

Effect of collisions on the distribution of molecules with respect to vibrational levels of excited electronic states in a gas discharge

S. N. Andreev, M. A. Kerimkulov, B. A. Mirzakarimov, Yu. B. Konev, V. N. Ochkin, S. Yu. Savinov, M. V. Spiridonov, S. N. Tskhaï, and L. I. Shumskaya

P. N. Lebedev Physics Institute, Russian Academy of Sciences of the USSR, Moscow

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Correlations in the vibrational distributions of N_2 and CO molecules in the ground and excited electronic states in a gas-discharge plasma have been studied by laser and classical emission spectroscopy. Variation of the pressure of the CO– N_2 –He–Xe– O_2 gas mixture from 5 to 300 Torr revealed the effect of vibrational relaxation of N_2 ($C^3\Pi$) and CO ($A^1\Pi$). The effective relaxation cross sections for the vibrational levels $v = 1-4$ of nitrogen and $v = 1-6$ of carbon monoxide have been determined. The cross sections are proportional to the index of the vibrational level. They are large in absolute value, $\sim 1 \text{ \AA}^2$. They have no temperature dependence over the range 500–1200 K. A new method is proposed for estimating the shape of the high-energy part of the electron velocity distribution and for determining the vibrational temperatures of the electronic ground states. This method is based on measurements of the intensity in the spectra of transitions which start from excited electronic states.

1. INTRODUCTION

In the nonequilibrium plasma of a discharge in a molecular gas, the energy is carried primarily by molecules in electronic ground states, which are distributed among a large number of vibrational-rotational levels. The shape of these distributions has a fundamental effect on essentially all processes which occur in the plasma. There is thus good reason for the effort which is being expended on developing quantitative methods of classical and laser spectroscopy for diagnostics of molecules in electronic ground states.

A simple experimental solution to the problem of determining the vibrational temperatures of diatomic molecules under very nonequilibrium conditions was proposed in the earliest studies in this direction.¹⁻³ It was in those studies that the difference between the effective temperatures in different electronic states was first stressed. Interrelationships were pointed out between the various types of distributions of molecules among vibrational levels in the ground states (v^0) and the emitting electronically excited states (v). This method for measuring vibrational temperatures has subsequently been refined repeatedly. There is only one important circumstance associated with the design of the present study which we should point out here.

Correlations in the v^0 and v distributions were established in Refs. 1–3 for low-density plasmas. Those studies were restricted to low densities because at low densities a molecule does not undergo collisions capable of redistributing the densities of its vibrational states which are produced by the excitation mechanism over the time τ_r , corresponding to the radiative lifetime of the state from which the detected transitions start.

In the case of the N_2 ($C^3\Pi$) molecule, for example, which is the one most commonly used in plasma diagnostics, this lifetime is $\tau_r \sim 10^{-8}$ s. At a pressure $P \approx 1$ Torr, the time scale between particle collisions is $\tau_c \sim 10^{-7}$ s. The condition mentioned above is satisfied at pressures $P \leq 10$ Torr. This is of course a “lower” estimate, since not every single collision will cause transitions between different levels v . It

has not been possible to reduce the uncertainty in these estimates, because there has been essentially no study of the vibrational relaxation of electronically excited molecules.

In a low-density plasma, the method of relative intensities in the vibrational structure of electronic bands is widely used to find the vibrational energy in a variety of objects: arcs, plasma-chemistry reactors, laser active media, plasma jets, etc. (Refs. 1–9, for example). In several cases the reliability of this method has been tested by more elaborate independent measurements.^{10,11}

Several attempts have been made to use this method for plasmas at higher gas pressures, ≥ 100 Torr. Although the results obtained, in our opinion, are in good logical agreement with other measurements of plasma properties (e.g., Refs. 12 and 13), the validity of such studies remains an open question.

Our purposes in the present studies were to use independent methods to investigate the distributions of N_2 and CO molecules with respect to vibrational levels of the ground and excited electronic states over a broad range of gas pressures in a glow discharge, to compare the results, and to detect manifestations of a vibrational relaxation of electronically excited molecules.

2. EXPERIMENTAL CONDITIONS, PROCEDURE, AND APPARATUS

2.1. The system studied

The measurements were carried out in the positive column of a glow discharge in a (1:4:15:0.5:0.03) CO– N_2 –He–Xe– O_2 gas mixture, which is typical of a CO laser. We used a water-cooled glass discharge tube with an inside diameter $2R = 6$ mm. The total length of the tube was 105 mm; the length of the discharge zone along the tube axis was 90 mm. The electrodes were in side branches. The discharge current was $i = 5-40$ mA. The pressure of the gas mixture was $P = 5-300$ Torr. The experiments were carried out as the gas flowed slowly, at ≈ 0.5 m/s, through the dis-

charge zone. The flow was monitored on the basis of the rate of outflow from the vessel of known volume.¹⁴

2.2. Diode laser spectroscopy

The populations of the levels of the $\text{CO}(X^1\Sigma)$ molecules were determined by diode-laser spectroscopy. The layout of the spectrometer and its characteristics are described in Refs. 15 and 16. The CO absorption spectrum was measured over the interval 4.8–5.2 μm at a resolution $\sim 10^{-4} \text{ cm}^{-1}$. It was possible to reliably detect individual vibrational-rotational lines corresponding to $v^0 \rightarrow v^0 + 1$ vibrational transitions with $v^0 \leq 9$. The typical spectra contained ~ 200 lines of transitions with rotational quantum numbers $j^0 \leq 40$. During intense vibrational-rotational excitation, the populations of the levels coupled by radiative transitions were comparable. The procedure for analyzing the absorption spectra in such a situation is described in Refs. 15 and 16.

2.3. CARS spectroscopy

The populations of levels with $v^0 \leq 3$ of $\text{N}_2(X^1\Sigma)$ molecules were determined by the method of coherent anti-Stokes Raman scattering (CARS). We used a CARS spectrometer based on a pulsed YAG laser and a dye laser. The length of the output pulses was $\sim 10^{-8} \text{ s}$, and the repetition frequency was 20 Hz. The output energy of the YAG laser was $\approx 40 \text{ mJ}$ per pulse; the corresponding figure for the dye laser was $\approx 3 \text{ mJ}$. The resolution of the spectrometer was $\approx 0.2 \text{ cm}^{-1}$. We used a collinear system for bringing the laser beams together. The spectrometer and the procedure are described in more detail in Refs. 17 and 18.

2.4. Emission spectroscopy

The populations of the vibrational levels of the electronically excited $\text{CO}(A^1\Pi)$ and $\text{N}_2(C^3\Pi)$ molecules were determined from the relative intensities of the vibrational bands in the electronic spectra with the help of an apparatus based on a modified DFS-8 spectrometer.¹⁹ In the case of $\text{CO}(A^1\Pi)$ molecules, the measurements were carried out on the basis of 4⁺ bands of the $A^1\Pi - X^1\Sigma$ system: (1–7), (2–8, 9, 10), (3–9, 10, 11), (5–11, 12, 13), (6–13, 14, 15, 16), and (7–15, 16, 17). In other words, we determined the populations of levels $v = 1-7$. For $\text{N}_2(C^3\Pi)$ we used bands of the 2⁺ system: (0–2, 3), (1–3, 4), (2–4, 5), (3–5, 6), and (4–6, 7). It was thus possible to obtain the population distributions among all five vibrational levels ($v = 0-4$) belonging to this state. A check was made to ensure that there was no

reabsorption. The necessary data on the spectroscopic constants, the Franck-Condon factors, and the radiative lifetimes of the states are given in Refs. 20–22.

2.5. The volume studied in the measurements

All the results of the spectral measurements correspond to the paraxial zone of the discharge. In the method of diode spectroscopy, the light from the diode laser was collimated into a beam $\leq 1 \text{ mm}$ in diameter. In the CARS method, the laser beams were focused on the discharge axis, at the middle of the tube. The region in which the scattered light was generated in this case had a dimension $\approx 3 \text{ mm}$ along the discharge axis and a dimension $\approx 0.1 \text{ mm}$ transverse with respect to this axis. A system of diaphragms selected the light from a paraxial zone 2 mm in diameter in the recording of the emission electronic spectra from the end of the tube.

The electric field was measured by probes.

3. RESULTS AND DISCUSSION

3.1. Distribution of molecules with respect to levels of the electronic ground states

Figure 1a shows representative distributions of $\text{CO}(X^1\Sigma)$ molecules with respect to j^0 vibrational levels for several v^0 vibrational states. These results are plotted as the populations N_{j^0} per unit statistical weight g_{j^0} versus the rotational energy, in semilogarithmic scale. All the plots are linear, with a common rotational temperature (which in this case, with $P = 80 \text{ Torr}$ and $i = 15 \text{ mA}$, is $T_{\text{rot}} = 580 \pm 15 \text{ K}$). This was the situation under all the conditions studied. We identify the rotational temperature with the gas temperature T_g .

Studies of the distribution of N_2 and CO molecules with respect to the vibrational levels of the electronic ground states show that these distributions can be thought of as Treanor distributions for the groups of lower levels.²³ Two parameters are sufficient to describe them: T_1 and T_g . Here $T_1 = E_1 k^{-1} \ln(N_0 N_1^{-1})$, where E_1 is the size of the first vibrational quantum, k is the Boltzmann constant, and N_0 and N_1 are the populations of the zeroth and first vibrational levels. Figure 1b illustrates the situation with distributions of $\text{CO}(X^1\Sigma)$ molecules with respect to the levels v^0 , as a semilog plot versus the vibration energy E_{v^0} . Also shown here are calculated Boltzmann and Treanor distributions for $T_1 = 3530 \text{ K}$ and $T_g = 580 \text{ K}$.

Some of the measurements of T_1 and T_g are summarized in Fig. 2, as a plot versus the pressure at currents of 5

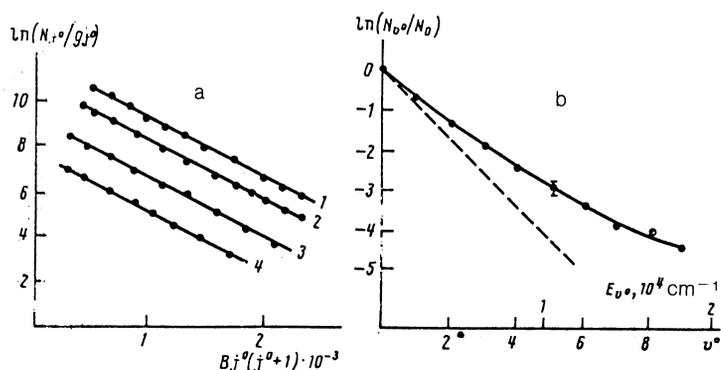


FIG. 1. Illustrative distributions of $\text{CO}(X^1\Sigma)$ molecules with respect to vibrational-rotational levels ($P = 80 \text{ Torr}$, $i = 15 \text{ mA}$). a: Distributions with respect to rotational levels ($T_{\text{rot}} = 580 \pm 15 \text{ K}$). 1— $v^0 = 1$; 2— $v^0 = 2$; 3— $v^0 = 3$; 4— $v^0 = 4$. b: Distributions with respect to vibrational levels. Points—Experimental data; solid line—Treanor distribution ($T_1 = 3530 \text{ K}$, $T_g = 580 \text{ K}$); dashed line—Boltzmann distribution ($T = 3530 \text{ K}$).

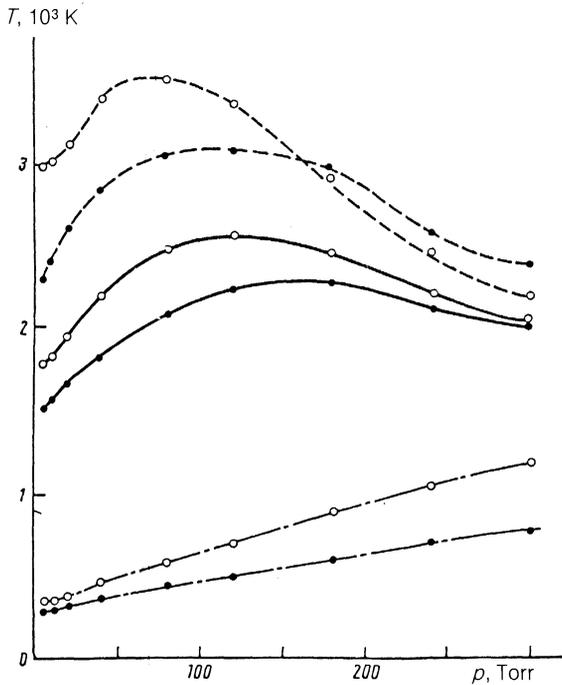


FIG. 2. The gas temperature T_g and the vibrational temperature T_1 versus the gas pressure. ●— $i = 5$ mA; ○— $i = 15$ mA. Solid lines) $T_1^{N_2}$; dashed lines) T_1^{CO} ; dot-dashed lines) T_g .

and 15 mA. The error in the determination of the temperature is less than 3%. We see that T_g increases monotonically with increasing pressure, because of the increase in the energy deposition at a fixed current. The plots for the vibrational temperatures are not monotonic. In the initial stage, the values of T_1 increase, because of an increase in the energy deposition and a decrease in the role played by relaxation at the walls, due to a decrease in the diffusion rate. At high pressures, the decrease in T_1 stems from an increase in the role of vibrational-translational (VT) relaxation due to the increase in T_g .

It is interesting to compare the values of T_1 for oscillators with various vibrational quanta. If the time scales for the intramode (VV) and the intermode (VV') exchange are shorter than the VT relaxation time, the relationship between vibrational temperatures is given by the familiar theoretical expression (Ref. 23, for example)

$$T_1^{CO} T_g E_1^{N_2} - T_1^{N_2} T_g E_1^{CO} = T_1^{N_2} T_1^{CO} (E_1^{N_2} - E_1^{CO}). \quad (1)$$

Relation (1) is widely used in calculations on relaxation systems. However, it is usually difficult to analyze the initial conditions in detail, particularly when the plasma is a gas discharge. It is thus useful to carry out an experimental test of expression (1). Such a test was recently attempted in Ref. 24, where a study was also made of the relationship between $T_1^{N_2}$ and T_1^{CO} in a discharge plasma with cryogenic cooling and a rapidly flowing gas. However, while the vibrational temperatures of CO were measured by a direct ir-luminescence method in Ref. 24, the value of T_1 was found by the method of Refs. 1–3, which we mentioned in the Introduction. As a result, the interval of conditions studied was extremely narrow, primarily in terms of the gas density. The

results of the measurements of Ref. 24 turned out to agree with (1). Our direct measurements also support relation (1) over the entire range of conditions studied, to within the small measurement errors.

3.2. Vibrational-excitation temperatures in electronically excited states

The measurements show the the vibrational distributions of the $N_2(C^3\Pi)$ molecules can be described quite accurately as Boltzmann distributions over the entire range of conditions studied. Figure 3 shows a typical plot of the populations N_v of the $N_2(C^3\Pi)$ vibrational levels versus the level energy, for a mixture pressure $P = 40$ Torr and a current $i = 15$ mA. We see that the distribution can be characterized by an effective vibrational temperature T_{vib} , which is determined by the slope. Table I shows values of T_{vib} for several sets of conditions.

The situation is slightly different in the case of the vibrational distributions of $CO(A^1\Pi)$. The plot is generally non-linear. The excitation temperature,

$$T_{exc}^{CO}(v) = (E_v - E_{v-1}) [k \ln(N_{v-1} N_v^{-1})]$$

is independent of the level index v in this case. In addition, for the levels with $v \geq 3$ the experimental points conform to a straight line. In other words, there is a constant excitation temperature T_{exc} . This behavior was found under all conditions studied. It is thus possible to introduce the concept of a vibrational temperature $T_{vib} = T_{exc}(v \geq 3)$, which characterizes the vibrational distribution of $CO(A^1\Pi)$. The results of measurements of this parameter are also shown in Table I.

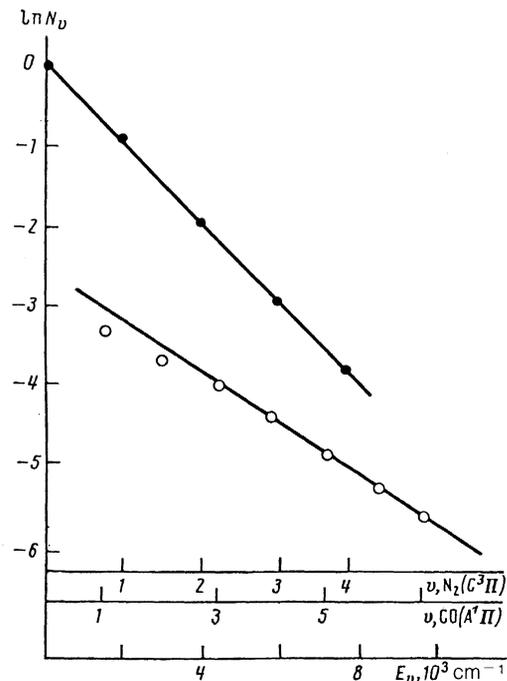


FIG. 3. Distributions of (●) $N_2(C^3\Pi)$ molecules and (○) $CO(A^1\Pi)$ molecules with respect to vibrational levels v ($P = 40$ Torr, $i = 15$ mA).

TABLE I. Value of the effective vibrational temperature T_{vib} of the electron-excited molecules, K.

Molecule	i , mA	P , torr					P , Torr				
		5	10	20	40	80	120	180	240	300	
N_2 (C ³ H)	5	{ 2650 ± 70 2600	2550 ± 60 2500	2400 ± 60 2440	2500 ± 60 2545	2770 ± 80 2755	2600 ± 70 2670	2490 ± 60 2775	2380 ± 60 2655	2320 ± 60 2770	
	15	{ 2700 ± 80 2670	2500 ± 60 2460	2400 ± 60 2450	2750 ± 80 2770	2800 ± 80 2850	2800 ± 90 2850	2660 ± 70 2810	2390 ± 70 2625	2350 ± 60 2525	
CO (A ¹ H)	5	{ 4100 ± 100 4100	4400 ± 100 4500	4600 ± 100 4500	4700 ± 100 4700	4300 ± 100 4400	3750 ± 100 4000	— 3870	— 3580	— 3410	
	15	{ 5100 ± 150 5000	4400 ± 150 4500	5000 ± 150 5100	4700 ± 150 4600	5000 ± 150 5140	3800 ± 100 4130	3430 ± 100 3790	3050 ± 90 3420	2940 ± 80 3190	

Note. The upper value of T_{vib} for each value of i corresponds to the experimental data, and the lower value is theoretical.

3.3. Calculation of the vibrational distributions of electronically excited molecules without relaxation

Once the vibrational distributions of the molecules in the electronic ground states are known, the distributions in the electronically excited states can be calculated. One of the primary mechanisms for the filling of excited electronic states of molecules in the plasma of a glow discharge is direct electron impact. Making the further assumption that the only mechanism which empties these levels is radiative decay, we can write

$$N_v = n_e A_v^{-1} \sum_{v^0} \langle v_e \sigma_{v^0 v} \rangle N_{v^0}, \quad (2)$$

where n_e and v_e are the density and velocity of the electrons in the plasma, $\sigma_{v^0 v}$ is the cross section for the excitation of level v from level v^0 of the electronic ground state, and A_v is the probability for the radiative decay of level v .

Relation (2) underlies the method of Refs. 1–3 for solving the inverse problem of reconstructing the vibrational distribution in the electronic ground state, N_{v^0} , from data on the distribution in the excited state, N_v . The excitation of molecules by electron impact occurs in accordance with the Franck–Condon principle: $\sigma_{v^0 v} \propto q_{v^0 v}$, where $q_{v^0 v}$ is the Franck–Condon factor.^{25–27} As was shown in Refs. 28 and 29, the rate constant $\langle v_e \sigma_{v^0 v} \rangle$ is proportional to not only $q_{v^0 v}$ but also a factor reflecting the value of the electron distribution function $f(\varepsilon)$ at threshold excitation energies $\varepsilon_{v^0 v}^*$. In this case (2) becomes

$$N_v = \text{const} \cdot A_v^{-1} \sum_{v^0} q_{v^0 v} (\varepsilon_{v^0 v}^*)^{1/2} f(\varepsilon_{v^0 v}^*) N_{v^0}. \quad (3)$$

The difficulty in correctly choosing $f(\varepsilon_{v^0 v}^*)$ over a broad range of conditions is that measurements by probe methods generally do not yield reliable information at pressures $P > 10$ Torr. For this reason, $f(\varepsilon)$ was calculated by solving the Boltzmann equation. The method for calculating $f(\varepsilon)$ in gas mixtures containing vibrationally excited molecules has now been worked out in detail and tested. It is described in Refs. 30 and 31, among other places. To improve the reliability and accuracy of the calculations to the extent possible, we used experimental values of the gas temperature T_g , of the reduced electric field E/N (N is the total gas density, determined with allowance for thermal displacement), and the populations of the vibrational levels of the molecules (in particular, in order to deal with superelastic collisions correctly). Figure 4 shows some illustrative $f(\varepsilon)$ distributions, along with plots of the parameter E/N versus the gas pressure, for currents $i = 5$ and $i = 15$ mA. In the energy interval 2–6 eV we see some significant deviations from Maxwellian distributions. These deviations stem from the presence of resonant cross sections for the excitation of N_2 and CO vibrations.^{30,31} There is another point here which is of importance to the discussion below: At energies $7 \leq \varepsilon \leq 14$ eV, the shape of the distribution $f(\varepsilon)$ is approximately Maxwellian, although the average energies in these regions are generally not the same as the average energies for the overall distributions. The apparent reason for this result is that for $\varepsilon > 7$ eV electrons are exciting various electronic states of the molecules and ionizing them in a large number of elementary processes, and the overall set of the cross sections for these

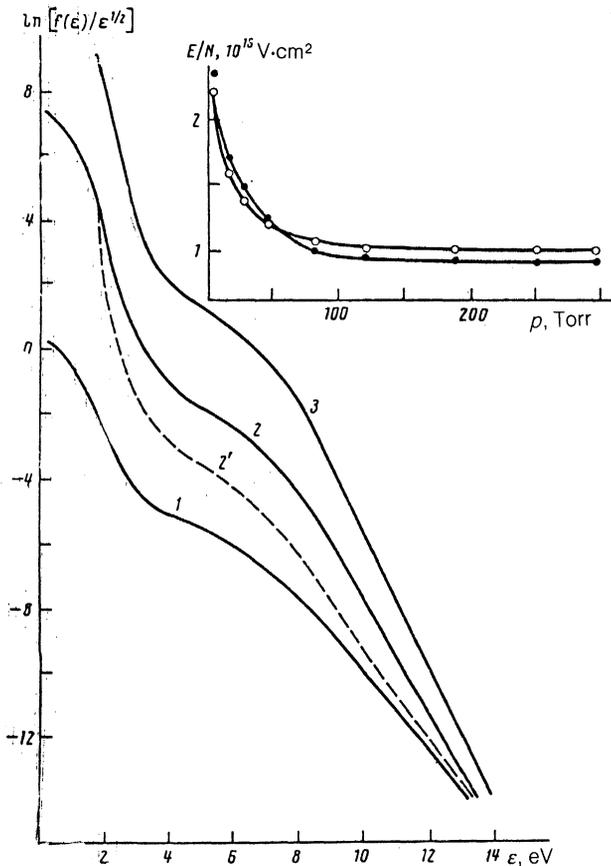


FIG. 4. Electron energy distributions for several experimental conditions (arbitrary units). 1— $P=5$ Torr, $i=5$ mA; 2, 2'— $P=40$ Torr, $i=15$ mA (line 2' was calculated without consideration of the vibrational excitation of the molecules); 3— $P=300$ Torr, $i=15$ mA. The corresponding values of the average energy $\bar{\epsilon}$ (eV) are as follows: 1) 0.954; 2) 0.599; 2') 0.602; 3) 0.527. The inset shows the pressure dependence of E/N . ●— $i=5$ mA; ○— $i=15$ mA.

processes is generally not of a clearly expressed resonant nature.

Analysis of the results calculated from (3) shows that the calculated distributions are essentially the same as the experimental distributions at pressures $P < 120$ Torr. This result is also illustrated by Table I, which reveals a close agreement between the theoretical and experimental values of the vibrational temperatures in this region. This fact also confirms our initial assumption that the levels are excited by direct electron impact.

At higher pressures, we see some systematic discrepancies. Specifically, the measured effective vibrational temperatures $T_{\text{vib}}^{\text{N}_2}$ and $T_{\text{vib}}^{\text{CO}}$ are lower than the theoretical temperatures. We believe that this difference stems from vibrational relaxation of electronically excited molecules

3.4. Effect of relaxation processes

Comparing the theoretical and experimental data, we can generate a quantitative description of the effect of collisions on the vibrational distributions of the electronically excited molecules. In analyzing vibrational-relaxation processes, we need to consider VV, VV', and VT processes. We first note that collisions of electronically excited particles (VV processes) can be ignored, since the density of these

particles in a gas-discharge plasma is much lower than the density of particles in electronic ground states.

Collisions of electronically excited particles with molecules in electronic ground states (VV' processes) should lead to vibrational distributions of $\text{CO}(A^1\Pi)$ and $\text{N}_2(C^3\Pi)$ with temperatures $T_{\text{vib}}^{\text{CO}*}$ and $T_{\text{vib}}^{\text{N}_2*}$ which are related to the vibrational temperatures T_1^{CO} and $T_1^{\text{N}_2}$ molecules in the electronic ground states by relation (1). It can be shown that for $P > 120$ Torr, in essentially all cases studied, the temperatures $T_{\text{vib}}^{\text{CO}*}$ and $T_{\text{vib}}^{\text{N}_2*}$ should have been higher than the calculated effective vibrational temperatures $T_{\text{vib}}^{\text{CO}}$ and $T_{\text{vib}}^{\text{N}_2}$. For example, at $P=240$ Torr and $i=15$ mA we have $T_{\text{vib}}^{\text{CO}*} = 6800$ K, in comparison with $T_{\text{vib}}^{\text{CO}} = 3420$ K. Actually, the measured vibrational temperatures in this pressure range are lower than the theoretical values. The implication is that the efficiency of VV' processes is considerably lower than the efficiency of VT processes in these cases.

We can thus assume, in a first approximation, that the populations of the vibrational states are changed only by one-quantum VT-relaxation processes. Using the principle of detailed balance, we can easily write the system of equations

$$N_0^0 = N_0 [1 + (N_1/N_0) \bar{k}_{1,0}], \quad (4)$$

$$N_v^0 = N_v [1 + \bar{k}_{v,v-1} - (N_{v+1}/N_v) \bar{k}_{v+1,v}],$$

where N_v^0 is the population of level v in the absence of relaxation,

$$\bar{k}_{v,v-1} = A_v^{-1} k_{v,v-1} \left[1 - \frac{N_{v-1}}{N_v} \exp\left(-\frac{E_v - E_{v-1}}{kT_g}\right) \right], \quad (5)$$

and $k_{v,v-1}$ is the rate of vibrational relaxation of electronically excited molecules, given by

$$k_{v,v-1} = \sum_i [i] \bar{v}^i \bar{\sigma}_{v,v-1}^i. \quad (6)$$

Here $[i]$ is the density of particles of species i of the gas mixture, \bar{v}^i is the average velocity of the relative motion of the relaxing particles and the particles of species i , and

$$\bar{\sigma}_{v,v-1}^i = \frac{\langle v^i \sigma_{v,v-1}^i \rangle}{\bar{v}^i}$$

is the effective cross section for the transition $v \rightarrow v-1$ in a collision with particles of species i .

For the $\text{N}_2(C^3\Pi)$ molecules, all five levels are observed experimentally, and Eqs. (4) are a closed system. In addition to the constants $\bar{k}_{1,0}$, $\bar{k}_{2,1}$, $\bar{k}_{3,2}$, $\bar{k}_{4,3}$, the ratio N_0^0/N_0 is unknown, since theory and experiment give us only the relative quantities N_v and N_v^0 . For the mixture under study here we have

$$\begin{aligned} k_{v,v-1} = & [\text{He}] \bar{v}^{\text{He}} \{ \bar{\sigma}_{v,v-1}^{\text{He}} + 0.1 \bar{\sigma}_{v,v-1}^{\text{N}_2} + 0.025 \bar{\sigma}_{v,v-1}^{\text{CO}} + 0.006 \bar{\sigma}_{v,v-1}^{\text{Xe}} \\ & + 0.002 \bar{\sigma}_{v,v-1}^{\text{O}_2} \} = [\text{He}] \bar{v}^{\text{He}} \bar{\sigma}_{v,v-1}^{\text{eff}}. \end{aligned} \quad (7)$$

Here $\bar{\sigma}_{v,v-1}^{\text{eff}}$ is the effective cross section for relaxation under the influence of all components of the mixture.

In the region in which relaxation is manifested, $120 < P < 300$ Torr, the gas temperatures are $T_g = 500\text{--}1200$ K. A solution of (4) with (5) and (7), for the entire range of conditions, shows that the set of observed vibrational distributions of $N_2(C^3\Pi)$ can be described well by a single set of cross sections $\bar{\sigma}_{v,v-1}^{\text{eff}}$, which are independent of T_g :

$$\begin{aligned}\bar{\sigma}_{1,0}^{\text{eff}} &= 0,11 \pm 0,01 \text{ \AA}^2, & \bar{\sigma}_{2,1}^{\text{eff}} &= 0,23 \pm 0,03 \text{ \AA}^2, \\ \bar{\sigma}_{3,2}^{\text{eff}} &= 0,34 \pm 0,08 \text{ \AA}^2, & \bar{\sigma}_{4,3}^{\text{eff}} &= 0,32 \pm 0,08 \text{ \AA}^2.\end{aligned}$$

For $CO(A^1\Pi)$, Eqs. (4) are not a closed system, since no emission from the $v = 0$ level was detected experimentally. We accordingly used seven equations of the system (4), with $v = 0\text{--}6$, and the auxiliary assumptions

$$\bar{\sigma}_{2,1}^{\text{eff}} = 2\bar{\sigma}_{1,0}^{\text{eff}}, \quad \sum_{v=0}^7 N_v^0 = \sum_{v=0}^7 N_v.$$

The first of these assumptions is made by virtue of the analogy with the corresponding expression for $N_2(C^3\Pi)$. The second assumption corresponds to our initial condition that the overall efficiency of the quenching of the electronic state is low. In this case, a solution of Eqs. (4) showed that, as in the preceding case, the set $\bar{\sigma}_{v,v-1}^{\text{eff}}$ satisfying the observations does not depend on T_g :

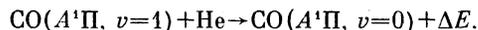
$$\begin{aligned}\bar{\sigma}_{1,0}^{\text{eff}} &= 0,4 \pm 0,1 \text{ \AA}^2, & \bar{\sigma}_{2,1}^{\text{eff}} &= 0,8 \pm 0,2 \text{ \AA}^2, & \bar{\sigma}_{3,2}^{\text{eff}} &= 1,3 \pm 0,4 \text{ \AA}^2, \\ \bar{\sigma}_{4,3}^{\text{eff}} &= 1,7 \pm 0,5 \text{ \AA}^2, & \bar{\sigma}_{5,4}^{\text{eff}} &= 2,2 \pm 0,5 \text{ \AA}^2, & \bar{\sigma}_{6,5}^{\text{eff}} &= 2,7 \pm 0,7 \text{ \AA}^2.\end{aligned}$$

Note that the effective cross sections $\bar{\sigma}_{v,v-1}^{\text{eff}}$ are much higher than the corresponding cross sections for the electronic ground states ($\sim 10^{-5}\text{--}10^{-7} \text{ \AA}^2$). Note also that the cross sections for each molecule are related by $\bar{\sigma}_{v,v-1}^{\text{eff}} \approx v\bar{\sigma}_{1,0}^{\text{eff}}$, which are known from the classical theory of vibrational relaxation, derived for molecules in the electronic ground states (Ref. 23, for example). The cross section $\bar{\sigma}_{4,3}^{\text{eff}}$ for $N_2(C^3\Pi)$ is an exceptional case. The probable reason is that the $v = 4$ level is the last or highest bound level in this electronic term.

Comparing with the results available on molecules in electronic ground states, we conclude that the independence of the effective cross sections from the gas temperature over a wide range of this temperature is evidence that the mechanism for VT processes in this case is not the Landau–Teller mechanism.²³ A possible explanation for this behavior is that the mechanism for the vibrational relaxation of $N_2(C^3\Pi)$ and $CO(A^1\Pi)$ appears to be similar to the mechanism for the relaxation of the NO molecule, whose electronic ground term is again a Π state. This term is split into two closely spaced terms. Nonadiabatic transitions occur between the vibrational levels of these terms.³² These transitions have a high probability. The temperature of this probability is not described by the adiabatic Landau–Teller theory.

Because of the complex composition of the gas mixture which was used, there is no hope of unambiguously assigning the cross sections given above to any specific partner in a collision with an electronically excited molecule. A more productive approach for resolving this question would be to carry out some special experiments like those which we are

reporting here, but on gas mixtures consisting of a small impurity of the molecules of interest in a relaxing gas. Nevertheless, one can suggest that the He atoms make the greatest contribution under our conditions. In the first place, their density is highest. Second, they lead to a high collision rate, because of their small mass. Along the same line, it would be useful to make a comparison with the results of Ref. 33, where the cross section $\sigma_{1,0} = 0.45 \text{ \AA}^2$ was found for the process



This value is the same as the one which we found.

4. MEASUREMENT OF THE VIBRATIONAL TEMPERATURES OF MOLECULES IN ELECTRONIC GROUND STATES IN TERMS OF ELECTRONIC-VIBRATIONAL BANDS

4.1. Conventional procedure

As we mentioned in the Introduction and in Subsection 3.3, a relation of the form (2) was proposed in earlier studies for reconstructing the N_{v^0} distributions in the electronic ground states from the vibrational distributions of N_v in excited electronic states. The first studies¹⁻³ in this direction used the very simple approximation that the rate constants for the excitation of electronic-vibrational levels are simply proportional to Franck–Condon factors: $\langle v_e \sigma_{v^0,v} \rangle \propto q_{v^0,v}$. That approximation is evidently justified only (a) if the average energy of the electron distribution is high in comparison with the difference between the excitation thresholds for different electronic-vibrational levels v or (b) at low vibrational temperatures of the ground state, such that the excitation occurs from the lowest levels v^0 .

Further analysis^{28,29} showed that this approximation is not satisfactory for many entities of practical importance, in which case the excitation cross sections must be averaged over the electron velocity. This step requires the use of relation (3), which in turn complicates the method. For example, if a universal relationship between the vibrational temperatures T_{v^0} and T_v of the ground and excited states is established through an approximation,¹⁻³ a family of such curves must be used in order to take the averaging into account. Each member of the family is characterized by two parameters: the shape of $f(\epsilon)$ and the vibrational temperature of the ground state. Furthermore, when we note that the shape of $f(\epsilon)$ depends on the vibrational temperature of the ground state, we see that in practice it will be extremely difficult to choose these parameter values.

The recommendations offered in Ref. 29 regarding the approximation of $f(\epsilon)$ —recommendations which have been justified for low gas densities—can hardly be extended to a broad range of conditions.

For these reasons, and also on the basis of the results of the present study, in which these circumstance have been taken into account systematically, we wish to offer a new procedure for using this method.

4.2. Maxwellian approximation of the high-energy part of the electron distribution; use of the spectra of two molecules

Here we make use of the circumstance, mentioned in Subsection 3.3, that $f(\epsilon)$ can be approximated at high energies by a Maxwellian function

$$f_M(\varepsilon) = \text{const} \cdot \varepsilon^{1/2} \exp\left(-\frac{3}{2} \frac{\varepsilon}{\bar{\varepsilon}_{\text{eff}}}\right). \quad (8)$$

We will not attempt to find a definite value of an effective average energy $\bar{\varepsilon}_{\text{eff}}$ to describe this part of $f(\varepsilon)$. We consider vibrational distributions with temperatures $T_{\text{vib}}^{(1)}$ and $T_{\text{vib}}^{(2)}$ for the two electronically excited molecules. We find the results

$$T_1^{(1)} = f_{T_g}^{(1)}, T_{\text{vib}}^{(1)}(\bar{\varepsilon}_{\text{eff}}), \quad T_1^{(2)} = f_{T_g}^{(2)}, T_{\text{vib}}^{(2)}(\bar{\varepsilon}_{\text{eff}}). \quad (9)$$

We can then eliminate the quantity $\bar{\varepsilon}_{\text{eff}}$.

This procedure can be implemented numerically. We first solve the direct problem of finding T_{vib} for both molecules, for given values of T_g , $T_1^{(1)}$, and $T_1^{(2)}$. We vary ε_{eff} :

$$T_{\text{vib}}^{(1)} = \varphi_{T_g}^{(1)}, T_1^{(1)}(\bar{\varepsilon}_{\text{eff}}), \quad T_{\text{vib}}^{(2)} = \varphi_{T_g}^{(2)}, T_1^{(2)}(\bar{\varepsilon}_{\text{eff}}). \quad (10)$$

We then calculate families of (10) for various values of T_1 .

Figure 5 shows an example of such a family for the case which we have considered here, of the 4^+ system of CO, at $T_g = 460$ K, which corresponds to a pressure of 40 Torr and a current of 15 mA in the experiments. The value of $\bar{\varepsilon}_{\text{eff}}$ was varied over the range 0.4–4 eV in steps of 0.18 eV. The value of T_1^{CO} was varied over the range 500–5000 K in steps of 180 K. With the value of $T_{\text{vib}}^{\text{CO}}$ known from experiments, we can construct one dependence as in (9) from the points at which the curves of the corresponding family in (10) intersect the straight line $T_{\text{vib}}^{\text{CO}} = \text{const}$ [$T_{\text{vib}}^{\text{CO}}(A^1\Pi) = 4700$ K, in the example at hand] (Fig. 5). Figure 6 shows the results of such a construction for our case of CO($A^1\Pi$) and also for N₂($C^3\Pi$), under the same conditions [$T_{\text{vib}}^{\text{N}_2}(C^3\Pi) = 2750$ K]. On the other hand, the values of the vibrational temperature T_1 of the various molecules correspond to relation (1), as we verified above. When we combine (9) and (1), we can find T_1^{CO} , $T_1^{\text{N}_2}$, and $\bar{\varepsilon}_{\text{eff}}$. We can solve this system of equations in the following way. By eliminating $\bar{\varepsilon}_{\text{eff}}$ from (9), we find $T_1^{\text{N}_2} = \psi(T_1^{\text{CO}})$. The values of T_1 can then be found at the point at which this curve intersects a plot of (1).

In practice, because of measurement errors and the

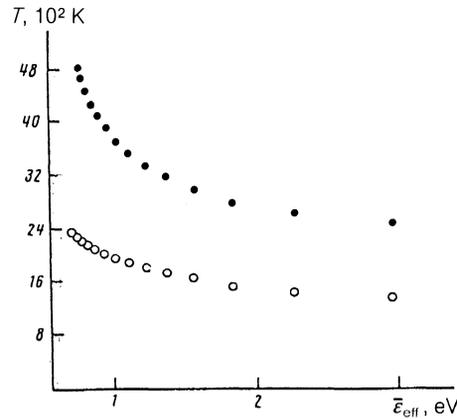


FIG. 6. The vibrational temperatures (●) T_1^{CO} and (○) $T_1^{\text{N}_2}$ versus $\bar{\varepsilon}_{\text{eff}}$. The gas temperature is $T_g = 460$ K; $T_{\text{vib}}^{\text{CO}}(A^1\Pi) = 4700$ K; $T_{\text{vib}}^{\text{N}_2}(C^3\Pi) = 2750$ K.

nonrigorous approximation in (8), there may be no intersection. In this case, the values of $T_1^{\text{N}_2, \text{CO}}$ will correspond to the point at which the curves come closest together. For our example, this procedure yields the values $T_1^{\text{N}_2} = 2295$ K and $T_1^{\text{CO}} = 3530$ K, which agree well with the values found in direct experiments: $T_1^{\text{N}_2} = 2240$ K (CARS) and $T_1^{\text{CO}} = 3400$ K (diode spectroscopy).

The procedure proposed here has been tested over the entire range of experimental conditions studied. The test confirmed that this procedure is valid. In several cases, the error in the reconstruction of the values of T_1 reaches 20%. Analysis shows that the primary source of error is the deviation of the actual distribution $f(\varepsilon)$ from (8). The difficulty arises because the approximation (8) has to be extended over a fairly broad interval of ε , since the excitation thresholds of the 4^+ bands of the CO system lie in the interval 5.7–9.4 eV, while those of the 2^+ bands of the N₂ system lie in the interval 8.6–12 eV. These results lead us to conclude that in order to improve the accuracy of the method we should seek states of electronically excited molecules for which the entire set of vibrational levels is excited by electrons in an energy interval as narrow as possible.

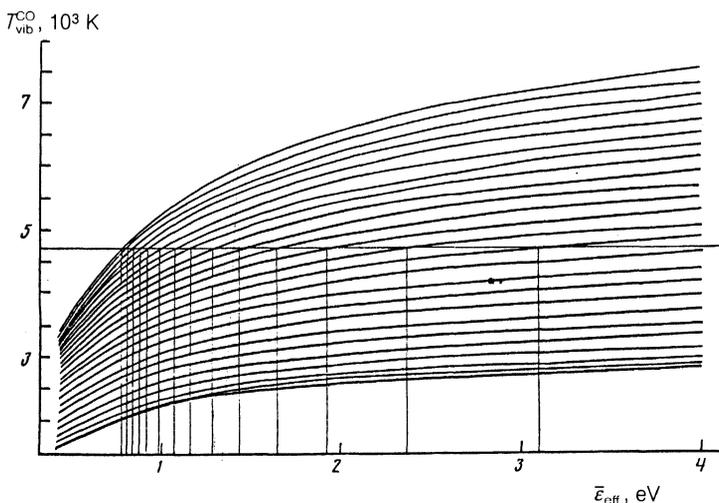


FIG. 5. Vibrational temperatures $T_{\text{vib}}^{\text{CO}}(A^1\Pi)$ versus the effective average energy $\bar{\varepsilon}_{\text{eff}}$ of the high-energy part of $f(\varepsilon)$. The gas temperature is 460 K. The various curves correspond to different vibrational temperatures T_1^{CO} of the ground state. Specifically, T_1^{CO} was varied from 500 K (lower curve) to 5000 K, at steps of 180 K. The horizontal line corresponds to $T_{\text{vib}}^{\text{CO}}(A^1\Pi) = 4700$ K.

4.3. Use of excited electronic states with an equilibrium internuclear distance close to the internuclear distance in the electronic ground state

The spread in the threshold values $\varepsilon_{v^0v}^*$ in (3) can be minimized if the matrix of Franck–Condon factors q_{v^0v} is approximately diagonal, i.e., if

$$\sum_{v, v^0} q_{v^0v \neq v^0} \ll q_{v^0v = v^0}$$

In this case the only differences in the values of $\varepsilon_{v^0v}^*$ are those which stem from the anharmonicity, which can in principle be ignored for our purposes here. It then follows immediately from (3) that the vibrational distributions should be “duplicated”: $N_v \propto N_{v^0}$. It turns out that this exceptionally simple result fits nicely with an equally simple possibility for making use of this result in connection with the CO($B^1\Sigma$) state, which gives rise to the Angstrom bands $B^1\Sigma - A^1\Pi$. The matrix q_{v^0v} for the transition $X^1\Sigma - B^1\Sigma$ has a structure of such a nature that for $v^0 \neq v$ the values of q_{v^0v} are at least two orders of magnitude smaller than the diagonal terms.

Our calculations show that for the temperature intervals $T_1^{\text{CO}} = 500\text{--}5000$ K, and $T_g = 100\text{--}1000$ K and for the interval $\bar{\varepsilon}_{\text{eff}} = 0.4\text{--}5$ eV the relation $T_{\text{vib}}^{\text{CO}*}(B^1\Sigma) = T_1^{\text{CO}}$ holds to within 3%. The reason for this small discrepancy is that all the off-diagonal terms q_{v^0v} have been taken into account in the complete matrix.²² The bands of the CO Angstrom system thus constitute an essentially ideal thermometer for determining T_1^{CO} . If we use the relative intensities of transitions from the levels CO($B^1\Sigma, v = 0, 1$), we do not need to know the value of T_g . However, it is still necessary to find T_g if it is necessary to determine $T_1^{\text{N}_2}$ from (1).

Recalling the discussion in the preceding subsection (4.2), we easily see another possibility for determining the behavior of the distribution function $f(\varepsilon)$ in the high-energy

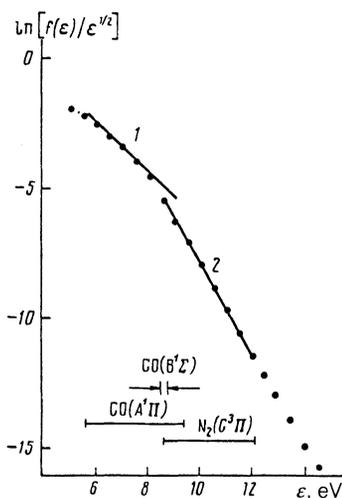


FIG. 7. Part of the function $f(\varepsilon)$ for the discharge conditions $P = 40$ Torr and $i = 15$ mA. The points are calculated from the Boltzmann equation. Solid lines 1 and 2 show an approximation parts of $f(\varepsilon)$ by Maxwellian functions with effective average energies $\bar{\varepsilon}_{\text{eff}}$ found from the spectral measurements. 1—Measurements based on the 4^+ system and the Angstrom system of CO, with $\bar{\varepsilon}_{\text{eff}} = 1.2$ eV; 2—measurements based on the 2^+ systems of N_2 and the Angstrom system of CO, with $\bar{\varepsilon}_{\text{eff}} = 0.8$ eV.

region of the excitation of the electronic states of interest, on the basis of emission measurements. For example, going back to our case of the discharge conditions $P = 40$ Torr and $i = 15$ mA, we note that the measurements yield $T_g = 460$ K, and $T_1^{\text{CO}} = T_{\text{vib}}^{\text{CO}}(B^1\Sigma) = 3400$ K. We then repeat the procedure described above. Specifically, we construct the function (9) [the upper curve in Fig. 6, which corresponds to $T_{\text{vib}}^{\text{CO}}(A^1\Pi) = 4700$ K], from which we find $\bar{\varepsilon}_{\text{eff}} = 1.2$ eV at $T_1^{\text{CO}} = 3400$ K. This effective average energy pertains to the region 5.7–9.4 eV of $f(\varepsilon)$. This region is responsible for the excitation of the 4^+ spectrum of the CO system.

We could carry out some similar manipulations with the results found in measurements of the intensities of the 2^+ system of N_2 . For this purpose we first work from (2) and the value $T_1^{\text{CO}} = 3400$ K at $T_g = 460$ K to find $T_1^{\text{N}_2} = 2240$ K. Using (9) [the lower curve in Fig. 6, which corresponds to $T_{\text{vib}}^{\text{N}_2}(C^3\Pi) = 2750$ K] with $T_1^{\text{N}_2} = 2240$ K, we find $\bar{\varepsilon}_{\text{eff}} = 0.8$ eV. This value pertains to electrons in the energy interval 8.6–12 eV, which are responsible for the excitation of $\text{N}_2(C^3\Pi)$.

Figure 7 shows a part of the function $f(\varepsilon)$. In addition to the Maxwellian regions $\varepsilon = 5.7\text{--}9.4$ eV and $\varepsilon = 8.6\text{--}12$ eV, which correspond to the data mentioned above, we show a theoretical function from the family in Fig. 4. The agreement is good.

4.4. Effect of vibrational relaxation in excited electronic states in measurements of the vibrational temperatures of ground states

This effect is important at pressures $P > 100$ Torr, as was shown above. Once the cross sections and the corresponding rate constants for vibrational relaxation have been determined, there are various ways to take them into account. Apparently the simplest way is to use relation (4) to reconstruct from the experimental populations N_v some values of N_v^0 , which are not distorted by relaxation processes. In other words, we would reconstruct the values which are formed directly by the mechanism of electron-impact excitation. Beyond this point, all the procedures described in Subsections 4.2 and 4.3 remain valid.

5. CONCLUSION

In this study we have combined the methods of laser and classical emission spectroscopy to analyze the origin of the distributions of molecules with respect to vibrational levels of electronically excited states during excitation of electron shells by direct electron impact under the conditions prevailing in a steady-state gas-discharge plasma. The study was carried out over a broad range of gas densities, so it has been possible to see the effect of the vibrational relaxation of short-lived electronically excited states of $\text{N}_2(C^3\Pi)$ and CO($A^1\Pi$) molecules. We have determined effective cross sections for vibrational relaxation in the CO– N_2 –He–Xe– O_2 gas mixture. The general procedure proposed here, which also includes calculations of the electron energy distributions, can be recommended for similar studies of the kinetics of electronically excited molecules in plasmas of various chemical compositions, for a longer list of molecules and their electronic states.

On the basis of the experience gained in these studies,

we have proposed a new version of the method for determining the vibrational temperatures of diatomic molecules in electronic ground states from the intensities in the vibrational structure of electronic spectra. The effect of the electron energy distribution and of vibrational relaxation has been taken into account.

We are indebted to N. N. Sobolev for interest in this study and for discussing it.

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