Measurement of the temperature and spectroscopy of discharge-excited vibrational-rotational states by the CARS method

V. V. Smirnov and V. I. Fabelinskiĭ

P. N. Lebedev Physics Institute, USSR Academy of Sciences
(Submitted 10 August 1978)
Pis'ma Zh. Eksp. Teor. Fiz. **28**, No. 7, 461–465 (5 October 1978)

Resolved spectra of discharge-excited vibrational-rotational transitions are obtained. The constants of the vibrational rotational interaction as functions of the vibrational quantum number, as well as the vibrational and rotational temperatures are measured.

PACS numbers: 52.80.Hc, 33.10.Jz, 33.20.Fb

We have obtained fully resolved spectra of the vibrationally excited states, and measured the vibrational and rotational temperatures in a gas discharge in N_2, by the method of spectroscopy of coherent anti-Stokes Raman scattering of light (CARS). In views of the large brightness of the scattered radiation, this method made it possible to register the spectrum against the background of strong glow of a gas-discharge plasma. The principle of the CARS method and the features of its experimental realization are described in several reviews.[1,2] This method was first used for the investigation of a gas discharge in Refs. 3 and 4.

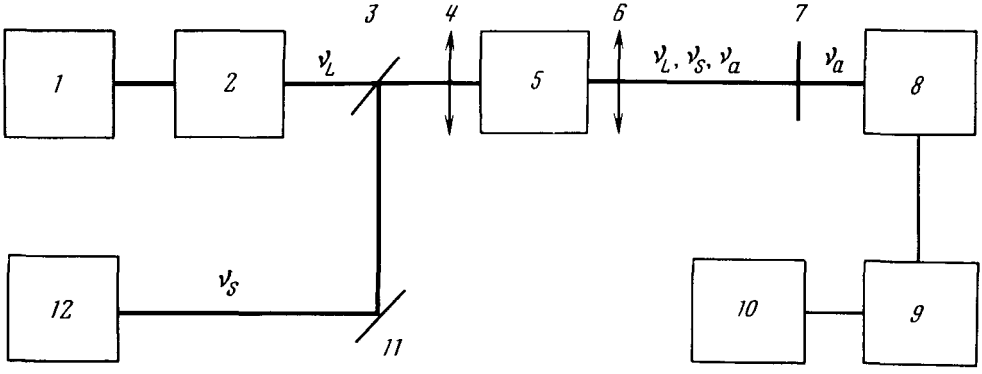

FIG. 1. Experimental setup: 1) YAG : Nd laser (TEM_{00}, $P_L = 5$ mW, $f = 12.5$ Hz, $\Delta\nu_L = 0.01$ cm^{-1}), 2) second-harmonic generator (DCDA, $\eta = 30\%$), 3, 11) mirrors, 4, 6) lenses with $f = 10$ cm, 5) discharge cell, 7) filter, 8) FEU-79 photomultiplier, 9) strobed integrator, 10) automatic recorder, 12) rhodamine-6G dye laser (TEM_{00}, $P_S = 2$ kW, $f = 12.5$ Hz, $\Delta\nu_S = 0.1$ cm^{-1}).

1. The vibrational and rotational temperatures can be determined from the relative intensity of the individual rotational components within a single band (T_{rot}) and in different vibrational bands (T_v):

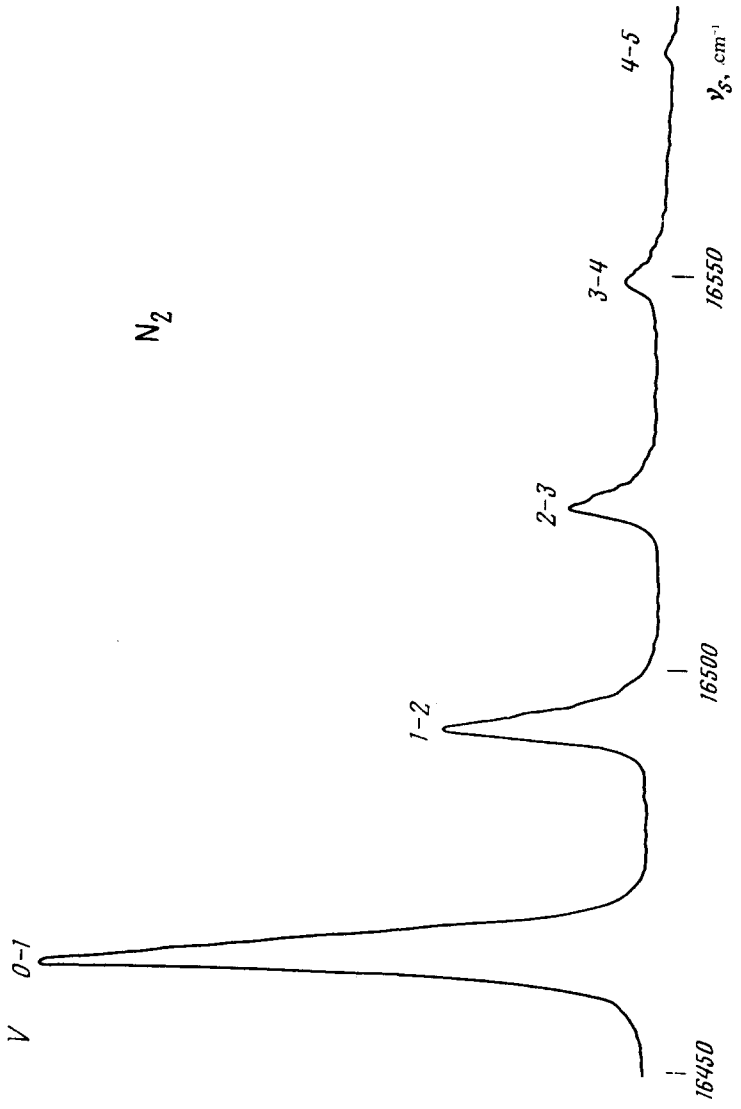

FIG. 2. Vibrational CARS spectrum of nitrogen in a discharge.

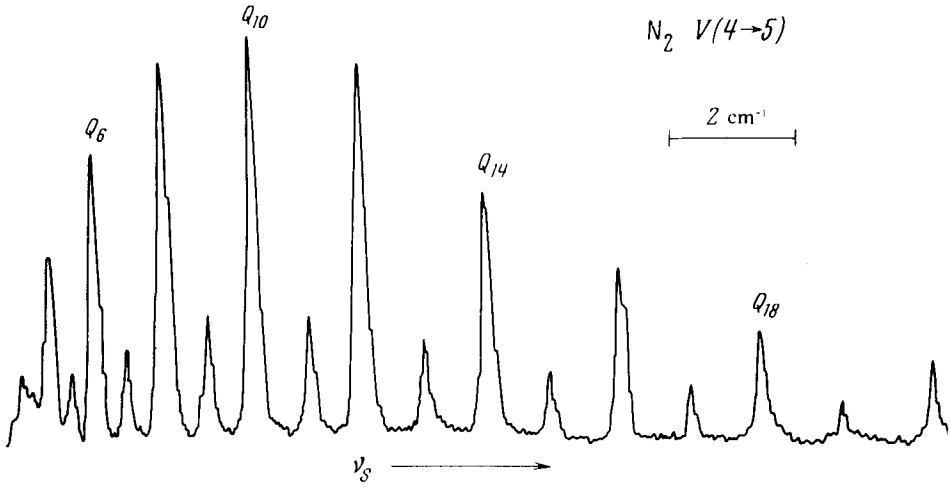

FIG. 3. Structure of Q branch of vibrational transition $v = 4 \rightarrow v = 5$ (resolution 0.1 cm^{-1}).

$$\frac{I_{v,\,J'}}{I_{v,\,J}} = \frac{(2J'+1)^2}{(2J+1)^2} \exp\left\{-\frac{2hc\,B_v}{k\,T_{\text{rot}}}\,[J'(J'+1) - J(J+1)]\right\}, \tag{1}$$

$$\frac{I_{v',J}}{I_{v,J}} = \frac{(v'+1)^2}{(v+1)^2} \exp\left\{-\frac{2hc}{kT_v}\,(\nu_e - 2\nu_e x_e)\right\}, \tag{2}$$

where I_{vJ} is the intensity of the scattering in the CARS spectrum for the transition $(J,v \rightarrow J,v+1)$ with frequency

$$\nu_{v,\,J} = \nu_e - 2\nu_e x_e - a_v J(J+1) \tag{3}$$

v and J are the vibrational and rotational quantum numbers, B_v is the rotational constant, and (3) has been written out in the notation of Ref. 5.

Expressions (1) and (2) are valid under the assumption that the line width and the scattering cross section do not depend on J, the structure of the Q branch is completely resolved, and a Boltzmann distribution has been established both in the vibrational and in the rotational subsystems.

2. We have obtained in our experiments the vibrational–rotational spectra of the Q branch of nitrogen in a gas glow discharge $U = 10$ kV and $I = 7$ mA, in a tube of 15 mm diameter with a discharge-gap length 10 cm at a nitrogen pressure 12 Torr. The CARS spectrometer setup is shown in Fig. 1. This spectrometer yielded spectra that made it possible to determine the population distribution and the vibrational temperature up to levels with $v = 6$. Figure 2 shows a spectrogram of the vibrational transitions. By introducing for each pair of levels some vibrational temperature T_v and using

(2), we obtain $T_v = 2850 \pm 100$ K for $v = 0 \rightarrow 1$, $T_v = 3100 \pm 100$ K for $v = 1 \rightarrow 2$, $T_v = 3400 \pm 150$ K for $v = 2 \rightarrow 3$, and $T_v = 3500 \pm 200$ K for $v = 3 \rightarrow 4$. This points to a noticeable deviation of the distribution of the upper-level populations from a Boltzmann distribution.

To determine the rotational temperature we obtained resolved spectra of the Q branches of the individual vibrational–rotational transitions (see Fig. 3). The distribution of the individual rotational components in the spectra agreed with the Boltzmann distribution with a temperature $T_{\text{rot}} = 395 \pm 15$ K.

3. In the presence of stable molecules in the discharge, the strong population of the upper vibrational states makes it possible to register high-resolution CARS spectra and to obtain spectral information on the structure of molecular states with high vibrational quantum numbers. In the case of molecule dissociation, we can investigate the vibrational–rotational structure of the dissociated fragments. The spectral resolution of the CARS method is determined by the line widths of the employed lasers and it is limited by the Doppler line width. We investigated experimentally the rotational structure of high vibrational states. From the resolved Q-branch spectra we determined the constants α and γ in the formula

$$B_v = B_e - \alpha (v + 1/2) + \gamma (v + 1/2)^2 + \ldots$$

and, using the value of B_0 measured in Ref. 6, obtained the relation

$$B_v = 1{,}99875 - (0{,}01816 \pm 0{,}0003)(v + 1/2) + (0{,}00023 \pm 0{,}00005)(v + 1/2)^2.$$

The authors thank P.P. Pashinin for constant interest in the work, V.N. Zhiganov for help with the experiments, and L.M. Fabelinskaya for help with the reduction of the experimental results.

[1]S.A. Akhmanov and N.I. Koroteev, Usp. Fiz. Nauk **123**, 405 (1977) [Sov. Phys. Usp. **20**, 899 (1977)].
[2]W.M. Tolles, J.W. Nibler, J.R. McDonald, and A.B. Harvey, Appl. Spectroscopy **31**, 253 (1977).
[3]J.W. Nibler, J.R. McDonald, and A.B. Harvey, Opt. Commun. **18**, 371 (1976).
[4]W.M. Shaub, J.W. Nibler, and A.B. Harvey, J. Chem. Phys. **67**, 1883 (1977).
[5]G. Herzberg, Infrared and Raman Spectra of Polyatomic Molecules, Van Nostrand, 1947.
[6]B.P. Stoicheff, Can. J. Phys. **32**, 630 (1954).