. We know that the levels of different spin modifications are not coupled by relaxation. If only D_2O molecules in the ground state belonging to the ortho-modification condense, then the absorption on transitions of the para-modification, including the lowest, $1_{01}-2_{12}$, should correspond to a fixed number of molecules in this modification and should react to only an increase in the gas temperature. This is what we observe experimentally. Figure 3 shows K as a function of P_0 for the two transitions $1_{01}-2_{12}$ and $5_{14}-5_{23}$ of the para-modification. The gas temperature found from these results turns out to be the same as that measured in the ortho-modification, and the value of ΔN is zero, within the measurement errors (Fig. 2).

The apparent reason for the pronounced selectivity of the process by which the molecules combine with each other is a substantial anisotropy of the D_2O-CO_2 intermolecular interaction potential. The molecules that experience the strongest attraction are water molecules which do not have time to change their relative orientation during the collision. This condition imposes a severe restriction on the dipole rotational fre-

quency ($< 10^{11} \text{ s}^{-1}$), which makes the combining of molecules likely for only D_2O molecules from the rotational ground state.

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