Spectroscopy of vapors of low-volatility compounds supercooled in a supersonic stream

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A pressing problem for molecular spectroscopy and related methods of study of the molecular structure of molecules, and also for the development of gasdynamic lasers, is that of obtaining low-volatility compounds in a gaseous phase at translational and rotational temperatures near absolute zero and with densities sufficient for recording the spectra. It is demonstrated that the conditions for such deep supercooling can be produced in a supersonic flow. Three systems are considered. In the first, supercooling occurs on supersonic escape of pure vapor from a furnace or shock tube. In the second, the vapor escapes together with an inert gas. In the third (proposed by us), the vapor diffuses into the boundary layer of a supersonic flow of a cold inert gas through a porous wall of the furnace parallel to the flow. With respect to its parameters the third system is the most promising. The method may also be applied in investigations of inorganic polymer molecules and of compounds with inert gases. From the viewpoint of gasdynamics, the method opens new opportunities for diagnostics of supersonic flows.

At the present time, the principal methods used to investigate the molecular composition of low-temperature plasma and vapors of nonvolatile compounds are spectroscopy (optical, microwave, and photoelectronic), mass spectrometry, and electron diffraction. However, the development of these methods has been hindered in many respects by the following circumstance. At high temperatures (1000—3000°C), the only ones at which many molecules can exist, the populations of their excited states (rotational and vibrational) become increased at the expense of the low-lying states. As a result, an appreciable increase takes place in the number of observed spectral transitions. The rotational structure of each band broadens, and the maximum of its intensity is lowered and shifts towards larger quantum numbers. Simultaneously, an increase takes place in the Doppler width of the rotational-structure lines, and this results in a decrease in their intensity at the maximum. Thus, the structure of the spectrum becomes so much more complicated and overlapping that its interpretation for the purpose of obtaining information on the system of the energy states of the molecule and its structure becomes extremely difficult and frequently even impossible. The difficulties becomes aggravated with increasing number of atoms and with increasing molecular weight of the molecules.

A way out of the resulting situation is theoretically clear: it is necessary to lower the population of the excited states of the molecules by supercooling the plasma or the vapor to 10—50°K, in such a way that the molecules do not associate and no essential change takes place in the composition of the gas phase. In spectroscopy, so far, the problem of reducing the rotational and vibrational structures of the spectrum has been solved only partially. For example, the investigated molecules are obtained from volatile compounds as unstable intermediate products by electric discharges at low pressure or by pulsed photolysis. The freezing of the investigated molecules in a crystal lattice of inert gases at 4—20°K has uncovered new possibilities for investigating the vibrational and electronic spectra of the molecules. However, this method does not solve the problem of determining all the energy states of the free molecules, since the intermolecular interaction results in a loss of information on the rotation of the molecules, and the geometry of the molecule can become strongly distorted. To deactivate the excited electronic states and to decrease the Doppler width of the spectral lines, one uses sometimes molecular beams, but in these beams the relaxation of the vibrational and rotational states is extremely small. Thus, it is necessary to have new and more effective methods of reducing the vibrational and rotational structures of the spectra and at the same time decreasing the line width.

In 1969, Milne and Greene[1,2] pointed out the possibility of using the well-known phenomenon of supercooling of gases and vapors in supersonic streams for spectroscopic investigations. This method, however, has not been considered in detail anywhere. It is necessary to realize the principal idea and develop it methodologically. We consider below three methods of supercooling gases and vapors in supersonic streams for the purpose of spectroscopic study.

It must be emphasized that the problem is not limited to structure investigations with the aid of spectroscopy, electron diffraction, or mass spectrometry. It is also directly connected with problems of practical importance in gas dynamics and gas-dynamic lasers. In particular, study of the spectral distribution of the intensity in molecular bands will make it possible to determine the vibrational and rotational temperature distributions, and also the concentrations of different components over the zones of a supersonic stream.

1. SUPERCOOLING OF A VAPOR IN SUPERSONIC OUT FLOW

In principal, the simplest method of supercooling is based on the escape of vapor (in this section we do not distinguish between gas and vapor) through a nozzle or an orifice with a diameter larger than the effusion diameter into a region with sufficiently low pressure. The source of the vapor can be an oven or a shock tube. The vapor is cooled as a result of the conversion of the thermal energy into translational energy of the stream. If we neglect the friction of the vapor against the wall and possible chemical reactions, this process can be regarded as adiabatic. Then the stream parameters are connected by the relation[3,4]

$$\frac{T_0}{T}=\left(\frac{p_0}{p}\right)^{(\gamma-1)/\gamma}=\left(\frac{n_0}{n}\right)^{\gamma-1}=\frac{\gamma-1}{2}M^2+1. \qquad (1)$$

Here T is the temperature, p is the pressure, n is the number of molecules per cm^2, $\gamma \equiv c_p/c_v$ is the ratio of the specific heats, M is the Mach number, which is equal to the ratio of the stream velocity and the sound velocity in the given zone of the stream, and the subscript zero pertains to the initial parameters.

Reduction of the rotational and translational temperatures of gases to a few degrees Kelvin has been obtained in several experiments with supersonic streams. The corresponding published data are given in Table I. The translational temperature T_{trans} was determined with the aid of a time-of-flight mass spectrometer, and the rotational temperature T_{rot} from the rotational structure of the spectrum excited by an electron beam. Table I illustrates the dependence of the state of the gas or vapor in the stream on T_0, p_0, and d_{cr} (d_{cr} is the so-called critical diameter of the orifice or the minimal diameter of the nozzle).

There exist, however, factors that limit the possibility of attaining low temperatures in supersonic streams. Foremost for this method is the phenomenon of "freezing," when the vapor density drops during the course of expansion to such an extent that the collisions between the molecules practically cease, and the decrease of n and p is no longer accompanied by a decrease of T and an increase of M, i.e., relation (1) ceases to hold. In[8] they obtained a semiempirical formula for the frozen value of M in a free jet (a free jet is a stream that escapes from an orifice and is not bounded by the walls of a nozzle). For convenience we write this relation in the form

$$M_{\text{fr}}=B[p_0 d_{\text{cr}}/\Lambda(T_0,\ p=1)]^{\alpha}, \qquad (2)$$

where Λ is the mean free path of the molecules and B and α are constants that depend on the substance and on the range of values of T_0.

TABLE I. Temperature and degree of condensation in supersonic streams of gases and vapors (published data).

Case No.	Gas or vapor	Initial conditions			Method of observation and reference	Results of observations		
		T_0, °K	p_0, atm	d_{cr}, mm		T_{trans}, °K	T_{rot}, °K	Products and degree of condensation
1	Ar	300	5	0.10	ms [5]			$Ar_2 : Ar = 0.06$
2	Ar	300	2	0.01	ms [5]			$Ar_2 : Ar = 0.007$
3	N_2	300	~0.02	25.4	s [6]	28.8 *	34.5	None noted.
4	N_2	300	~0.20	25.4	s [6]	5.15 *	8.7	None noted
5	N_2	300	$p_0 d_{\text{cr}} = 15$ Torr-mm		s, tof c [7]	30	40	None noted
6	N_2	300	$p_0 d_{\text{cr}} = 480$ Torr-mm		s, tof [7,8]	7	10	None noted
7	N_2	300	0.13	5	s, [9]		10	None noted
8	N_2	78	0.105	0.42	to [10]			$N_2 : (N_2)_x = 0.43$, $x = 160$
9	N_2	78	0.92	0.42	to [10]			$N_2 : (N_2)_x = 0.0015$, $x = 6500$
10	Xe	300	0.53	0.2	e [11]			70% Xe_2
11	CO_2	300	1	0.23	to [5]			$(CO_2)_2 : CO_2 = 0.01$
12	CO_2	295	$\leqslant 0.13$	0.59	tof [12]	60	60 *	Condenses at $p > 0.08$
13	UF_6	295	$\leqslant 0.13$	0.59	tof [12]	160		Does not condense
14	SF_6	300		0.01	to [13]			Does not condense
15	Rb	+100 **	0.033	0.15	to [14]			4% Rb_2
16	Rb	+100 **	0.4	0.15	to [14]			26% Rb_2
17	Cs	+150 **	0.13	0.06	to [14]			6% Cs_2
18	Cs	+150 **	0.13	0.11	to [14]			10% Cs_2
19	Cs	+70 **	0.13	0.11	to [14]			16% Cs_2
20	Zn	925	0.013 – 0.04	0.2	to [15]			Does not condense

*The temperature was estimated from other parameters of the stream.

**This is the amount by which the nozzle is superheated relative to the evaporator, whose temperature determines p_0.

Note: Observation methods: ms – mass spectroscopic, tof – time-of-flight mass spectral, s – spectrum excited by electron beam, e – electron diffraction method.

For different degrees of freedom of the molecules to become relaxed, it is necessary to have different numbers of intermolecular collisions N. For relaxation of oscillations, N is usually very large, on the order of 10^3 and more[16]. The first to be frozen is therefore the vibrational temperature T_{vib}. For example, Rebrov and Sharafutdinov[17] investigated the escape of CO_2 ($d_{\text{cr}} = 0.96$ mm, $p_0 = 490$ Torr). At $T_0 = 1200$°K, the vibrational temperature freezes at the level $T_{\text{vib}} = 980$°K.

Gordon et al.[14], investigating the association (molecule formation) of alkali metals in supersonic escape of vapor (cases 15–19 of Table I) assumed that practically the entire association energy remains in the form of the vibrational energy of the molecules, where $T_{\text{vib}} \sim 3000$°K. Hagen and Henkes[12] observed that escape of UF_6 (case 13 of Table I) at $p_0 = 0.4$ Torr occurs almost without vibrational relaxation, whereas at $p_0 = 80$ Torr the escape is accompanied by practically complete relaxation of the vibrational energy, and this energy is quite high: even at room temperature it amounts to almost half the internal energy of the gas.

In our subsequent estimates we shall not take into account the vibrational energy of the molecules, i.e., we assume $\gamma = 7/5$ for diatomic or linear polyatomic molecules, and $\gamma = 8/6$ for nonlinear polyatomic molecules. It should be remembered, however, that when vibrations are taken into account γ approaches unity, i.e., a given ratio T_0/T corresponds to larger values of p_0/p, n_0/n, and M. For monatomic gases, as is well known, $\gamma = 5/3$.

Rotational relaxation usually calls for 5–10 collisions, as many as or barely more than translational relaxation[18-20]. Therefore rotational freezing sets in only slightly ahead of the translational freezing, as seen from Table I (cases 3–6). There is a known[21] relation between the Mach numbers corresponding to rotational and translational freezing in a free jet:

$$\frac{M_{\text{trans fr}}}{M_{\text{rot fr}}}\approx\left[\left(\frac{\gamma-1}{{}^{2}/_{3}}\right)^{3/4}\left(\frac{\gamma}{{}^{5}/_{3}}\right)^{2/3}\frac{N_{\text{rot}}}{{}^{5}/_{4}}\right]^{6/11}, \qquad (3)$$

where γ takes the rotation into account, and n_{rot} is the number of collisions necessary for rotational relaxation.

Let us proceed to estimate the parameters of the system. They are determined by the temperature T_0 of the initial vapor, the temperature T which we wish to attain for the spectral investigation of the vapor, and a vapor density n sufficient for their spectral investigation at the temperature T. We assume here $T_0 = 1300$°K, $T_{\text{rot}} = 20$°K, and $n = 10^{14}\ \text{cm}^{-3}$. The initial data for the choice of these quantities are given in Sec. 4.

From relation (1) we obtain M, and then from the condition $M_{\text{rot.fr}} \geq M$ we calculate with the aid of formula (2) the lower limit of the value of $p_0 d_{\text{cr}}$, if we know the corresponding values of B and α. There are very few such data in the literature. For helium, argon ($\gamma = 5/3$) and methane ($\gamma = 8/6$), the values of B and α were obtained in[8], but only as applied to translational freezing. For methane it is therefore necessary first to change from $M_{\text{rot.fr}}$ to $M_{\text{trans.fr}}$ with the aid of formula (3). In addition to these gases, there are also data on nitrogen ($\gamma = 7/5$)[21], namely the dependence of $M_{rot.fr}$ on p_0d_{cr} but only for $T_0 = 300°K$ and $M_{rot.fr} \leq 13$, so that our extrapolation will be very crude. The calculated values of p_0d_{cr} are 4.9×10^{-2}, 3.6×10^{-1}, 60 and 150 atm-mm for He, Ar, N_2, and Ch_4, respectively. We see from these results that at reasonable values of d_{cr} (~1 mm), an acceptable value of p_0 is obtained only for a monatomic gas. Thus, deep supercooling of polyatomic vapors by this method calls for values of p_0 which are completely unattainable for compounds with variable volatility.

The use of the considered method is also restricted by the association of the molecules in the vapor. We shall discuss this in greater detail in the next section. We note for the time being that, according to Table I, the association is small only in those cases when the vapor in the initial state is very far from saturated (cases 1–7 and 11–15). In the very same cases, when the vapor is close to saturated, several dozen percent or even practically all the molecules become associated (cases 8–10, 16, 18, 19). Thus, this method is suitable in practice only for relatively small supercoolings of the vapor. Notice should be taken, to be sure, of one other important advantage of this method, namely, to produce low pressure in a volume into which a supersonic stream escapes one can use cryogenic evacuation with the aid of liquid nitrogen. This simplifies the system greatly in comparison with the two other methods which will be considered later on.

2. SUPERCOOLING OF A VAPOR IN SIMULTANEOUS ESCAPE OF AN INERT GAS AND VAPORS OF LOW-VOLATILITY COMPOUNDS

It is clear from the foregoing analysis of the supersonic streams that only monatomic gases, owing to the high value of γ, make it possible to lower the temperature by a factor of several times 10 at a moderate initial pressure p_0. If a monatomic gas contains a small amount of the vapor of a low-volatility compound (such that the value of γ for the mixture remains close to $5/3$), then obviously the vapor will be cooled to practically the same temperature as the gas. This method was proposed by Milne and Greene[1,2] and called "isolation in a free jet," in analogy with the method of matrix isolation, over which it has the advantage of being practically completely free of intermolecular interaction. At specified T_0 and T, the initial vapor pressure in this method is determined by the required final density of the vapor. For $n_v(T) = 10^{14}$ cm^{-3} (the subscripts v and g will henceforth denote vapor and gas, respectively), under the previous conditions ($T_0 = 1300°K$, $T = 20°K$) we get $M = 13.9$, $p_{0.v} = 9.3 \times 10^{-3}$ atm. Thus, the initial pressure of the helium or argon needed to attain $T = 20°K$ before "freezing" sets in (see the preceding section) also ensures a vapor dilution sufficient to obtain $\gamma \approx 5/3$.

The association of the vapor molecules is much lower in the considered method than in the former one, because of the low value of p_0 and the faster escape velocity. However, it is precisely the association which imposes the principal limitations on the applicability of the considered method. This is evidenced, in particular by cases 3, 5, 8, and 10 of Table II, which gives the published data on association in mixtures.

TABLE II. Degree of condensation in supersonic streams of mixtures of gases and vapors (mass-spectral measurements, published data)

Case No.	Mixture	Initial conditions			Products and degree of condensation	Reference
		T_0, °K	p_0, atm	d_{cr}, mm		
1	He + 1% CO_2, N_2O, SO_2, Xe	300	0.26	0.51	Does not condense	[22]
2	Ar + N_2	300		0.01	Fraction of Ar does not change when N_2 is added	[13]
3	Ar + 25% CO_2	300	20	0.01	There is practically no Ar_2, a quantity of $(CO_2)_2$ larger than without Ar is observed; $ArCO_2$, Ar_2CO_2, $Ar(CO_2)_2$ ... are observed	[13]
4	Ar + 25% CO_2	300	<3	0.01	$ArCO_2 > (CO_2)_2$	[13]
5	Ar + 4% CO_2	300	1	0.23	$Ar_2 : Ar = 5 \cdot 10^{-7}$, $(CO_2)_2 : CO_2 = 0.07$	[5]
6	Ar + 4% SF_6	300	40	0.01	$(SF_6)_2 : SF_6 = 0.0026$	[13]
7	Ar + 10% SF_6 + 10% CO_2	300	40	0.01	$SF_6(CO_2)$ and $SF_6 \cdot CO_2 \cdot Ar$ are observed	[13]
8	Ar + Traces of H_2O	300	5	0.05	$Ar : Ar_2 : H_2O : (H_2O)_2 = 1 : 0.045 : 0.006 : 0.006$ $Ar : Ar \cdot H_2O : Ar_2 \cdot H_2O : Ar(H_2O)_2 = 1 : 0.0015 : 0.00045 : 0.00045$	[5]
9	N_2 + 2.4% Hg	588	7	*	Does not condense	[23]
10	N_2 + 2.4% Hg + 0.15% Rb	588	7	*	50% Hg is condensed	[23]

*Square nozzle measuring 4.32 x 1.24 cm.

Association in supersonic streams was considered in detail by a number of authors (see, e.g.,[7,14,24]). For our purposes it suffices to consider it quantatively, estimating only the number of collisions between the molecules of the vapor during the course of escape. We start from the assumption that $\gamma = \gamma_g$ and $T_{rot} = T_{trans} = T$. From the well-known expressions for the Mach number and the average time between collisions of the molecules, we can find the number dZ of collisions between one molecule of the vapor and others along a stream path dL:

$$dZ = \frac{4\sigma_v^2 n_v}{M}\left(\frac{\pi m_g}{\gamma_g m_v}\right)^{1/2} dL, \qquad (4)$$

where σ is the gaskinetic diameter of the molecule and m is the molecular weight. Thus, the number of intermolecular collisions in a given region is inversely proportional to the Mach number and does not depend on the temperature.

Introducing n/n_0 in place of n and L/d_{cr} in place of L, expressing n/n_0 in terms of M, and integrating, we obtain

$$Z = 4\left(\frac{\pi m_g}{\gamma_g m_v}\right)^{1/2} \sigma_v^2 n_{0,v} d_{cr} \int\limits_0^{L/d_{cr}} \frac{1}{M}\left(\frac{\gamma_g - 1}{2} M^2 + 1\right)^{1/(1-\gamma_g)} d\left(\frac{L}{d_{cr}}\right).$$

Let us consider a concrete example. We take a heavy diatomic vapor with $m_v = 150$ and $\sigma_v = 5 \times 10^8$ cm and helium gas. The stream diameter in the investigated region is assumed equal to 1 cm. After determining M from T_0 and T we obtain[3,4] $d_{cr} \approx 0.76$ mm.

We consider two variants: a) a nozzle in which the supersonic (expanding) part has a profile such that $M = 10$ at the exit and the stream is uniform over the entire cross section[25]; b) a free jet escaping from an orifice into a vacuum; for the values of M on the jet axis at $L/d_{cr} > 1$ we know the approximate relation[26]

$$M \approx 3.26(L/d_{cr} - 0.075)^{2/3} - 2/[3.26(L/d_{cr} - 0.075)^{2/3}].$$

Assume that the subsonic (contracting) part has in both cases a curvature radius equal to the critical diameter.

For the subsonic part, calculation yields 28.4 collisions. For the supersonic part, the results of the calculations are shown in Fig. 1. Far from all collisions lead to condensation, so that we can only draw qualita-

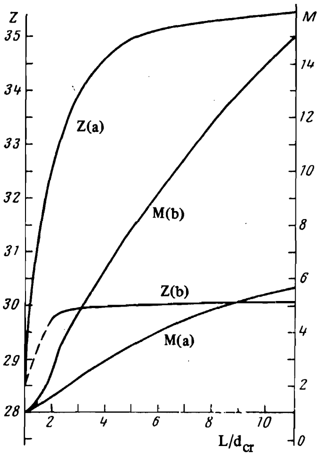

FIG. 1. Mach number M and number of collisions Z of one vapor molecule with others as function of L/d_{cr} on the axis of a supersonic nozzle (a) and on the axis of a free jet (b). Only the supersonic part of the stream is shown, but L/d_{cr} and Z are reckoned from the start of the subsonic part. The dashed part of the Z curve (b) was not calculated, so that the position of this curve relative to the ordinate axis is approximate.

tive conclusions from our calculations. In the subsonic part, there will be so many collisions that if the vapor in the oven is saturated, then it will in the main become condensed. The number of collisions in the supercooling region can be decreased by a factor of several times by superheating the vapor in the oven, for example, if the supercooling sets in only at M = 1, i.e., at $p_V = 3.7$ Torr and T = 980°K. However, even in this case the number of collisions is significant, particularly in the case of a nozzle (owing to its large length and the slow growth of M).

Thus, the considered method is suitable only if a sufficient vapor pressure can be obtained under superheating conditions, or else in the case when the observations are possible at a much lower density of the investigated vapors ($n_V \sim 10^{12}\,\mathrm{cm}^{-3}$). For electronic absorption spectra, such small n_V are sufficient only in exceptional cases. We can, however, investigate microwave spectra, as was done in the cited paper of Greene and Milne[2]. We can also investigate the emission spectra excited by an electron beam or by a weak high-frequency discharge. Using a laser technique and modern methods of registration, good results can be obtained by investigations of resonance fluorescence.

We emphasize one more an interesting field of application, for which the method considered in this section, as well as the method considered below, produce unique possibilities, namely the investigation of compounds with inert and other gases, examples of which are given in Table II.

3. SUPERCOOLING OF A VAPOR WHEN IT IS INJECTED INTO THE BOUNDARY LAYER OF A COLD SUPERSONIC STREAM

With the aim of reducing to the minimum the initial vapor pressure and the association of its molecules, we propose the following (third) method. It follows from formula (4) and Fig. 1 that in the region of large M the number of collisions of the vapor molecules with one another is very small. It is therefore desirable to avoid mixing of heated gases with gas in the subsonic region, where the principal association of the particles takes place, and to introduce the vapor directly into the supersonic region of a stream of inert cold gas, for example through a porous oven wall parallel to the stream. The region between the unperturbed stream (the parameters of which will now be denoted by the subscript ∞) and the wall (subscript w) is called the boundary layer. In this layer we have $T_W \geq T \geq T_\infty$, $n_{V,W} \geq n_V \geq 0$, $0 \leq U \leq U_\infty$ (U is the stream velocity), etc.

Let us estimate the conditions under which specified temperature and vapor density are reached in the external sublayer (the one facing the stream) of the boundary layer. The methods of calculating a supersonic boundary layer are quite crude. We use approximate equations for the cross section of the boundary layer on a plane semi-infinite plate[3,4]

$$p_W = p = p_\infty, \quad \frac{U}{U_\infty} = \frac{T_0 - T_W}{T_{0\infty} - T_W} = \frac{C_W - C}{C_W}$$

$$C = \frac{n_V m_V}{n_V m_V + n_g m_g}.$$

Here T_0 and p_0 denote, as before, the parameters of the gas at rest, which in the case of adiabatic expansion acquires a temperature T and a pressure p, but T_0 and p_0 for the boundary layer are not equal to the gas parameters in the reservoir. The equations are solved for specified $T_{0\infty}$ and M_∞ by successive approximations. To this end it is necessary to fix the value of $(p_g/p_V)_W$, which is unknown to us. It is determined by the intensity of the injection of the vapor, which should not be too large, since otherwise a shock wave is produced ahead of the injection region in the stream, and the temperature behind this shock increases sharply. Variation of $(p_g/p_V)_W$ in the range from 1 :9 to 9 :1 affects the results little, especially if $m_g \ll m_V$. We thus obtain the dependence of p_V/p_g, U/U_∞, and M on T. Absolute values of p and $p_{V.W}$ are obtained when we specify the required n_V for a certain sublayer T. The calculation was performed by us with a computer using the same initial data as for the second method. The results for six cases (different gases, T_0 and M) are given in Table III. The values of $p_{V.W}$, p_0 and the Reynolds number Re were calculated at $(p_g/p_V)_W = 9$. The Reynolds numbers (for their definition, see, e.g.,[3,4]) were obtained at a boundary-layer length L = 1 cm. It follows from their values that the boundary layer is apparently laminar under the considered conditions.

Figure 2 shows the distribution of certain parameters of the boundary layer as functions of the temperature for case 5 of Table III. It is interesting to note that n_V remains practically constant and relatively high ($\sim 0.2 n_{V.W}$) from hot to very cold layers. The reason is that the decrease in the fraction of the vapor in the gas-vapor mixture is partly offset by the increase of the density of the mixture with decreasing temperature.

The possibility of spectral investigations in the low-temperature sublayer of the boundary layer is determined to a considerable degree by its thickness δ. The usual estimation of δ as a quantity on the order of $L/\mathrm{Re}^{1/2}$ gives patently undervalued results in our case, since it does not take the high temperature of the wall into account. When T_W is taken into account, one of

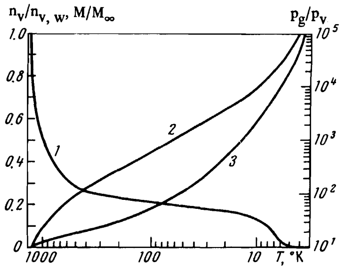

FIG. 2. Distribution of the ratios $n_V/n_{V.W}$ (curve 1), p_g/p_V (2) and M/M_∞ (3) over the cross section of the boundary layer for case 5 of Table III.

TABLE III. System parameters at which a vapor density $n_v = 10^{14}$ cm^{-3} is reached in the boundary layer sublayer with $T = 20°K$.

Parameters	Case No.					
	1	2	3	4	5	6
Gas	Ar	Ar	He	He	He	He
M_∞	7	5	5	7	16	5
$T_{0,\infty}$, °K	300	80	80	300	300	4
T_∞, °K	17.3	8.57	8.57	17.3	3.47	0.43
U_∞, 10^4 cm/sec	5.42	2,73	8.62	17.14	17.56	1.93
$p_{v,w}$, Torr	0.149	$3.11 \cdot 10^{-2}$	0.110	0.48	$7.88 \cdot 10^{-2}$	$6.39 \cdot 10^{-2}$ *
$p_{0,\infty}$, Torr	1860	82,5	292	6010	54600	169
10^{-5} Re	3.78	2.19	1.70	2.81	22.4	35.6

*In the sublayer with $T = 1.5°K$, the required n_v is reached at $p_{v.w} = 0.09$ Torr.

the approximate methods (see[4]) yields $\delta \sim 1$ cm at $L = 1$ cm. The use of this method to calculate the distribution of T with respect to the geometrical coordinate y perpendicular to the oven wall is meaningless in our case, since the method is based on the assumption $T(y = \delta) = T_\infty$, and for us it is important that $T(y \rightarrow \infty) = T_\infty$.

It is even more difficult to estimate the degree of association of the vapor in the cold sublayer. It can be assumed, however, that the trajectories of an appreciable fraction of the vapor molecules in the external sublayer start from the region in which the stream is in contact with the oven wall, and lie entirely in the region $M \approx M_\infty$. These molecules will not associate in practice. Another part of the vapor enters the cold sublayer from the sublayers with low M, and becomes partly associated along its path, but the products of the association remain mainly in the hot sublayers, owing to the larger molecular weight.

The estimates presented allow us to conclude that the proposed method is perfectly realistic. The initial vapor pressure and the association of the vapor molecules are lower than in the two preceding methods. It becomes unnecessary to heat the initial gas. Slight dimerization of the inert gas, for example argon, is possible, but the absorption spectrum of Ar_2 lies in the far vacuum ultraviolet[27]. A more significant obstacle may be the association of gas atoms with the molecules of the investigated vapor. At the same time, as already mentioned, the products of such an association are themselves interesting research objects.

4. SUPERCOOLED-VAPOR DENSITY NEEDED TO OBTAIN THE SPECTRUM

Thus, of the three methods considered for supercooling vapor in a supersonic stream, the most promising for spectral research is, in our opinion, the last method. It must be emphasized, however, that concrete circumstances may change this choice. For example, investigation of compounds with inert gases is apparently best carried out by the second method, while the first method is best for the study of dimers.

Much depends also on the minimal vapor density n_v necessary for spectral investigations. The smaller the value of n_v, the lower can the initial vapor pressure $p_{0.v}$ be in the second and third methods. According to our estimates, the value $n_v \sim 10^{14}$ cm^{-3} suffices for photographic registration of the electronic absorption spectrum at the following typical values of the decisive factors[28-30]: 1) spectral region—500 nm, 2) oscillator strength of electron-vibrational transition—10^{-3} [31-33], 3) fraction of molecules situated on the investigated vibrational level—20%, 4) high resolving power of the spectral instrument -10^6, for it is precisely in this case that the advantage of the supercooling become manifest, 5) length of optical path—10 cm, 6) observed optical density at the maximum of the most intense line of the band—0.3, 7) molecular weight, on which the Doppler line width Δ depends—150, 8) molecular rotational constants on which the fraction g of the integrated intensity of the band due to the most intense line of the band depends—$B'' = 0.117$ cm^{-1} and $D'' = 2 \times 10^{-8}$ cm^{-1}, 9) rotational temperature—20°K. The choice of the last quantity is based on the fact that for the indicated molecular constants and other parameters and for T_{rot} equal to 4, 20, 300 and 1000°K, we have, in the case of the electronic $^1\Pi - {}^1\Sigma$ transition, values of g respectively equal to[30] 0.0875 (line of Q branch, J = 3), 0.0393 (J = 7), 0.0102 (J = 29), and 0.00565 (J = 54). Therefore, taking $\Delta(T_{trans})$ into account, the values of n_v are related like 0.45 :1 :5.6 :15. Supercooling to $T = 4°K$ calls for very high $p_{0.g}$ and $p_{0.v}$, and is therefore more difficult to realize, and at $T = 300°K$ the supercooling effect is lost to a considerable degree. We therefore chose $T_{rot} = 20°K$ and assumed that $T_{trans} = T_{rot}$.

At other values of the listed factors, n_p can change by one order or more. Thus, the use of photoelectric registration, and also of high-sensitivity spectral methods of microwave spectroscopy, resonance fluorescence, etc., offers prospects for greatly decreasing n_v. This will make it possible either to lower $p_{0.v}$ and accordingly reduce the association of the molecules, or to obtain an even lower temperature of the supercooled vapor.

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