DETERMINATION OF THE VIBRATIONAL TEMPERATURE OF CARBON MONOXIDE USING THE ELECTRON BEAM

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The work reported here has led to an expression showing the variation of the intensity ratio for electron-beam-excited electron-vibrational carbon monoxide bands with the vibrational temperature. The experimentally measured vibrational temperatures agree with gas temperatures behind a sonic jet with quenched vibrational temperatures.

Passage of a high-energy electron beam through a low density gas gives rise to several band systems, the excitation mechanism varying from band to band.

Electron-beam measurements of vibrational temperatures in rarified gases are based on the relation holding between the emissivity of the electron-vibrational band of the molecular spectrum and the population of the lower molecular vibrational levels.

It has been shown in [1] that electron-beam diagnostics of low-density gas streams must be limited to those bands of the molecular spectrum which can be excited directly, bands excited through a gaskinetic collision mechanism being unsuitable for this purpose. This is equivalent to requiring that the gas molecules be excited out of their ground states by primary beam electrons and that the band-emitting level not have cascade population. A second requirement is that the lifetime of the emitting level be short.

The bands in the electron-beam-excited emission spectrum of carbon monoxide have been studied in [2]. There it was shown that the only bands suitable for electron-beam diagnostics of carbon monoxide are those of the first negative system of the CO^+ molecular ion ($B^2\Sigma^+ \rightarrow X^2\Sigma^+$ transitions). This band system falls in the 2000-2500 Å range, a region of the spectrum which is accessible to quartz optics; its excitation and emission mechanism are shown schematically in Fig. 1. The beam electrons carry gas molecules from their $X^1\Sigma^+$ ground state into the $B^2\Sigma^+$ state of the CO^+ ion. Since the vibrational levels of this latter state are very short-lived ($4 \cdot 10^{-8}$ sec [3]), perturbations arising from gaskinetic collisions can be considered as of minor significance up to pressures of the order of 0.2 mm Hg at 300°K [2]. Higher excited states of the CO^+ ion do not come into play here, since the $B^2\Sigma^+$ state does not have cascade population. Under these conditions, the emission intensity of the (v_2', v_2'') electron-vibrational band is given by the expression

$$I_{v_2'v_2''} = K(\lambda_{v_2'v_2''}) N_{v_2'} h \nu_{v_2'v_2''} c A_{v_2'v_2''} \tag{1}$$

regardless of the type of optical system used in examining the spectrum. Here the subscript 2 indicates states of the CO^+ ion; v_2' is the number of the vibrational level of the $B^2\Sigma^+$ state; v_2'' is the number of the vibrational level of the $X^2\Sigma^+$; $K(\lambda)$ is a scale factor for the measuring system, a quantity which varies with the emission wavelength and includes the system's transmission coefficient; $N_{v_2'}$ is the population of the vibrational level v_2'; $\nu_{v_2',v_2''}$ is the transition wave number; h is the Planck constant; and c is the velocity of light.

The vibrational levels of the ground state will be well populated if the temperature is reasonably high. The rate of excitation of vibrational level v_2' of the $B^2\Sigma^+$ state by an electron beam of current density i will then be given by [4, 5]

$$\xi = \frac{ci}{e} \sum_{v_1''} N_{v_1''} P_{v_2'v_1''} \tag{2}$$
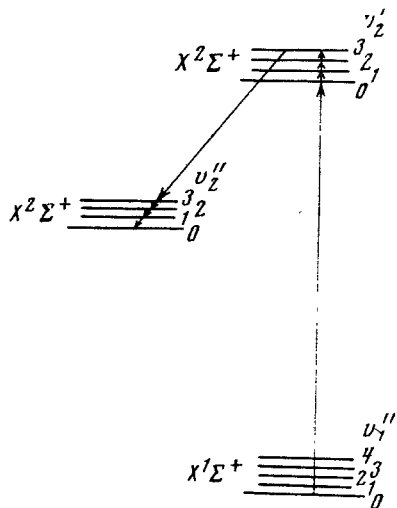
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Fig. 1

$N_{V_1''}$ being the population of vibrational level v_1'' of state $X^1\Sigma^+$, c_1 is a constant, the value of which will vary with the system of units, e is the charge on the electron, and $P_{v_2', v_1''}$ is the strength of high-speed electron-beam excitation of the vibrational band.

With no allowance for quenching collisions, the rate of deexcitation of level v_2' will be determined by transitions from level v_2' to all levels v_2'' of the $X^2\Sigma^+$ state transitions between vibrational levels of the $B^2\Sigma^+$ state being neglected

$$3 = N_{v_2'} \sum_{v_2''} A_{v_2'v_2''}. \tag{3}$$

At equilibrium, the rate of excitation must equal the rate of deexcitation. From this it follows that

$$N_{v_2'} = \frac{c_i}{e} \sum_{v_1''} P_{v_2'v_1''} N_{v_1''} \Big/ \sum_{v_2''} A_{v_2'v_2''}. \tag{4}$$

The intensity of high-speed electron-beam electron-vibrational band excitation from the ground state is given by the equation [6]

$$P_{v_2'v_1''} = \left| \int \psi_{v_2'}(r)\, G(r)\, \psi_{v_1''}(r)\, dr \right|^2. \tag{5}$$

Here $G(r)$ is the perturbation integral for excitation of level v_2' by electron impact, and $\psi_{v_2'}(r)$ and $\psi_{v_1''}(r)$ are the respective nuclear wave functions for the $B^2\Sigma^+$ and $X^1\Sigma^+$ states.

Neglecting the dependence of the perturbation integral on the distance of internuclear separation, one has that

$$P_{v_2'v_1''} = |G_e|^2 q_{v_2'v_1''} \tag{6}$$

$$q_{v_2'v_1''} = \left| \int_0^\infty \psi_{v_2'}(r)\, \psi_{v_1''}(r)\, dr \right|^2, \tag{7}$$

$q_{v_2'v_1''}$ being the Franck–Condon factor for the excitation process.

Drawing on Eqs. (1), (4), and (6), and assuming the ground state vibrational-level populations to follow the Boltzmann equation, the expression for the intensity ratio for two bands with different upper levels takes the form

$$\frac{I_{v_2'v_2''}}{I_{v_{2a}'v_{2a}''}} = \frac{K(\lambda_{v_2'v_2''})\, v_{v_2'v_1''}\, i_{v_2'v_2''} \left[\sum_{v_1''} q_{v_2'v_1''} \exp(-G_{v_1''} hc/kT) \right] \Big/ \sum_{v_1''} A_{v_2'v_2''}}{K(\lambda_{v_{2a}'v_{2a}''})\, v_{v_{2a}'v_{2a}''}\, A_{v_{2a}'v_{2a}''}\, i_{v_{2a}'v_{2a}''} \left[\sum_{v_1''} q_{v_{2a}'v_1''} \exp(-G_{v_1''} hc/kT) \right] \Big/ \sum_{v_{2a}''} A_{v_{2a}'v_{2a}''}}. \tag{8}$$

Here $G_{v_1''}$ is the energy of vibrational level v_1'' of the ground state, T is the vibrational temperature, and k is the Boltzmann constant.

The scale constants depend on the wavelength and are, in general, unknown; the right-hand side of Eq. (8) is a function of the ratio of these constants, $K(\lambda_{v_2'v_2''})/K(\lambda_{v'_{2a}v''_{2a}})$, for given values of transition probabilities $A_{v_2'v_2''}$ and $A_{v'_{2a}v''_{2a}}$. Determination of the scale constants would require that the optical system be specially calibrated with respect to a standard light source, a matter of considerable difficulty since one would be working in the ultraviolet region of the spectrum. These constants were eliminated by dividing (8) by the expression for the intensity ratio for these same bands at a vibrational temperature so low that the population of the upper vibrational level can be neglected in comparison with that of the zeroth level. For carbon monoxide, this condition is met even at 300°K. The expression for the reduced band-intensity ratio then takes the form

$$F(T) = \left(\frac{I_{v_2'v_2''}}{I_{v_{2a}'v_{2a}''}} \right)_T \left(\frac{I_{v_2'v_2''}}{I_{v_{2a}'v_{2a}''}} \right)_{T=300°K}^{-1} = \frac{q_{v_{2a}'0} \sum_{v_1''} q_{v_2'v_1''} \exp(-G_{v_1''} hc/kT)}{q_{v_2'0} \sum_{v_1''} q_{v_{2a}'v_1''} \exp(-G_{v_1''} hc/kT)}. \tag{9}$$
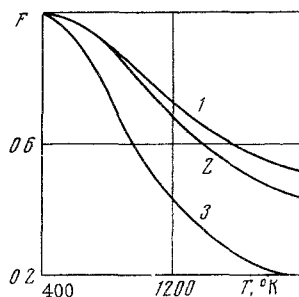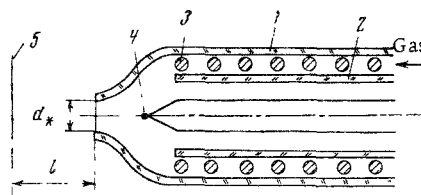
Fig. 2

Fig. 3

Fig. 4

Equation (9) contains only the Franck−Condon factors for band excitation and the ground state energy parameters. The Franck−Condon factors in question here are given by expressions of the type of (7) for the various vibrational levels of the $X^1\Sigma^+$ and $B^2\Sigma^+$ states. Values obtained in this way are given in [6]. Rather precise values of the vibrational energy levels of the $X^1\Sigma^+$ state can be found in [7].

Equation (9) is transcendental in T and of a form which does not, in general, have a solution. The vibrational temperature was obtained by developing the F(T) function on the Mir−1 computer, working in 50° steps from 400 to 2000°K. The results of these calculations on the band-intensity ratios I_{01}/I_{23}, I_{12}/I_{23} and I_{03}/I_{36} for the first negative system of the CO^+ ion are shown in Fig. 2. Curves corresponding to fixed upper vibrational level and different lower vibrational levels coincide, just as predicted by Eq. (9). The result is that the intensity ratios I_{03}/I_{25} and I_{03}/I_{36} are identical with the ratios I_{01}/I_{23} and I_{01}/I_{34}. Analysis shows that the most suitable bands for the present purposes would be those for which $\Delta v = v_2' - v_2'' = -3$, i.e., the bands 0.3, 1.4, 2.5 and 3.6. The band-intensity ratios I_{01}/I_{12} and I_{03}/I_{14} were found to be only weakly temperature dependent.

The calculated results of Fig. 2 can be used to obtain vibrational temperatures for any experiment in which the intensity ratios of these selected bands have been measured. The accuracy of such determination will depend on the accuracy of measurement of the band-intensity ratios, on the validity of describing the excitation process in terms of Franck−Condon factors, and on the accuracy of determination of the values of these factors.

The results of these calculations have been compared with values of the F(T) function for the first negative system of CO^+ bands as measured during expansion of carbon monoxide in vacuum.

Measurements were made in a low-density aerodynamic tube [8], working in the free carbon monoxide flow behind a sonic nozzle. The gas was excited by a 20 keV electron beam and the emitted light focussed by a quartz lens onto the slit of an SPM-2 monochromator equipped with a quartz prism and an FÉU-39 photomultiplier. The unamplified signal from the multiplier was recorded with an ÉPP V-60 potentiometer. Band intensities were recorded on the tape of the apparatus, the spectrum being scanned throughout the sequence of $\Delta v = -3$ and $\Delta v = -1$ bands. The error of determination of the intensity ratios was fixed by the stability of operation of the photomultiplier and potentiometer, and amounted to no more than ± 2%.

The electron beam was generated by a magnetically focussed two-lens electron gun which gave a narrow well-defined beam in the working area of the low-density aerodynamic tube. By using a separate vacuum system, it was possible to reduce the pressure of the neighborhood of the cathode element of the gun to 10^{-5} mm Hg, even with pressures in the working area of the aerodynamic tube as high as 1 mm Hg.

The electron emitter was a vacuum-baked tablet of tantalum hexacarbide. Stability of emission was attained by having a tungsten wire heater to heat the tablet to at least 1600°C. All of the heated elements of the cathode of the gun were made from either molybdenum or tantalum.

A 20-keV accelerating potential was applied to the cathode of the gun, and the control potential applied to a special control electrode. By carefully stabilizing the accelerating and control potentials, and the magnetic lens currents, it was possible to obtain a 2-3 ma beam, 1.5-2 mm in diameter, which would remain stable to within ~2% over an 8 h operating period.

The gas was heated in an exchanger of the type shown schematically in Fig. 3. The nichrome coil heating element 3 was inserted in the space between the two coaxial quartz tubes 1 and 2. The outermost of these tubes was constructed to form a sonic nozzle of 3 mm critical diameter. The gas temperature was determined with the aid of the standard platinum−platinum-iridium thermocouple 4. The temperature and pressure of the gas in the forechamber were determined through the inner tube. The electron beam 5 was set 10 mm from the nozzle opening.

The retarding pressure was selected so that the vibrational temperature could be frozen at a value close to that of the retarding medium. It has been shown in [9] that the relaxation time of carbon monoxide at $1500°K$ is 10^{-3} sec·atm, or $5.4 \cdot 10^{-3}$ sec at a maximum retarding pressure of 140 mm Hg. Thus, the time required for vibrational relaxation was considerably greater than the $6 \cdot 10^{-4}$ sec required for passage of the gas from the point at which the temperature was to be measured to the point at which spectral observations were to be carried out. By working in the free flow it was possible to obtain narrow bands with low rotation temperature thus avoiding the possibility of band overlap.

Experiments were carried out over the interval from 300 to $1100°K$. Heater problems made it impossible to go to higher temperatures. The results on the band-intensity ratios I_{01}/I_{23} and I_{03}/I_{36} are shown in Fig. 4., the full curves indicating calculated values, and the circled points, values obtained experimentally. The agreement here was to within ± 5%, the limit of error in the measurement of F(T). The fact that temperatures obtained from the 2.3 and 3.6 bands agreed to within the limits of experimental error could be taken as indirect indication of Boltzmann law vibrational-level populations in the ground state of the molecule at the quenched temperature.

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