Investigation of kinetic processes in molecular nitrogen by the CARS method

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The first report is given of the use of a wide-band variant of CARS (coherent anti-Stokes Raman scattering) spectroscopy in a study of the kinetics of distribution of nitrogen molecules between nonequilibrium excited vibrational states. The values of the rate constants of energy exchange between electronic and vibrational levels are found and the parameters of the V–V exchange are determined.

§ 1. INTRODUCTION

Systems of molecules excited to a strongly nonequilibrium state plays an important role in laser physics and in the physics of low-temperature plasmas, and they are used widely in research on physical and chemical kinetics. The most effective method of creating a strongly nonequilibrium molecular gas is excitation by an electric discharge. In this case the distribution of energies between the various degrees of freedom of molecules is governed by the kinetics of excitation of molecules by electrons, as well as by the kinetics of intramolecular (internal) and intermolecular energy exchange. The usual method for investigating these processes involves a study of macroscopic manifestations of a strong nonequilibrium, such as determination of the characteristic time for the establishment of a thermal equilibrium,[1] measurement of the lifetime of a population inversion between some energy levels of molecules, measurements of the velocities of propagation of acoustic and strong shock waves,[2] etc. However, difficulties encountered in a theoretical interpretation of the results obtained by these methods impose familiar restrictions when information is being extracted about elementary processes that govern the physical kinetics of strongly nonequilibrium molecular media. In this respect the recently developed method of coherent anti-Stokes Raman scattering (CARS) has certain fundamental advantages.[3]

The CARS method makes it possible to determine not only the temperature, density, and chemical composition of gases, but also the populations of the individual vibrational and electronic levels of the molecules. This method is particularly effective in studies of kinetic processes in gases composed of homonuclear molecules (for example, H_2, O_2, and N_2) the high symmetry of which imposes a strong hindrance on the optical transitions between vibrational and many electronic states, resulting in major restrictions on the use of the conventional spectroscopic methods. The CARS technique is based on the process of coherent four-wave parametric interactions $\omega_A = 2\omega_L - \omega_S$, where ω_A is the frequency of the recorded anti-Stokes signal and ω_L and ω_S are the frequencies of the biharmonic excitation (the difference $\omega_L - \omega_S$ is tuned to the molecular-vibration frequency Ω). The radiation at the anti-Stokes frequency ω_A appears in a direction governed by the phase-matching condition: $\mathbf{k}_A = 2\mathbf{k}_L - \mathbf{k}_S$, where $\mathbf{k}_L$, $\mathbf{k}_S$, and $\mathbf{k}_A$ are the wave vectors of the radiations with the relevant frequencies.

There are two different variants of the CARS spectroscopy. In the narrow-band variant both lasers (ω_L, ω_S) generate practically monochromatic radiation and the CARS signal appears only at one frequency ω_A. Therefore, when a CARS spectrum has to be determined in a wide range of wavelengths, it is necessary to tune synchronously the emission wavelength of one of the lasers (by varying, for example, ω_S) and the recording wavelength. This method has high sensitivity and good spectral resolution, and it has been used to study the vibrational kinetics of nitrogen.[4] However, a serious shortcoming of a system with consecutive (point-by-point) recording of a spectrum is that the signal is not recorded simultaneously in different parts of the spectrum so that the recording process has to be repeated many times. Moreover, this lack of simultaneity of the recording process results in strong distortions of the spectra because of the instability of radiations emitted by the pump lasers.

The method of parallel recording of a spectrum (i.e., the wide-band variant of CARS) is free of these shortcomings.[5] In this variant one of the lasers generates radiation in a relatively wide spectral range ($\Delta\omega_S$) and the CARS signal is recorded simultaneously in a wide frequency band $\Delta\omega_{AS}$. This method ensures the minimum statistical scatter of the results because it makes it possible to determine in practically one biharmonic laser pulse the populations of several vibrational levels of molecules when the energy difference between them is not constant due to the molecular anharmonicity. Successful applications of the wide-band CARS variant in tackling the problems in vibrational kinetics is reported, for example, in Ref. 6 describing a study of vibrations of polyatomic molecules excited by two-frequency (biharmonic) laser pumping.

We shall report the use of the wide-band CARS variant in a study of the kinetics of the distribution of nitrogen molecules between vibrational states. The fundamental difference between our experiments and those published so far is the high degree of excitation of the vibrational and electronic degrees of freedom of molecules, with spatial homogeneity of the investigated medium retained. Consequently, in contrast to Ref. 4, we were able to record for the first time an increase in the degree of vibrational excitation of molecules because of the relaxation of energy from electronic states.
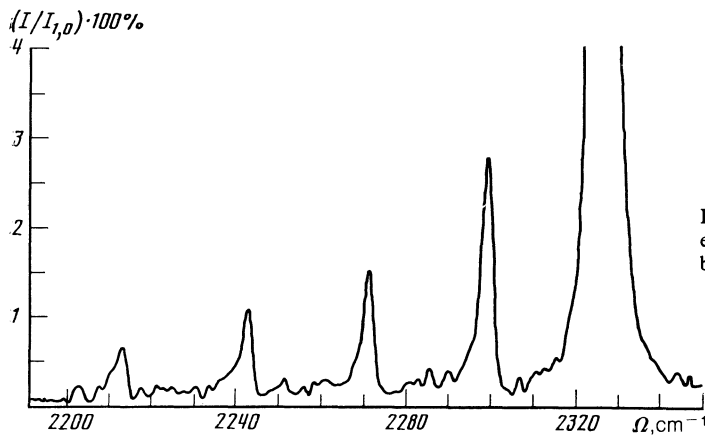
FIG. 1. Coherent anti-Stokes Raman scattering spectrum of vibrationally excited nitrogen, obtained after a time delay of 400 nsec relative to the beginning of a current pulse.

Moreover, in contrast to Ref. 4, we were able to monitor the plasma parameters simultaneously with the process of recording of the CARS spectra. All this not only made it possible to refine the results of previous investigations designed to determine the rate constant of the vibrational–vibrational (V-V) exchange, but to obtain for the first time the experimental values of the rate constants of electron-impact excitation of various vibrational levels of molecules and also the fraction of the energy transferred from the electronic degrees of freedom (as a result of their quenching) to various vibrational levels of the N_2 molecule. The use of numerical calculations in an analysis of our experimental results enabled us to select the correct normalization of the cross section for scattering of an electron by an N_2 molecule.

§ 2. LASER SPECTROSCOPIC SYSTEM FOR THE APPLICATION OF THE WIDE-BAND CARS VARIANT. METHOD AND EXPERIMENTAL RESULTS

A wide-band CARS spectrometer was based on a YAG:Nd^{3+} laser emitting the TEM_{00} mode. The radiation from a master oscillator was amplified by two amplifiers, frequency-doubled ($\lambda_L = 532$ nm), and then used as a laser pump ω_L. The unconverted part of the radiation at the wavelength $\lambda = 1.06\,\mu$ was filtered off from the second-harmonic radiation, frequency doubled, and used to pump an organic-compound laser. The active medium of the organic-compound laser was a solution of 6, 6-aminophenolene in ethanol. A laser attachment ensured that wide-band pump radiation was supplied at the Stokes frequency ($\lambda_S = 606$ nm, $\Delta\lambda = 9$ nm), which corresponds to tuning of the difference $\omega_L - \omega_S$ to the frequency of the Raman resonance of the nitrogen molecule at $\Omega = 2331$ cm^{-1}. A collinear phase-matching scheme was used for the waves participating in the CARS process. Laser beams of frequencies ω_L and ω_S were combined on a dichroic mirror and focused in the investigated object. The CARS spectra were recorded by a multichannel optical analyzer. In addition to this procedure, the spectral range was determined using the same spectrometer and it was found to be 150 cm^{-1} when the resolution was 1.5 cm^{-1}. The use of wide-band excitation at the frequency ω_S in combination with the parallel recording by the multichannel optical analyzer made it possible to dispense with monitoring of the laser pump powers, necessary in the case of

narrow-band CARS spectrometers with consecutive recording of the spectra.

Our CARS spectrometer made it possible to record high-quality spectra of molecular nitrogen as a result of just one laser shot. Moreover, the signal/noise ratio was improved by the process of storage of the output data from a certain number of cycles in the multichannel optical analyzer. The maximum sensitivity of this wide-band CARS spectrometer, defined in terms of detection of the nitrogen molecules in the ground state, was $\sim 10^{17}$ molecules/cm^3.

Nonequilibrium excitation of the nitrogen molecules was due to pulsed self-sustained discharge of ≈ 200 nsec duration (measured at half-maximum of the current pulse). The discharge was initiated between two circular electrodes of 1.7 cm^2 area each and separated by a distance of 1 cm. Reproducibility of the initial conditions was ensured and the pulse repetition frequency was increased by slow circulation of the gas. The main experiments were carried out on nitrogen of technical purity at a pressure of 60 Torr. The current in a homogeneously burning discharge reached 260 A when the voltage across the discharge gap was ≈ 5 kV.

We recorded the CARS spectra of nitrogen in the range of delay times 400 nsec–1 msec from the beginning of the current pulse when the precision of the synchronization was ≈ 100 nsec. The spectra were normalized to the spectrum of the organic-compound laser and to the curve representing the channel sensitivity of the analyzer. The whole process of acquisition, analysis, and readout of the experimental results was controlled by a computer in accordance with a specially written program.

Figure 1 shows a characteristic CARS spectrum of excited nitrogen for a time delay amounting to 400 nsec. The CARS spectra made it possible to determine the relative populations of the vibrational levels by the following procedure.[4] The CARS intensity of an individual vibrational–rotational transition is

$$I_{v,\,v+1} = k^2 [n_v - n_{v+1}]^2 (v+1)^2,$$

where k is a coefficient independent of the level number v; n_v is the relative population of this level. Simple operations yield the normalization condition

$$-(m+1)n_{m+1} + \sum_{v=0}^{m} n_v = \frac{1}{k} \sum_{v=0}^{m} I_{v,v+1}^{1/2},$$
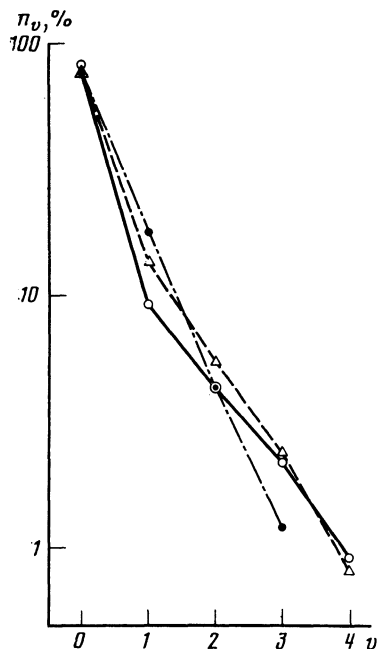
FIG. 2. Distributions of the populations of nitrogen molecules between various vibrationally excited states at different time delays: 400 nsec (continuous lines), 3.2 μsec (dashed lines), 1.4 msec (dash-dot lines).

where $m + 1$ is the number of vibrational–rotation transitions recorded in the CARS spectrum. Assuming that $n_{m+1} = 0$ and that

$$\sum_{v=0}^{m} n_v = 100 \ \%,$$

we obtain the following recurrence formula for the relative population n_v of the level v:

$$n_v = n_{v+1} + [I_{v,v+1}^{1/2}/(v+1)]\left(100\% \Big/ \sum_{v=0}^{m} I_{v,v+1}^{1/2}\right). \qquad (1)$$

The distributions of the populations of various vibrationally excited states of the nitrogen molecule, reconstructed by such a method for time delays of 400 nsec, 3.2 μsec, and 1.4 msec, are plotted in Fig. 2. The kinetics of changes in the relative populations of the levels $v = 0$–4 is shown in Fig. 3.

It should be pointed out that, although the rotational structure of the CARS spectra was not resolved completely, a change in the translational temperature of the gas could be determined from the envelope of the rotational structure. The results of such a determination indicated that the translational temperature T was not affected (to within 50 °C) for delays up to 1.4 msec.

§ 3. THEORETICAL MODEL FOR CALCULATIONS. VALUES OF RATES OF ELEMENTARY PROCESSES

The CARS method makes it possible to determine the evolution in time, governed by the kinetics of excitation and deexcitation of various vibrational states, of the distribution of the populations of molecular levels. It is therefore natural to expect that the experimental results can be used to obtain quantitative information on the rates of the principal ele-

mentary processes which govern the nonequilibrium of the molecular excitation in a low-temperature gas-discharge plasma.

Vibrational excitation of molecules in a gas-discharge plasma is mainly the result of their collisions with high-energy electrons:

$$N + e \xrightarrow{K_e(v)} N(v) + e. \qquad (2)$$

In addition to the e–V processes, the distribution of populations of vibrationally excited molecules is governed by the V–V exchange process between molecules:

$$N(v) + N(v') \xrightarrow{K_{v,v-1}^{v',v'+1}} N(v-1) + N(v'+1), \qquad (3)$$
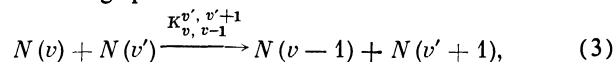
as well as by the V–T relaxation processes of excited molecules:

$$N(v) + N \xrightarrow{K_{v,v-1}} N(v-1) + N. \qquad (4)$$
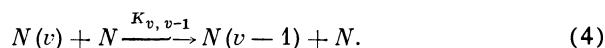
Here, $K_e(v)$, $K_{v,v-1}^{v',v'+1}$, and $K_{v,v-1}$ are the rate constants of the e–V, V–V, and V–T processes.

Estimates obtained using the constants of the reactions (3) and (4) taken from Refs. 4, 7, and 8 show that the characteristic times of the V–V and V–T processes in molecular nitrogen at $p = 60$ Torr are considerably greater than 400 nsec, which was the minimum delay in our experiments. Therefore, the CARS spectra obtained with a delay of ≈ 400 nsec relative to the beginning of a current pulse carry information on the vibrational distribution function of molecules established exclusively by the e–V processes. The results of
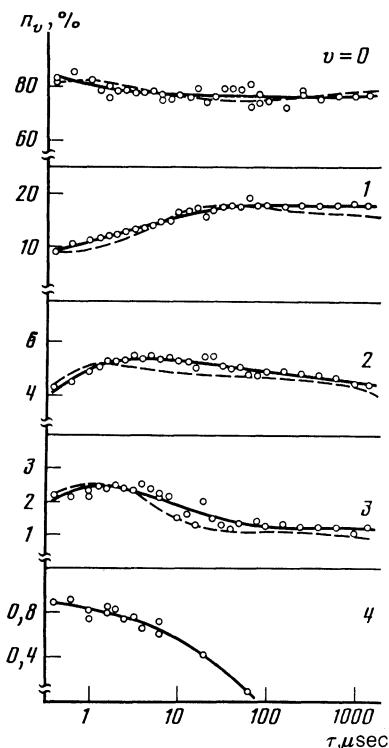

FIG. 3. Time dependence of the relative populations of the levels $v = 0$–4. The points represent the experimental results, the continuous curves are approximations by a fourth-degree polynomial, and the dashed curves are the results of calculations.

TABLE I.

v	1	2	3	4
$K_e(v)$, cm^3/sec, exper. values	$(8.0\pm1)\cdot10^{-9}$	$(4.1\pm0.5)\cdot10^{-9}$	$(2.1\pm0.2)\cdot10^{-9}$	$(8.6\pm0.4)\cdot10^{-10}$
$K_e(v)$, cm^3/sec, calc.	$6.0\cdot10^{-9}$	$3.5\cdot10^{-9}$	$1.95\cdot10^{-9}$	$1.67\cdot10^{-9}$

the calculations reported below indicate that under our experimental conditions we can ignore multistage excitation of the vibrational levels by electrons. Therefore, the kinetics of changes in the vibrational distribution function is described over short times by the following equation:

$$dN(v)/dt = K_e(v)n_e N(0); \qquad (5)$$

here, n_e is the density of electrons in the interior of a plasma, which can be determined by measuring the current density in the discharge using the familiar dependence of the drift velocity of electrons on the ratio E/N (Ref. 9), where E is the electric field in the bulk of the plasma and N is the concentration of the molecules. Under our experimental conditions (allowing for the voltage drops in the electrode layers) the parameter E/N at the half-amplitude of a voltage pulse was ≈ 200 Townsend (Td). Calculations indicated that in fields of this kind the constant $K_e(v)$ depends quite weakly on the parameter E/N [when E/N is increased from 100 to 200 Td, the value of $K_e(v)$ falls by a factor less than 1.2]. When this circumstance is allowed for, the experimentally determined values of the populations of vibrational levels $N(v)$ at the end of a discharge pulse of known duration τ can be used to find the pulse-average value of the constant

$$K_e(v) = N(v)/n_e N\tau.$$

The values of $K_e(v)$ determined in this way are listed in Table I.

The rate constant of the excitation of various vibrational molecular levels $K_e(v)$ by electrons is determined by the nature of the distribution function $f(\varepsilon)$ of the electron energies ε and by the cross sections $\sigma_v(\varepsilon)$ of the processes described by Eq. (2):

$$K_e(v) = \int_0^\infty \sigma_v(\varepsilon) f(\varepsilon) d\varepsilon.$$

In turn, the function $f(\varepsilon)$ is governed by the ratio E/N and by the cross sections of the processes of interaction of electrons with the N_2 molecule. A comparison of the calculated values of $K_e(v)$ with those found experimentally makes it possible to determine the most reliable set of the cross sections for the interaction of electrons with the N_2 molecule.

In a theoretical determination of the constants $K_e(v)$ we used the familiar method[10] to calculate the electron energy distribution function: the values of the cross sections for the vibrational excitation of nitrogen molecules were taken from Ref. 11. These calculations gave values of $K_e(v)$ underestimated by a factor exceeding 2 compared with those found experimentally. Such a large difference cannot be explained by the scatter of the experimental parameters. An

agreement with the experimental results can be obtained by retaining the relative values of the cross sections of the vibrational levels[11] but doubling the absolute normalization factor. The results of such a calculation are presented in Table I. We can see that this ensures a reasonable agreement with the experimental results for the excitation of the first three vibrational levels. The considerable discrepancy between the values of the excitation rate constant of the last observed level may be explained by the fact that in the analysis of the experimental results we ignored the excitation of all higher ($v > 4$) vibrational levels. The total population of these levels may be comparable with the population of the highest of the observed levels.

It should also be pointed out that the knowledge of the populations of the various vibrational states of the N_2 molecule immediately after the end of a discharge current pulse makes it possible to find the fraction of the Joule energy η_v used to excite the vibrational degrees of freedom. Under our experimental conditions this quantity was $\eta_v = 30\%$, whereas a calculation carried out using the set of cross sections from Ref. 11 gave $\eta_v = 14\%$. Doubling of the cross sections for the vibrational excitation compared with Ref. 11 made it possible to account for the experimental value of η_v.

After the end of a current pulse the e–V processes play no significant role in the dynamics of relaxation of the vibrational distribution function. However, the changes of the populations of the various vibrational states of the N_2 molecule are governed by the V–V and V–T processes. Therefore, the experimental results on the time dependences of the populations of the vibrational levels of molecules obtained for this stage make it possible to find the rate constants of energy exchange between various molecular states. With this in mind, we carried out a numerical integration of a system of kinetic equations describing the dynamics of behavior of 50 vibrational levels of nitrogen, together with the equation for the gas temperature. We described the constants $K_{v+1,v}^{v',v'+1}$ (V–V exchange) and $K_{v,v-1}$ (V–T relaxation) by the familiar approximations[7]:

$$K_{v+1,v}^{v',v'+1} = Q_{10}\frac{(v+1)(v'+1)}{[1+\delta(v+1)][1-\delta(v'+1)]}\exp[-\delta_{VV}|v-v'|], \qquad (6)$$

$$K_{v,v-1} = P_{10}v(1-\delta v)^{-1}\exp(v\delta_{VT}), \qquad (7)$$

where Q_{10} and P_{10} are the probabilities of the corresponding processes; δ is a spectroscopic constant; δ_{VV} and δ_{VT} are the reciprocal radii of the V–V and V–T exchange processes.

These calculations showed that the degree of excitation of a gas achieved in our experiments allowed us to consider just the one-quantum exchange processes. The initial condi-
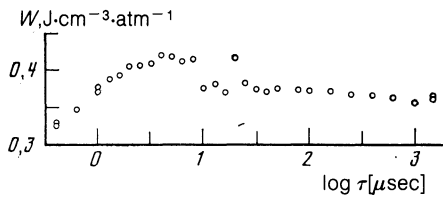
W, J·cm^{-3}·atm^{-1}

FIG. 4. Time dependence of the total energy W stored in the first four vibrational levels of the nitrogen molecules.

tions in our calculations were set by the experimentally determined vibrational distribution function established immediately after the end of a discharge current pulse. Since we determined the populations of only the first four vibrational levels, which corresponded to a weaker excitation of the higher levels, the populations of the levels with the vibrational numbers $v > 4$ were assumed to be initially zero or were found by linear extrapolation of the values of the measured populations. It should be pointed out straightaway that in all the calculations variants the translational temperature of the medium was found to be practically constant and this, firstly, agreed with the experimental results and, secondly, indicated that in the investigated time intervals the V–T relaxation processes were not yet important. Therefore, we matched the calculated and experimentally determined vibrational distribution functions by varying only the V–V exchange constant [Eq. (6)] and two parameters (Q_{10} and the V–V exchange radius δ_{VV}^{-1}) for each of which there were no reliable experimental data. Nevertheless, even simultaneous variation near the published[4,7,12] values of the parameters δ_{VV} (variation by a factor of 5) and Q_{10} (variation by an order of magnitude) failed to give a satisfactory description of the experimentally observed behavior of the level populations $N(2)$ and $N(3)$, particularly their rise during the first few microseconds (Fig. 3). Moreover, we failed to account for the time dependence of the total energy stored in the lower vibrational levels (a graph showing the time dependence of this energy is plotted in Fig. 4). An increase in the populations of the second and third vibrational levels could in principle be associated with the acquisition of energy from higher vibrational states, but the calculations indicated that the characteristic time of this process is considerably greater than in our experiments.

We feel that the most probable mechanism responsible for the increase in the populations of the first vibrational levels at the end of a discharge pulse was relaxation of metastable electronically excited nitrogen molecules, the excitation of which consumed about 70% of the energy deposited in the gas. Assuming that the most effective relaxation was the result of self-quenching of the lower metastable electronic states $A\,^3\Sigma_u^+$,

$$2N_2\,(A^3\Sigma_u{}^+) \xrightarrow{K_T} N_2\,(C^3\Pi_u) + N_2\,(X^1\Sigma_g{}^+, v), \qquad (8)$$
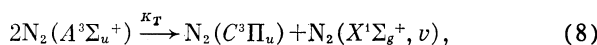
we used the experimental rise of the populations of the vibra-

tional levels a long time after the end of the discharge and the calculated value of the concentration of $N_2(A\,^3\Sigma_u^+)$ immediately after the end of the discharge pulse to find the rate constant of the process (8). The published value of this constant is known very inaccurately: $K_T = (0.2\text{–}2.6) \times 10^{-10}$ cm^3/sec (Ref. 13).

Such a calculation showed that an allowance for the process (8) can account also for the time dependences and values of the populations of the second and third levels $N(2)$ and $N(3)$ (Fig. 3) if we assume the following constants: $K_T = 5 \times 10^{-11}$ cm^3/sec [then 70% of the $N^2(X\,^1\Sigma_g^+, v)$ molecules are formed in the state with $v = 2$, and the remaining 30% molecules are in the state with $v = 3$]; $Q_{10} = 5 \times 10^{-14}$ cm^3/sec; $\delta_{VV} = 2.7T^{-1/2}[\mathrm{K}^{-1/2}]$. The value of the constant Q_{10} was within the range of the scatter of the published data, and the parameter δ_{VV} was 2.5 times less than the values given in Refs. 4, 7, and 12.

We therefore demonstrate experimentally that the wide-band CARS variant makes it possible to determine simultaneously the kinetics of population of several vibrational levels of molecules. The results of our measurements allowed us to determine quantitatively the contribution of various elementary processes to the dynamics of the population of the molecular levels in a low-temperature gas discharge plasma and to find the values of the rate constants of these processes.

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