Rotational nonequilibrium of $H_2{}^{16}O$ molecules in a supersonic rarefied water vapor stream

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An experimental investigation was made of the integrated absorption coefficient of the $H_2{}^{16}O$ molecules for the 1_{11}–2_{02}, 2_{02}–2_{11}, 3_{31}–4_{22}, and 4_{31}–5_{24} rotational transitions in the submillimeter range. The investigation was carried out using a planar supersonic stream of rarefied water vapor with the initial parameters $P_0 = 4$ Torr and $T_0 = 20$–150°C, which were close to the saturation line. The behavior of the integrated absorption coefficient was determined in the absence of condensation, at the begining of nonequilibrium condensation, and under conditions of advanced condensation in the stream. It was found that the distribution of the $H_2{}^{16}O$ molecules over the rotational levels was of nonequilibrium type and could not be described by the Boltzmann distribution with any rotational temperature. The reasons for this rotational nonequilibrium were analyzed.

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Intensive investigations are being made of supersonic gas streams by physical methods and the aim is to determine kinetic, spectral, and other characteristics of molecular gases under strongly nonequilibrium conditions. In the case of axisymmetric and planar supersonic rarefied gas streams there may be considerable temperature and density gradients and nonequilibrium gas condensation may take place. Spectral properties of water vapor under strongly nonequilibrium conditions are particularly interesting because this vapor is present in all the gases that participate in atmospheric and many other technical processes. Very little is known about the kinetics of rotational relaxation of polyatomic polar molecules under strongly nonequilibrium conditions.

The present paper reports a spectroscopic investigation of the rotational state of the $H_2{}^{16}O$ molecule in a planar stream of rarefied water vapor.

We used the method of monochromatic submillimeter spectroscopy, which makes it possible to determine accurately the difference between the numbers of molecules at rotational levels between which a transition takes place. A description of the gasdynamic part of the apparatus and of a computer-controlled automatic submillimeter spectrometer can be found in Ref. 1, together with a study of equilibrium water vapor streams in supersonic nozzles. To the best of our knowledge, ours is the first investigation of the rotational lines of the H_2O molecule under strongly nonequilibrium conditions.

THEORY OF THE SPECTROSCOPIC METHOD

We shall investigate the distribution of molecules over the vibrational levels of pure water vapor by measuring the integrated absorption coefficient at spectral lines in the rotational spectrum of the H_2O molecule. The integrated absorption coefficient I for a single line is given by

$$I=\int\limits_{-\infty}^{\infty}\alpha(\omega)d(\omega-\omega_{21}), \tag{1}$$

where $\alpha(\omega)$ is the absorption coefficient considered as a function of frequency and ω_{21} is the angular frequency corresponding to the center of the spectral line. According to the theory, the absorption coefficient can be described by the following expression in the case of collisional (impact) broadening corresponding to the conditions in our experiments[2]:

$$\alpha_{\text{theor}}(\omega)=\frac{4\pi^2\mu^2R}{3\hbar c}\omega G(\omega-\omega_{21})(n_1-n_2), \tag{2}$$

$$G(\omega-\omega_{21})=\left[\pi\nu_c\left[1+\left(\frac{\omega-\omega_{21}}{\nu_c}\right)^2\right]\right]^{-1}, \quad n_i=\frac{N_i}{g_i}, \quad i=1,2, \tag{3}$$

where $\tau=1/\nu_c$ is the average duration of the coherent interaction between molecules and the radiation field. Here, $\mu=1.8546+0.0006\ D$ is the dipole moment of the $H_2{}^{16}O$ molecule[3] and R is the strength of the spectral line, which is a dimensionless quantity of the order of unity and which, in the case of rotational transitions of a rigid asymmetric top, is found from the matrix elements of the direction cosines.[4] The values of R for the investigated transitions are given in Table I; c is the velocity of light and $\hbar$ is the Planck constant.

The form of the theoretical dependence $\alpha_{\text{theor}}(\omega)$ indicates that the experimentally determined absorption coefficient is a function of the type

$$\alpha_{\exp}(\omega)=\frac{\omega}{\omega_{21}}\frac{\alpha}{1+[(\omega-\omega_{21})/\gamma]^2}, \tag{4}$$

where α is the absorption coefficient at it maximum and 2γ is the width of the spectral line at its midamplitude. The integral in Eq. (1) can be calculated; we then have

$$I_{\exp}=\pi\alpha\gamma. \tag{5}$$

On the other hand, the theoretical value I_{theor} of the integrated coefficient can be found by integrating Eq. (2):

$$I_{\text{theor}}=\omega_{21}\sigma(n_1-n_2), \quad \sigma=4\pi^2\mu^2R/3\hbar c, \tag{6}$$

where σ is a quantity of the dimensions of a cross section, composed of the constants representing the mole-

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cule and spectral transition. The values of σ are listed in Table I.

It should be pointed out that the absorption coefficient α_{theor} and the integrated absorption coefficient I_{theor} are proportional to the difference between the number of molecules $n_1 - n_2$ per unit volume in one state of each of the rotational levels and g_i is the degeneracy of a level in respect of the projection of its momentum. Equating Eqs. (5) and (6), we obtain the following expression for the main quantity $n_1 - n_2$ determined in the experiments described below:

$$n_1-n_2=\pi\alpha\gamma/\sigma\omega_{21}. \tag{7}$$

From the experimental point of view, the measurement of the integrated absorption coefficient for a Lorentzian profile reduces to the determination of two parameters α and γ of Eq. (5), which can be found conveniently by plotting a curve of the (4) type through the experimental values $\alpha_{\text{exp}}(\omega)$. The method of analysis of the experimental data and determination of the Lorentzian curve parameters are considered in detail in Ref. 1.

In a theoretical analysis of a nonequilibrium state of a gas the interest lies not in the quantity $n_1 - n_2$ itself but in the relative population difference $n_{12}= (n_1 - n_2)/N$, where N is the total number of molecules per unit volume, so that in experiments one should determine not only I but also find independently the molecular concentration N.

If a gas is in a state of thermal equilibrium at a temperature T, then

$$n_{12}(T)=\frac{g_I}{Q(T)}[\exp(-\varepsilon_1/T)-\exp(-\varepsilon_2/T)], \tag{8}$$

where ε_1 and ε_2 are the energies of the levels; $Q(T)$ is the rotational partition function; g_I is the nuclear-spin degeneracy. In the case of the water molecule with the isotopic composition $H_2{}^{16}O$, the value of $Q(T)$ in the temperature range 150–400° K can conveniently be calculated from[2,5]

$$Q(T)=2(\pi T^3/ABC)^{1/2}, \tag{9}$$

where $A = 27.876 \pm 0.003\ \text{cm}^{-1}$, $B = 14.507 \pm 0.009\ \text{cm}^{-1}$, and $C = 9.288 \pm 0.002\ \text{cm}^{-1}$ are the rotational constants $H_2{}^{16}O$ for the ground vibrational state.[6] In the experiments described below we shall be concerned with transitions between the para-water levels so that $g_I = 1$ (Ref. 2).

In the determination of the integrated absorption coefficient we need to determine the coefficient α at various frequencies as well as to determine the absolute frequency ω of the radiation source. The absolute frequency measurements can be avoided and relative ones can be carried out if calibration measurements of I_0 are made for the same spectral transition in a gas in thermal equilibrium with a known temperature T_0 and molecular concentration N_0. In fact, in the relative measurements of the frequency the quantity $\tilde{I}$ contains an unknown but constant proportionality factor [see Eq. (5)]. The ratio of the integrated absorption coefficients does not conatin this factor:

$$\frac{I}{I_0}=\frac{\alpha\tilde{\gamma}}{\alpha_0\tilde{\gamma}_c}=\frac{n_1-n_2}{N_0 n_{12}(T_0)}. \tag{10}$$

Here, the tilde denotes the line widths and integrated absorption coefficients for relative values of the frequency. Thus, the determination of n_{12} reduces to the measurement for each spectral line of the quantities $\alpha\tilde{\gamma}$, $\alpha_0\tilde{\gamma}_0$, N_0, and T_0 and determination by an independent method of the molecular concentration N in that section of a supersonic stream which is intersected by an electromagnetic wave; $n_{12}(T_0)$ is calculated from Eq. (8). Calibration measurements can be conveninetly carried out for the values of N_0 and T_0 which are the initial parameters of a stream.

TABLE I.

Transition No.	Transition	E_1, cm^{-1}	E_1-E_2, cm^{-1}	R	$\sigma\cdot10^{18}$, cm^2
1	$1_{11}-2_{02}$	37.137	32.951	0.7549	1.0807
2	$2_{02}-2_{11}$	70.088	25.085	2.0752	2.9710
3	$3_{31}-4_{22}$	285.217	30.560	0.1615	0.2312
4	$4_{31}-5_{24}$	383.837	32.365	0.2619	0.3750

EXPERIMENTAL CONDITIONS

We employed a planar supersonic stream of low-density water vapor escaping from an acoustic nozzle into vacuum. The distribution of the gas parameters (the molecular concentration N per unit volume and gas temperature T) in the xy plane was calculated using the known parameters of the initial state of the gas (N_0, T_0). A calculation was made for a steady-state two-dimensional supersonic stream behind an acoustic nozzle; in this calculation use was made of a "natural" coordinate system formed by the lines of flow and normals to these lines.[7,8] In this method the whole flow field was divided into a number of stream tubes and the flow in each tube was determined by solving a one-dimensional problem; theinteraction between the tubes was assumed to occur at their boundaries via the pressure along the normal and via the derivative of the velocity pressure with respect to the opening angle of the tube. This calculation method made it possible to allow for the rotational relaxation of the molecules and homogeneous condensation of the gas in a stream.[8]

The calculations were made for the isentropic flow of a gas with a constant ratio of the specific heats $\varkappa = 1.33$. This value of $\varkappa$ correspond to the hypothesis of rotational equilibrium in the flow of the gas consisting of molecules with three rotational degrees of freedom. Figure 1 shows the dependence of T/T_0 on the coordinate x along the central stream line, and also profiles of T/T_0 along the transverse coordinate y at several distances measured from the edge of a sonic nozzle. The center of a microwave beam was located at a distance $2x/d = 5.5$, where $d = 12$ mm was the height of the throat (see also Fig. 2). The diameter of the microwave beam measured to the $1/e$ intensity was 4 mm (it is shown as a dashed half-cylinder in Fig. 1). At the center of the beam the relevant ratios were T/T_0

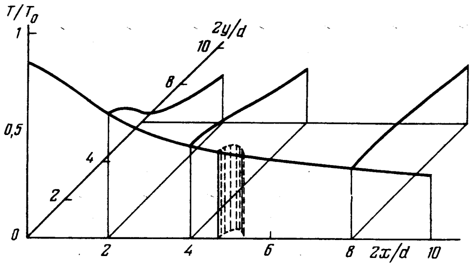

FIG. 1. Temperature distribution in a planar supersonic stream. The x axis coincides with the direction of motion of the gas. The y axis is perpendicular to the plane of symmetry of the stream and the origin is located at the edge of a supersonic nozzle; d is the height of the nozzle throat.

$= 0.4015$ and $N/N_0 = 0.06472$. The inhomogeneity of T/T_0 within the beam did not exceed 8% along the two coordinates.

Since the gas entered a vacuum chamber, where a constant pressure 0.1 Torr was maintained, the supersonic flow occurred in a confined spatial region. Figure 2 shows the boundaries of the stream and the position of the microwave beam relative to the acoustic nozzle. The initial water vapor pressure $P_0 = 4$ Torr was the same in all the experiments. The range of the initial temperatures $T_0 = 20-150°$ C was selected to that the zone of nonequilibrium condensation could be shifted along the stream relative to the point of observation, whose position was kept constant. According to the calculations,[8] at $20° C < T_0 < 50° C$ the point of observation was in the zone of advanced condensation, whereas at $50° C < T_0 < 100° C$ it was in the region of onset of nonequilibrium condensation, and for $T_0 > 100° C$ it was in the region of flow free of condensation.

RESULTS OF MEASUREMENTS

The rotational spectrum of the $H_2{}^{16}O$ molecule can be divided into two systems of levels, one of which corresponds to the total nuclear spin 0 (para modification) and the other to the total spin 1 (ortho modification). Radiative transitions between the levels of different modifications are forbidden by the selection rules.

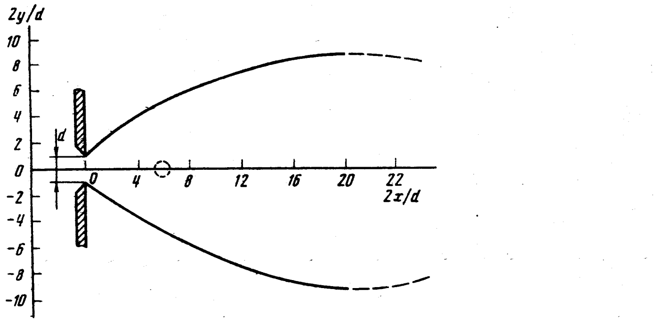

FIG. 2. Schematic representation of the observation conditions. The boundaries of a planar jet are shown up to the region with maximum broadening. The dashed circle identifies the position of the microwave beam.

Measurements of the population difference $n_1 - n_2$ were carried out for four pairs of rotational levels of the para modification (Table I), located both near the ground rotational state of the para modification (transitions 1, 2) and fairly high above the ground state (transitions 3, 4). The energy separation of a pair of rotational levels was approximately the same, ~30 cm^{-1}, so that the transition frequencies were within the same submillimeter spectral range. The results of measurements are plotted in Fig. 3 as the dependences on the initial temperature T_0 of the investigated water vapor. The quantity plotted in this figure is the nonequilibrium coefficient K, defined by

$$K = \frac{n_{12}}{n_{12}(T)} = \frac{\tilde{I}}{\tilde{I}_0}\frac{N_0}{N}\frac{n_{12}(T_0)}{n_{12}(T)}. \tag{11}$$

Equation (11) contains the measured quantity $\tilde{I}/\tilde{I}_0$ and the calculated quantities N/N_0 and $n_{12}(T_0)/n_{12}(T)$, where T and N are the parameters of the stream at the center of the probing microwave beam. The value $K = 1$ corresponds to rotationally equilibrium flow, whereas nonequilibrium flow is characterized by $K \gtrless 1$ and the degree of nonequilibrium is represented by the difference between K and unity. Table II gives the values of K_{exp} for $T_0 = 393°$ K, together with the experimental error; for comparison, this table includes also the values K_{calc} calculated for completely "frozen" flow, when the population of the rotational states is assumed to be constant beginning from the throat section.

DISCUSSION OF RESULTS

1. The values of the nonequilibrium coefficient given in Fig. 3 and Table II indicate that a supersonic stream of rarefied water vapor is strongly nonequilibrium relative to the rotational degrees of freedom of the H_2O molecule. The nonequilibrium population difference is exhibited by the levels high above the ground rotational state and close to this state. The nonequilibrium increases if homogeneous condensation of water vapor

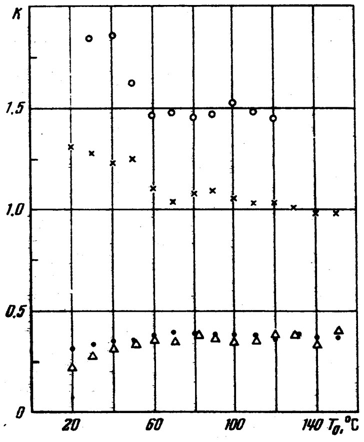

FIG. 3. Nonequilibrium coefficient K plotted as a function of the initial temperature of water vapor: ●) $1_{11}-2_{02}$; △) $2_{02}-2_{11}$; ×) $3_{31}-4_{22}$; ○) $4_{31}-5_{24}$. The value for a rotationally equilibrium stream is $K=1$.

takes place in the stream. To the authors' knowledge, this is the first case in which a considerable rotational nonequilibrium has been observed for supersonic flow of a gas consisting of polyatomic polar molecules of the asymmetric top type. The earlier reports have been concerned with diatomic nonpolar molecules of nitrogen,[9] in which case nonequilibrium is observed for high rotational levels $j=8-12$ in an axisymmetric low-pressure stream, and with linear polar molecules of OCS (Ref. 10), in which case the deviation from equilibrium is observed for lower rotational levels $j=0$, 1, and 2 for a gasdynamic source of a molecular beam.

2. The rotational temperature concept is frequently used in describing rotational nonequilibrium states, i.e., it is assumed that the distribution of molecules over the rotational levels is of the Boltzmann type but the rotational temperature T_r, which is a parameter of the distribution, differs from the gas temperature T. We shall show that in our case the distribution of molecules over the levels is not of the Boltzmann type.

It follows from Eq. (10) that the directly measureable quantity is n_1-n_2. The ratio of the population differences for two transitions can be used, together with Eq. (8), in determining the parameter T_r:

$$\frac{n_1-n_2}{n_1'-n_2'}=\frac{n_{12}(T_r)}{n_{12}'(T_r)}. \tag{12}$$

Figure 4 shows the values of T_r deduced from Eq. (12) for various transitions. For convenience, T_r is reduced to the initial temperature T_0. If the rotational temperature concept had been valid for the observed distribution, the points in the graph would have been grouped along some horizontal line. For example, in the case of equilibrium flow, these point would have been concentrated near the $T_r/T_0=0.4$ lines, whereas in the case of completely "frozen" flow they would have been near the $T_r/T_0=0.9$ line. Since the values of T_r/T_0 are distributed over the range 0.2–0.8, it follows that the rotational temperature concept cannot be introduced. The ratio of Eq. (12) applied to transitions 1 and 2 gives T_r close to the gas temperature.

3. The first proof of nonequilibrium of flow was based essentially on a calculation of the stream parameters T/T_0 and N/N_0 at the point of observation. This calculation was carried out assuming isentropy and equilibrium of the flow, which are, strictly speaking, inapplicable in our case. It is not yet possible to carry out a more general calculation of a rotational nonequilibrium in gasdynamic flow of water vapor because the selection rules have not yet been established for collisional rotational transitions of polar molecules of the asymmetric top type and the rates of elementary processes associated with the rotation of the H_2O molecule are not known for the temperature range below 300° K.

However, the second proof, based on an attempt to introduce the rotational temperature concept, did not rely on these calculations. The inability to describe the observed distribution of the H_2O molecules over the rotational levels by the Boltzmann function is also evidence of nonequilibrium nature of the flow in a supersonic water vapor stream. The formula (2) for the spectroscopic method implies an equiprobable distribution of molecules between the states with different projections of the momentum, and it is assumed that this assumption is obeyed.[2]

Transition	$\varkappa_{exp}$	$\varkappa_{calc}$	Transition	$\varkappa_{exp}$	$\varkappa_{calc}$
$1_{11}-2_{02}$	0.37±0.01	0.198	$3_{31}-4_{22}$	1.03±0.02	0.655
$2_{02}-2_{11}$	0.38±0.01	0.229	$4_{31}-5_{24}$	1.47±0.03	1.060

4. At this stage, the factors responsible for a rotationally nonequilibrium distribution can only be guessed.

The first and simplest hypothesis is that the observed distribution is the result of a transient process which occurs in the course of rapid cooling of water vapor. Since the average separation between the nearest rotational levels of the H_2O molecule in the lower part of the spectrum is $\Delta E \sim 30$ cm^{-1}, i.e., $\Delta E/T \approx 0.1$, then by analogy with hydrogen and deuterium[11] we can expect slow rotational relaxation, particularly at low temperatures in the supersonic part of the stream.

The second assumption is based on the fact that the parameters of water vapor are close to the saturation line and the flow is in condensational nonequilibrium. This means that the concentration of small entities such as dimers or trimers in nonsaturated vapor, and also of larger clusters in supersaturated vapor is less than the equilibrium concentration. The appearance and decay of clusters in which molecules are bound by the hydrogen bond are accompanied by the evolution or absorption of energy $\sim 2\times 10^3$ cm^{-1}, which is much greater than the average translational and rotational energy of a free molecule. In a condensationally nonequilibrium gas there is no equality between the direct processes of particle formation and decay. If we assume that the exchange of energy in the formation and decay occurs not only through the translational degrees of freedom but also involves the rotational degrees, we can then expect rotational nonequilibrium if allowance is made for the finite rotational relaxation rate.

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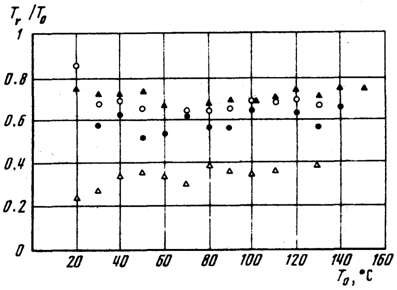

FIG. 4. Rotational temperature plotted as a function of the initial temperature of water vapor for various pairs of rotational transitions: △) $1_{11}-2_{02}$ and $2_{02}-2_{11}$; ●) $3_{31}-4_{22}$ and $4_{31}-5_{24}$; ▲) $1_{11}-2_{02}$ and $3_{31}-4_{22}$; ○) $1_{11}-2_{02}$ and $4_{31}-5_{24}$.

and also for a calculation carried out for a number of initial conditions, and to N. A. Irisova for discussing the problems associated with the performance of experiments.

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Nuclear relaxation in silicon in weak magnetic fields

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Nuclear spin lattice relaxation in silicon in weak magnetic fields was investigated with the aid of optical polarization of ^{29}Si nuclei. It was shown that a reduction in the magnetic field was accompanied by a reduction in the nuclear relaxation time due to an increased contribution of flip-flop and flip-flip transitions during the dipole–dipole interaction between the ^{29}Si nuclei and electrons localized on deep impurity levels, and also as a result of the influence of the local magnetic field due to the ^{29}Si nuclei in the silicon crystal.

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The degree of dynamic polarization of nuclear angular momenta in silicon doped with both deep and shallow donor impurities depends on the strength of the external longitudinal magnetic field in which the optical pumping process takes place, on the ratio of concentrations of the impurities introduced into the crystal, and on the nuclear spin-lattice relaxation time.[1,2] It has been shown[1] that silicon doped with gold and phosphorus, and optically pumped in weak magnetic fields, exhibits an inversion of nuclear magnetization when the magnetic field is varied. This phenomenon is connected with the different type of interaction between ^{29}Si nuclei and the oriented photoexcited electrons trapped in deep (gold) and shallow (phosphorus) donor levels, respectively. When a photoexcited conduction-band electron is trapped in a shallow donor level, its contact interaction with the ^{29}Si nucleus is found to predominate,[3] whereas, if the electron is trapped in a deep level, the dipole-dipole interaction is found to predominate. The dipole-dipole interaction between an electron localized in a deep donor center of the ^{29}Si nucleus then leads to the dynamic polarization of the nuclear angular momenta only in weak fields. This is connected with a particular ratio of the probabilities of flip-flop transitions, i.e., transitions with a mutual reorientation of electron and nuclear spins, and also transitions with a reorientation of only the nuclear spin, which are responsible for the nuclear spin-lattice relaxation, and the flip-flop transitions, i.e., transitions with simultaneous reorientation of both nuclear and electron spins.

By varying the longitudinal magnetic field, it may be possible to separate the contact and dipole-dipole interaction between the ^{29}Si nuclei and electrons localized in deep and shallow donor centers. In order to elucidate the phenomenon of inversion of nuclear magnetization, we must consider nuclear relaxation processes in weak magnetic fields. However the nuclear relaxation time is exceptionally difficult to measure under equilibrium conditions in the absence of illumination because the NMR signals characterizing the magnetization in the field are too weak. On the other hand, when silicon is illuminated with circularly polarized light, the degree of polarization of the ^{29}Si nuclei increases by several orders of magnitude, so that the nuclear relaxation processes can be investigated even in very weak magnetic fields.

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