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NONEQUILIBRIUM ROTATIONAL DISTRIBUTION FUNCTION FOR D_2O MOLECULES IN A RAREFIED SUPERSONIC JET

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An ever increasing interest in the study of rotational relaxation of polar molecules in a gaseous medium has recently been observed. For example, chemical lasers have elicited a series of theoretical and experimental papers on the rotational relaxation of HF molecules [1, 2]. For polyatomic molecules there also exist interesting and important problems, the solution of which requires an understanding of the laws of rotational relaxation. They include the behavior of water vapor in the upper layers of the atmosphere, the creation of gas-dynamic lasers (GDL) based on rotational transitions of molecules in the submillimeter range, clarification of the mechanism of action of masers, etc. The complexity of the rotational spectra of polyatomic molecules hinders the theoretical description of relaxation processes and the interpretation of experimental results, so that there are far fewer papers on rotational relaxation of polyatomic molecules than for diatomic molecules. There now exist models permitting a satisfactory description of the processes connected with rotational relaxation of molecules, such as the Polany—Woodall model [3]. There is an absence of such simple and convenient models for polyatomic molecules of the asymmetric-top type.

Rotational relaxation of the D_2O molecule in a rarefied supersonic argon jet was investigated in the present work. This was done earlier for diatomic, polyatomic, and linear molecules and molecules of the symmetric-top type [4, 5], while for molecules of the asymmetric-top type it is being done for the first time. The purpose of the work was to investigate the nonequilibrium distribution of molecules over the rotational levels during rapid cooling in a supersonic argon jet by the spectroscopic method and to construct a simple model permitting a satisfactory description of the populations of the rotational levels.

As the subject of observation we used a plane, supersonic argon jet with a small (less than 1%) admixture of D_2O vapor (Fig. 1). At such a concentration one can assume that relaxation takes place mainly due to D_2O—Ar collisions, and neglect D_2O—D_2O collisions. The difference in the populations of rotational levels connected with a radiative transition was measured by the method of submillimeter spectroscopy. A backward-wave tube (BWT) served as the radiation source. The probe beam was formed with Teflon lenses L_1 and L_2, passed through a polaroid P and a modulator M, intersected the jet, confined by Teflon walls, and was picked up by a gallium receiver through the lens L_3.

The initial gas pressure and temperature were 266 Pa and 293°K, respectively. The parameters of gas flow in the supersonic region were calculated by Skovorodko by the method of natural coordinates described in [6] for the case of the flow of a monatomic gas from a plane slot with a height of 0.72 cm. The calculated gas temperature in the measurement region was 65 ± 5°K. Conformity between the calculated and actual parameters of the gas stream was verified by measuring the pressure with a Pitot tube. The departure of the measured from the calculated pressure was 4% for the central streamline.

Teflon walls were set up to avoid expansion along the coordinate parallel to the slot. Boundary layers developed in the gas flow at the walls, and absorption in them could result in errors in the measurements. However, the temperature in the boundary layer is close to the stagnation temperature, and hence five times higher than the temperature of the main stream, so that the density in it is five times lower. The measurements were made for low rotational transitions, for which absorption decreases strongly with an increase in tempera-

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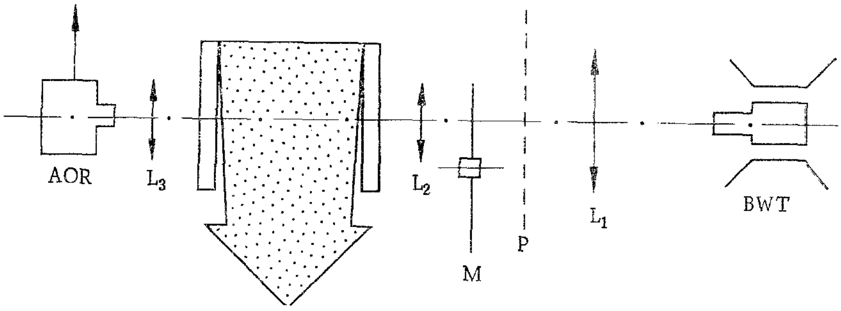

Fig. 1

ture. For these reasons absorption in the boundary layer does not exceed 1-2% for the absorption in the core of the supersonic jet.

Let us examine the diagram of the lower rotational levels of D_2O (Fig. 2). D_2O molecules can have a total spin of zero, one, or two. Molecules having an even nuclear spin comprise the para variant and those with an odd spin comprise the ortho variant. Collisional and radiative transitions between the different variants are forbidden with a high degree of accuracy. Therefore, for the majority of experimental situations the para and ortho systems can be treated as independent. The rotational levels of the D_2O para systems for which the measurements were made are shown in Fig. 2. The wave functions of the para variant of D_2O are transformed in accordance with irreducible representations A and B_1 of the D_2 group if the Oz' axis of the moving coordinate system is directed along the axis of symmetry of the D_2O molecule. In the quantization of an asymmetric top a division into (+) and (−) functions arises. Upon a reflection in a plane passing through the Oz' axis of the moving coordinate system the (+) functions do not change while the (−) functions change sign [7].

We recall that in molecular spectroscopy there is a division of levels into positive and negative, depending on whether the wave function changes sign upon an inversion of the coordinate system. To avoid confusion, we introduce the indices σ_+ and σ_- for the (+) and (−) functions, respectively.

In the tests we measured the integral absorption for the transitions indicated by arrows in Fig. 2. The integral absorption is proportional to the population difference Δn. For the conditions under which the observation was made we can calculate the equilibrium integral absorption, which is proportional to the equilibrium population difference Δn_e. The ratio of the measured to the equilibrium absorption will be $\Delta n/\Delta n_e$. These ratios are given in Table 1. Attempts to describe the experimental results on measuring the integral absorption using a Boltzmann distribution with any temperature met with failure. This is clearly seen from a comparison of the results for the transitions 3_{13}—3_{22} and 3_{22}—4_{13}, having the common level 3_{22}. We have a population difference from equilibrium of 0.35 for the first and 1.9 for the second, which is impossible for any positive temperature. This can be explained by the accumulation of particles at the 3_{22} level, which is connected with certain selection rules for collisional transitions, while the selection rules are connected with the symmetry of the shape of the molecule and the potential of the interaction of a molecule with an atom. It is convenient to write the potential in the form of an expansion in Wigner D functions. It turns out that terms of type A with an even index J' to the function $D^{J'}_{KM}$ and of type B_1 with an odd index alternate in the potential of the interaction of D_2O with an atom [8]. In [9] it was shown that terms of the potential of type A give rise to transitions with an even ΔJ

TABLE 1

Transition	1_{11}—2_{02}	2_{02}—2_{11}	2_{11}—2_{20}	3_{13}—3_{22}	4_{04}—4_{13}	4_{13}—4_{22}	3_{22}—4_{13}	3_{31}—4_{22}	4_{31}—5_{24}
Experiment	0,34	0,65	0,41	0,35	1,35	0,9	1,9	1,47	2,1
Calculation	0,54	0,60	0,39	0,34	1,35	0,91	1,41	1,87	3,95

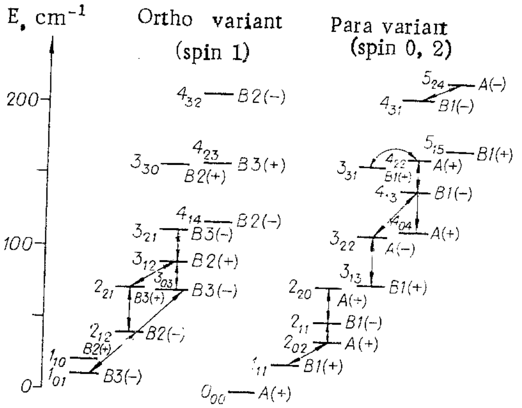

Fig. 2

while terms of type B_1 give rise to transitions with an odd ΔJ (ΔJ is the change in the total angular momentum of the molecule), and that group theory gives the following selection rules: $A \leftrightarrow A$ and $B_1 \leftrightarrow B_1$ for a potential of type A and $A \leftrightarrow B_1$ for a potential of type B_1. The combination of these rules with the parity selection rules leads to the fact that transitions between σ_+ and σ_- levels in collisions are forbidden.

For the interpretation of the nonequilibrium distribution we constructed a kinetic model of level-by-level rotational relaxation, based on the following assumptions.

1. Rotational relaxation in the σ_+ and σ_- systems takes place independently.

2. Within each system the probability of collisional transitions is given by the Polany–Woodall formula [3]

$$P_{ij} = C(2J + 1) \exp [-(D/kT)\Delta E_{ij}],$$

where C and D are constants; ΔE_{ij} is the energy gap between the levels; J is the total angular momentum of the upper level. The quantities C and D were assumed to be different for potentials of types A and B_1 and were denoted by the indices A and B_1, respectively. The probabilities of the reverse transitions were found from the principle of detailed equilibrium.

3. Slow collisional relaxation between the σ_+ and σ_- systems was described by the relaxation equation

$$dN^+/dt = -(N^+ - N_e^+)/\tau,$$

where $N^\pm$ is the total number of particles in the σ_+ and σ_- systems (the index e refers to equilibrium conditions); τ is the time of relaxation between the σ_+ and σ_- systems.

4. Rotational relaxation of a molecule of water, which is in the jet in the form of a small admixture, takes place in a gas in equilibrium with respect to translational degrees of freedom with a certain temperature T at each point of the flow. The temperature T is determined by calculation for a free two-dimensional jet of a monatomic gas [6]. It is assumed that the rotational energy of the D_2O molecule does not affect the gasdynamic parameters.

Since the probability of transitions without a change in J, due to the spherically symmetric term of the potential of the interaction of an atomic particle with a D_2O molecule, must dominate over the probabilities of other transitions, a coefficient α was introduced into the program. The coefficient α showed how many times greater is the probability of a transition with $\Delta J = 0$ than a transition with $\Delta J \neq 0$ for the same energy gap.

The system of kinetic equations was solved numerically in the section of gas flow from the critical cross section to the observation point for the 27 lowest levels of the D_2O para system. The parameters C, D, τ, and α were chosen from best agreement with the values of $\Delta n/\Delta n_e$.

Only the first seven values of $\Delta n/\Delta n_e$ were used in the search for the parameters. The data for the transitions 3_{31}–4_{22} and 4_{31}–5_{24} were excluded as insufficiently precise.

In Table 1 we present the experimental and calculated $\Delta n/\Delta n_e$ data for the following optimum parameters: $C_A = 1.5 \cdot 10^5$ Pa$^{-1}\cdot$sec^{-1}, $C_{B_1} = 1.1 \cdot 10^5$ Pa$^{-1}\cdot$sec^{-1}, $D_A = 5.8$, $D_{B_1} = 6.6$, $\tau^{-1} = 6.7 \cdot 10^2$ sec^{-1}, $\alpha = 5$.

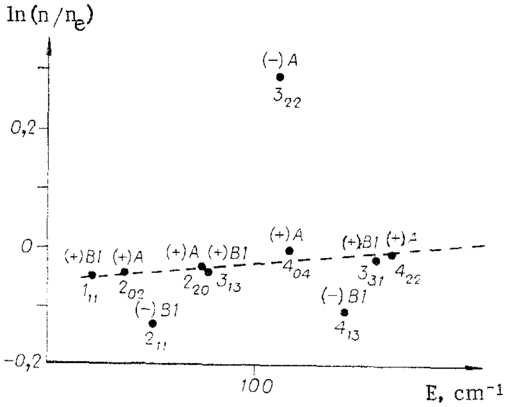

Fig. 3

If we compare the quantities C and D with the analogous quantities for a diatomic molecule, we find that they have close values. For example, if we write the relaxation rate for HF from [1] in the form of the Polany—Woodall formula, we obtain $C = 0.75 \cdot 10^5$ $Pa^{-1} \cdot sec^{-1}$ and $D = 5.8$.

The distribution function for the lower rotational levels can be reconstructed using the measured population differences. The dependence of ln (n/n_e) on the energies of the rotational levels is shown in Fig. 3. Here n is the experimentally determined population of the rotational level; n_e is the equilibrium population for the temperature 95°K; the points on the graph correspond to the rotational levels determined, the spectroscopic designations of which are given next to the points; the type of wave function of the level and its affiliation to the σ_+ and σ_- subsystems are also given. It is obvious that no definite rotational temperature can be ascribed to the distribution obtained, which is expressed in the absence of a linear energy dependence of ln (n/n_e). The fact that for all the levels of the σ_+ system the experimental points lie on a straight line corresponding to the temperature $T \approx 95$°K is interesting. This means that the lowest points of the σ_+ system can be described by a Boltzmann distribution with a temperature somewhat higher than the gas temperature. The populations of the levels of the σ_- system display no regularity. The difference in the behavior of the σ_+ and σ_- systems can be explained by the fact that the density of levels is almost twice as high in the σ_+ systems as in the σ_- system. The energy gap between the 2_{11}—3_{22} levels is twice as large as that between the 3_{22}—4_{13} levels which, with the strong exponential dependence of the transition probability on the energy difference, leads to the fact that at low temperatures the relative populations of the 3_{22}—4_{13} levels will be far closer to equilibrium than for 2_{11}—3_{22} levels. The relative populations of the 3_{22} and 4_{13} levels will also be closer to equilibrium than for the σ_+ system, since they are practically isolated, whereas in the σ_+ system there are seven closely spaced levels.

With a decrease in the gas temperature in the σ_+ system the molecules should accumulate at the 0_{00} level, while in the σ_- system they should accumulate at the 2_{11} level, but because of the low probability of the collisional transition 2_{11}—3_{22} at a low temperature they accumulate at the 3_{22} level.

Besides the low gas temperature, there may be one more factor causing the accumulation of particles at the 3_{22} level. If the predominant forces of the interaction of a molecule with an atom are dispersion forces, then collisional transitions with an even ΔJ predominate over transitions with an odd ΔJ. Within the σ_+ and σ_- systems one can isolate groups of levels with even and with odd J, which can be taken approximately as independent. The 3_{22} level is the lowest in one of these groups, and particles should accumulate at it upon rapid decrease in the gas temperature.

The model on the basis of which the calculations were made is approximate, since the Polany—Woodall formula was written for a system of rotational levels of a diatomic molecule. Moreover, a departure from the exponential dependence which is embedded in the Polany—Woodall formula was recently discovered [2]. However, the model is sufficiently simple and enables one to obtain satisfactory agreement with experiment and qualitatively predict new results. For example, for the 3_{31}—4_{22} and 4_{31}—5_{24} transitions, which were not included in the program of search for constants, the model gives qualitatively correct values of the integral absorption.

TABLE 2

Transition	$1_{11}-2_{02}$	$2_{02}-2_{11}$	$2_{11}-2_{20}$	$3_{13}-3_{22}$	$4_{04}-4_{13}$	$4_{13}-4_{22}$	$3_{22}-4_{13}$
Experiment	0,54	0,51	0,48	0,51	1,2	1,2	1,3
Calculation	0,54	0,52	0,53	0,32	1,18	1,33	1,28

Measurements of absorption similar to those described above were also made for higher concentrations of D_2O in the D_2O–Ar mixture. In this case we investigated the influence of the Ar pressure on the character of the nonequilibrium up to those pressures at which the distribution is fully in equilibrium. The Ar stagnation pressure was varied from 267 to 1066 Pa while the D_2O stagnation pressure equalled 20 Pa. It was found that such an admixture of D_2O vapor is sufficient to alter the form of the distribution.

The dipole–dipole interaction potential plays the main role for D_2O–D_2O collisions. This potential has a symmetry different from the symmetry of the D_2O–Ar potential and, as shown in [10], the following selection rules are valid for it: $\Delta J = 0, 1$, $A \leftrightarrow B_1$, transitions between σ_+ and σ_- states are not forbidden for it.

The influence of the potential of the dipole–dipole interaction on the relaxation can be taken into account if a correction with allowance for the corresponding selection rules is introduced into the model obtained earlier. Just as before, the correction had the form of the dependence of [1] with the parameters $C = 1.9 \cdot 10^5$ $Pa^{-1} \cdot sec^{-1}$ and $B = 6$. A comparison of the experimental results with the calculations is presented in Table 2.

The dependence of $\ln(n/n_e)$ on the energy of the level can be constructed just as above (Fig. 4). The equilibrium population for the comparison with the dependence at low concentrations also corresponds to 95°K.

D_2O vapor at a concentration of 7.5% alters the gasdynamic properties of the supersonic jet insignificantly, with the adiabatic constant changing from 1.67 to 1.64 and the equilibrium gas temperature at the measurement point increasing from 65 to 68°K.

However, it is seen from Fig. 4 that the temperature of the σ_+ system becomes 84°K, i.e., considerably closer to equilibrium. In this case the points of the σ_- system approach the points of the σ_+ system. Consequently, a relatively small admixture of D_2O considerably accelerates the relaxation. However, a single rotational temperature is absent, as before, and this can be verified as follows: By determining the rotational temperature from the ratio of the integral absorption for different transitions (as in [11]), we find that they differ for different pairs of levels. The dependence of the rotational temperatures on the argon pressure is shown in Fig. 5: points 1) 3_{13}–3_{22} and 3_{22}–4_{13}; 2) 2_{11}–2_{20} and 4_{04}–4_{13}; 3) 2_{02}–2_{11} and 2_{11}–2_{20}. As seen from Fig. 5, for the transitions 3_{13}–3_{22} and 3_{22}–4_{13} the rotational temperature goes to infinity for low pressures and becomes negative for 267 Pa. At pressures of about 1066 Pa the temperature is close to the equilibrium gas temperature for all the transitions.

Here the rotational temperatures for pairs of levels lying within the limits of 1 J prove to be close to the equilibrium temperature for any pressures (see Fig. 5). This evidently

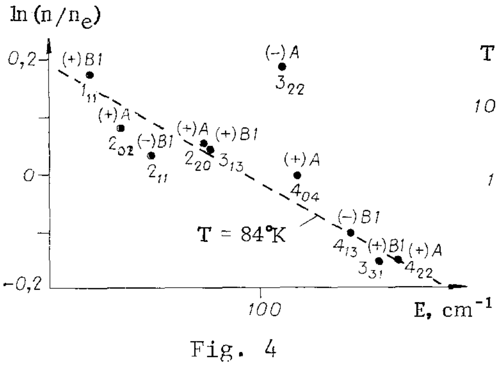

Fig. 4

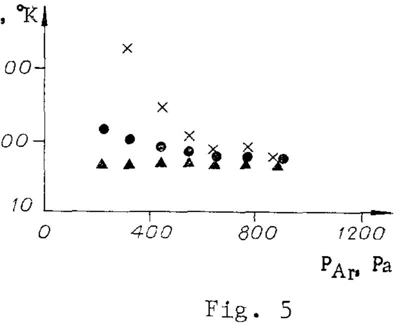

Fig. 5

TABLE 3

Transition	$2_{02}-2_{11}$	$1_{11}-2_{02}$
Experiment	0,2	0,13
Calculation	0,35	0,1

indicates the high probability of transitions due to the dipole—dipole interaction for ΔJ = 0.

It is interesting to demonstrate the possibility of applying the kinetic model for rotational relaxation obtained in this paper under other experimental conditions.

As mentioned above, supersonic gas streams provide a unique possibility for obtaining and investigating gaseous media at low temperatures. The states of a gaseous medium which develop in supersonic jets are nonequilibrium with respect to one or another parameter, as a rule. In particular, an argon jet with an admixture of D_2O molecules is nonequilibrium with respect to rotational levels of the molecules.

An experiment on measuring the time of relaxation of the population difference for the 1_{11}—2_{02} and 2_{02}—2_{11} transitions was set up in [12] under just the conditions of considerable rotational nonequilibrium of the molecular component of the gas mixture. The measurements were made by the saturation method under the conditions of a supersonic gas stream. The initial pressures of the components of the mixture were from 267 to 1066 Pa for argon and 20 Pa for D_2O, and the gas temperature of the mixture at the measurement point was 57°K. In these experiments it is important that the rate of change of the gasdynamic parameters, and hence the rate of change of the nonequilibrium distribution function, is considerably less than the relaxation rate upon a local departure from the nonequilibrium distribution function due to the action of saturating radiation. The nonequilibrium distribution function plays the role of the limit which the level population approaches after the action of the saturating radiation ends.

The time T_1 of relaxation of the populations under conditions corresponding to the experimental conditions of [12] can be calculated using the kinetic model. For this we solved the system of kinetic equations in the section of flow from the critical cross section to the observation point, as a result of which we obtained the nonequilibrium distribution function over the rotational levels. Then at the observation point we modeled 100% saturation, i.e., the populations of the pair of levels of the corresponding transition were equated. The subsequent solution of the system of kinetic equations downstream from the observation point showed that the difference in the populations of these transitions relaxes from zero to the value that would have occurred in the absence of saturating radiation. The time dependence of the relaxation was close to exponential with the characteristic relaxation time T_1. The relaxation times calculated in this way were compared with the experimentally determined times in [12] (Table 3).

This kinetic model was also used for numerical modeling of experiments on stationary saturation of the 2_{11}—2_{20}, 2_{02}—2_{11}, and 1_{11}—2_{02} rotational transitions of the D_2O molecule at room temperature for a stationary gas. Experimental values of T_1^{-1} as a function of the argon concentration in the D_2O—Ar mixture are presented in [13]. Theoretical curves obtained using this model are also presented there. The good agreement between the experimental and theoretical values indicates the possibility of using the kinetic model to calculate rotational relaxation at room temperature also.

The parameters C, D, τ, and α in the kinetic model of rotational relaxation were determined from experimental results obtained for the para system of the D_2O molecule. The rotational spectrum in the ortho system is somewhat different: The σ_+ and σ_- subsystems have about the same structure and the lower levels of the σ_+ and σ_- subsystems are located close to each other (see Fig. 2). Therefore, it is not obvious in advance that the kinetic model with parameters taken for the para system will also be applicable for the ortho system.

We used the kinetic model to calculate the values of $\Delta n/\Delta n_e$ in a supersonic gas stream for six pairs of lower rotational levels of the ortho system of the D_2O molecule (see Fig. 2, where the investigated transitions are indicated by arrows). For an experimental test of the calculated results we measured the values of $\Delta n/\Delta n_e$ by the method presented above for the same spectral transitions. The experimental and calculated values of $\Delta n/\Delta n_e$ are presented in Table

TABLE 4

Transition	$1_{01}-2_{12}$	$2_{12}-3_{03}$	$2_{12}-2_{21}$	$2_{21}-3_{12}$	$3_{03}-3_{12}$	$3_{12}-3_{21}$
Experiment	0,46	0,69	0,58	0,97	0,59	0,42
Calculation	0,46	0,55	0,50	0,88	0,68	0,50

TABLE 5

Transition	$1_{01}-2_{12}$	$2_{12}-3_{03}$	$2_{12}-2_{21}$	$2_{21}-3_{12}$	$3_{03}-3_{12}$	$3_{12}-3_{21}$
Experiment	0,44	0,56	0,35	1,0	0,52	0,54
Calculation	0,46	0,53	0,49	0,89	0,71	0,52

4 (the case of low D_2O concentrations) and in Table 5 (the case of high concentrations). The agreement between the calculated results and the experimental data with good accuracy allows us to conclude that the predictions given by the kinetic model for the ortho system of the D_2O molecule also have a good degree of reliability.

In the present work the D_2O molecule was chosen for investigation to facilitate experimental measurements using a BWT. The rotational spectrum of the D_2O molecule is almost completely similar to the spectrum of the H_2O molecule but is compressed in frequency compared with it, as a result of which a large number of spectral transitions fall in the region opened up by BWT spectroscopy. The similar arrangement of spectral levels in the rotational spectra of the D_2O and H_2O molecules and the coincidence of their multipole moments with high accuracy allow us to assume that the given kinetic model is also applicable for the calculation of processes of rotational relaxation of the water molecule.

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