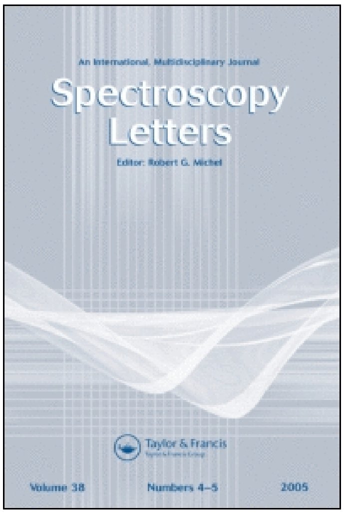

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Vibrational Temperatures of Some Molecules in a Hollow Cathode Discharge

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VIBRATIONAL TEMPERATURES OF SOME MOLECULES IN A HOLLOW CATHODE DISCHARGE

KEY WORDS : vibrational temperature, hollow cathode, excitation process, N_2, CN

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ABSTRACT

Investigation of vibrational energy distributions of molecules excited in a hollow cathode discharge has been presented here. The vibrational temperatures of the CN, N_2 and N_2^+ molecules have been measured at different experimental conditions. The excitation processes in HCD have been discussed.

INTRODUCTION

There has been a great, increasing interest in glow discharge sources, including a hollow cathode discharge (HCD), in the last years. These sources have found an application in spectrochemical analysis by atomic absorption , atomic fluorescence and atomic and molecular emission spectroscopy. The great attention, recently paid, to glow discharges is also due to the search for new atomization sources.[1,2] So far hollow cathode discharge lamps have mainly been employed for AAS and AAF although in emission, as well as other glow discharges, the hollow cathode has successfully been used to analyze various samples.[3-5]

In addition to atoms and ions low pressure plasma almost always consists of diatomic molecules. Intensities of diatomic molecular spectra indicate that under some experimental conditions a meaningful part of an analyzed element may exist as a diatomic compound. This has been successfully applied to determination of traces of some elements (e.g. fluorine[6,7]) by means of molecular spectra.

A number of studies has been devoted to measurements of excitation (atoms and ions) and rotational (molecules) temperatures in HCD[8-12] while problem of vibrational temperatures (vibrational energy distributions of molecules) has been rather omitted.

The present study has been undertaken to investigate vibrational energy distributions of selected molecules to extent our knowledge on spectroscopic characteristics of the hollow cathode discharge. Such an information could bring us more closely to understanding of mechanisms of energy exchanges between species being plasma components in HCD and better characterization of processes in this plasma source.

EXPERIMENTAL

A demountable hollow cathode lamp with a quartz window was used here. Conventional, uncooled cathodes were made of graphite and copper. Dimensions of the cylindrical cathodes were : 40 mm total length, 30 mm bore depth, 4 and 6 mm inner and outer diameter, respectively. The cathodes were empty or they contained a small amount (0.05 g) of solid ($CaCl_2$ or $Ca_3(PO_4)_2$) . Argon (with a small amount of nitrogen) flowing continuously through the lamp under a low pressure was a carrier gas. The discharge was operated at currents of 50, 75, 100 and 125 mA. Spectra were recorded by means of a monochromator (Bentham M300HR) using a holographic grating with 1800 grooves/mm. The monochromator cooperated with a microcomputer system (IBM PC/AT). The radiation from the hollow cathode discharge was focused on the entrance slit of the monochromator by a single spherical lens. The entrance slit widths of monochromator and photomultiplier were adjusted to obtain as high as possible high resolution at a reasonable level of signal and a good ratio of signal to noise. The radiation of the hollow cathode was taken from a zone located centrally in the analyzed plasma. Spectrum of a standard lamp of known intensity versus wavelength served to take into account a variation of a photomultiplier sensitivity with wavelength. Programs have been written in

TurboBasic and TurboPascal 5.0 to analyze files of collected spectroscopic signals, reduce data (determine temperatures) and review results in numeric and graphic forms.

MOLECULAR SPECIES EXCITED IN HCD

Spectra of atoms, ions (singly ionized atoms) and diatomic molecules have been excited in the hollow cathode discharge. A large number of both atomic and ionic lines of argon, being the carrier gas has been observed. Spectra of N_2, N_2^+ and CN (in discharge with the graphite cathodes) were prominent, quite well developed and intense. Some band spectra of the N_2 ($C^3\Pi$ - $B^3\Pi$), CN ($B^2\Sigma^+$ - $X^2\Sigma^+$) and N_2^+ ($B^2\Sigma^+$ - $X^2\Sigma^+$) molecules recorded at current of 100 mA are shown in Fig. 1. The CaCl and CuCl molecule spectra were recorded if $CaCl_2$ was placed in the copper cathode. The CaCl bands observed in the range 615 to 625 nm were very strong and severely overlapped. Bands of CuCl observed in the visible were relatively weak. The experiments were performed using a "dry" argon and only the OH $A^2\Sigma^+$ - $X^2\Pi$ 0-0 band at 306.36 nm of very low intensity was observed here. The NO bands were also very weak. At high currents (above 100 mA) weak band spectra of the C_2 and CO molecules could be recorded if graphite cathode was used. No bands of the PO molecule were identified in analyzed spectra.

Absolute intensities of species excited in HCD have changed with current, pressure (what is well known) and also depended on the composition of the plasma. The presence of both N_2 and CaCl has decreased

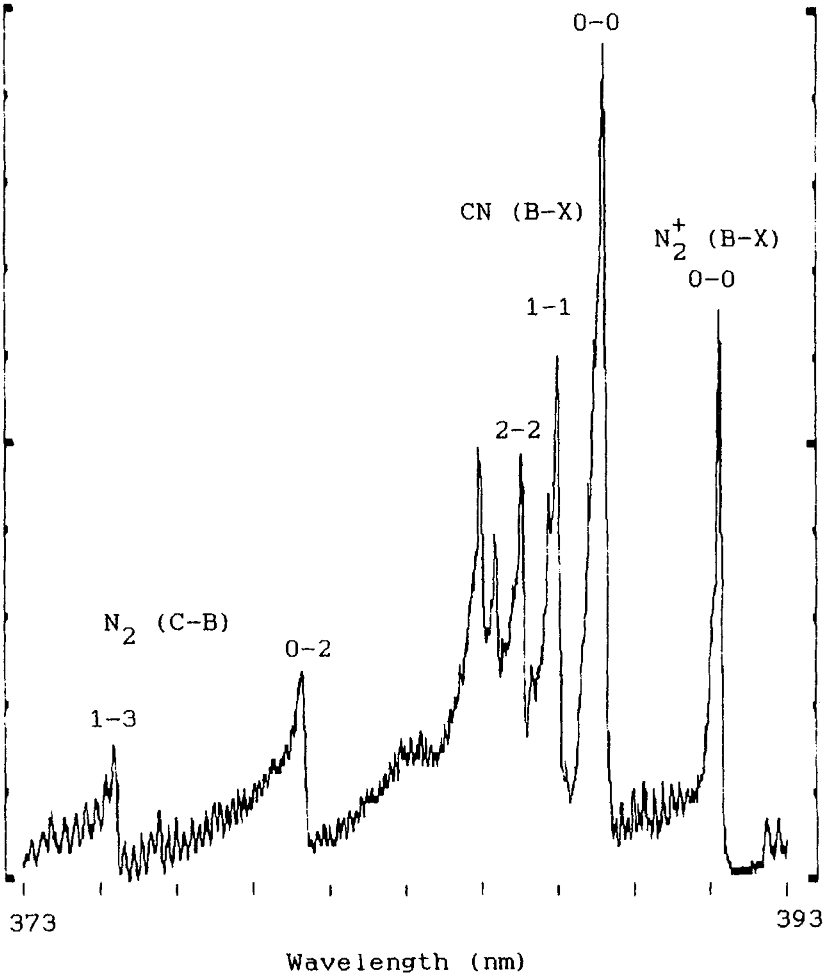

FIG. 1. A part of plasma emission spectrum excited in the hollow cathode discharge.

the intensities of copper and argon lines. The N_2, N_2^+ and CN spectra increased intensity with current, but only for the CN molecule the intensity rise was remarkable.

THEORY - BASIC RELATIONS

Diatomic molecules emit a great number of rotational lines which in the UV and visible spectral ranges correspond to electronic-vibrational-rotational transitions.

Rotational lines originating from the the same vibrational transition v'-v" form a band. The bands corresponding to the same electronic transition form a system. The band intensity, $I_{v'v''}$, which is a sum of intensities of rotational lines forming the band can be written[13]:

$$I_{v'v''} = C\, n_{v'}\, \nu^{4}_{v'v''}\, |R_e(\bar{r}_{v'v''})|^2\, q_{v'v''} \qquad (1)$$

where C - a coefficient, v' and v" - vibrational quantum numbers of the lower and upper states, $n_{v'}$ - number density of emitting molecules, Re - the electronic transition moment, $\bar{r}_{v'v''}$ - r-centroid, $q_{v'v''}$ - Franck-Condon factor, $\nu_{v'v''}$ - the band wavenumber.

Usually, $|R_e(\bar{r}_{v'v''})|$ is a constant value, in practice. Considering that fact one can easily obtain from Eq. (1) and the Boltzmann law applied to vibrational levels of diatomic molecule :

$$\ln\,(I_{v'v''}\nu^{-4}_{v'v''}q^{-1}_{v'v''}) = \text{const} - G(v')k^{-1}T^{-1}_{vib} \qquad (2)$$

where T_{vib} is the vibrational temperature, characterizing vibrational energy distributions, G(v') is the vibrational energy of the upper state. The vibrational energy of an electronic state is

$$G(v) = \omega_e(v+\frac{1}{2}) - \omega_e x_e(v+\frac{1}{2})^2 + \omega_e y_e(v+\frac{1}{2})^3 - \ldots \qquad (3)$$

where ω – vibrational constant, x and y – anharmonic constants, index "e" – denotes equilibrium constants. For most molecules, only values of ω_e and $\omega_e x_e$ are known,[14] but it is sufficient to calculate G(v) with quite good accuracy for low vibrational levels, which are as a rule used to determine the vibrational temperature.

MEASUREMENTS OF THE VIBRATIONAL TEMPERATURE

The N_2, N_2^+ and CN molecules have been used as thermometric species to determine vibrational energy distributions (the vibrational temperatures). Each molecule had a various origination. Neutral nitrogen was introduced in a small amount mixed with argon. The N_2^+ molecule was produced by a reaction of ionization of nitrogen. The CN molecule was the product of a reaction between the cathode nitrogen and carbon being the cathode material.

Bands of the $C^3\Pi - B^3\Pi$ system have been used for the N_2 measurements. Practically, all temperature measurements of N_2, reported so far, have been based on this band system. Bands of the $\Delta v = -2, -1, 0$ sequences have selected taking into account overlapping of individual bands by other atomic and molecular spectra. The N_2^+ spectrum observed here was

TABLE 1

Molecular bands and their spectroscopic data used for the vibrational temperature measurements (v' and v' – vibrational quantum numbers, G(v) – vibrational energy λ – wavelength, $q_{v'v''}$ – Franck–Condon factor).

Molecule (system)	v'	G(v') (cm^{-1})	v'–v"	λ (nm)	$q_{v'v''}$
N_2	0	1017	0–2	380.49	0.145
(B–X)	1	3016	1–3	375.54	0.202
			1–0	315.93	0.388
	2	4994	2–4	371.05	0.169
			2–1	313.60	0.335
	3	6986	3–5*	367.19	0.102
			3–2	311.67	0.204
N_2^+	0	1204	0–0	391.44	0.6509
(C–B)	1	3759	1–1	388.43	0.2226
CN	0	1077	0–0	388.34	0.9179
(B–X)	1	3200	1–1	387.14	0.7795
	2	5284	2–2	386.19	0.6754
	3	7326	3–3	385.47	0.5929
	4	9328	4–4**	385.04	0.5279

* – not in all the experiments the band was measurable

** – this band was not used in final calculation not well developed. The $B^2\Sigma^+ - X^2\Sigma^+$ 0-0 and 1-1 bands of N_2^+ have been measured. But if the CN bands were excited there was not possibility to measure the low intensity 1-1 band on the background of a strong spectrum of CN. The CN $B^2\Sigma^+ - X^2\Sigma^+$ band system was well developed. The most remarkable were bands of the $\Delta v = 0$ sequence. The N_2, N_2^+ and CN bands used for the vibrational temperature determination are listed with their wavelengths, vibrational energies of the upper states and values of Franck-Condon factors in Table 1. Only intensities of first bands in the analyzed sequences were easily measurable with a high accuracy. All next bands of the sequences were measured under conditions of considerable overlapping from other vibrational bands. This molecular background was carefully taken into account when determining the band intensities.

The measurements have been performed at various experimental conditions and the least squares procedure has been applied to determine the vibrational temperatures of the N_2 and CN molecules. The 4-4 band of the CN $B^2\Sigma^+-X^2\Sigma^+$ system was of much higher intensity than that expected from the Boltzmann distribution (due to overpopulation by the 5-5 band) and was not taken into account at final calculations of temperature.

The least squares procedure has been applied to determine the vibrational temperatures of the N_2 and CN molecules. The results obtained for N_2 and CN are listed in Table 2.

The vibrational temperature of N_2^+, evaluated from intensities of the 0-0 and 1-1 bands, has been determined to be between 6200 and 6700 K.

TABLE 2

The vibrational temperatures of the N_2 and CN molecules measured under different experimental conditions, in the Ar + N_2(traces) atmosphere at pressure of 7 Torr.

Molecule	Discharge cathode/sample	Current (mA)	T (K)
N_2	Cu	50	3200
	Cu/$Ca_3(PO_4)_2$	50	3500
		75	3100
	C/$Ca_3(PO_4)_2$	50	3100
		75	3000
		100	3300
		125	3400
CN	C/$CaCl_2$	50	6500
		75	6200
		100	6700
		125	5900
	C/$Ca_3(PO_4)_2$	50	6600
		75	6500
		100	6100

Chosen Boltzmann plots for the N_2 and CN molecules are shown in Fig. 2. It can be seen from Fig. 2 that the lowest vibrational levels of the N_2 $C^3\Pi$ and CN $B^2\Sigma^+$ states are populated here according to the Boltzmann distribution.

The vibrational temperatures of the CN and N_2^+ molecules are in a good agreement. The vibrational

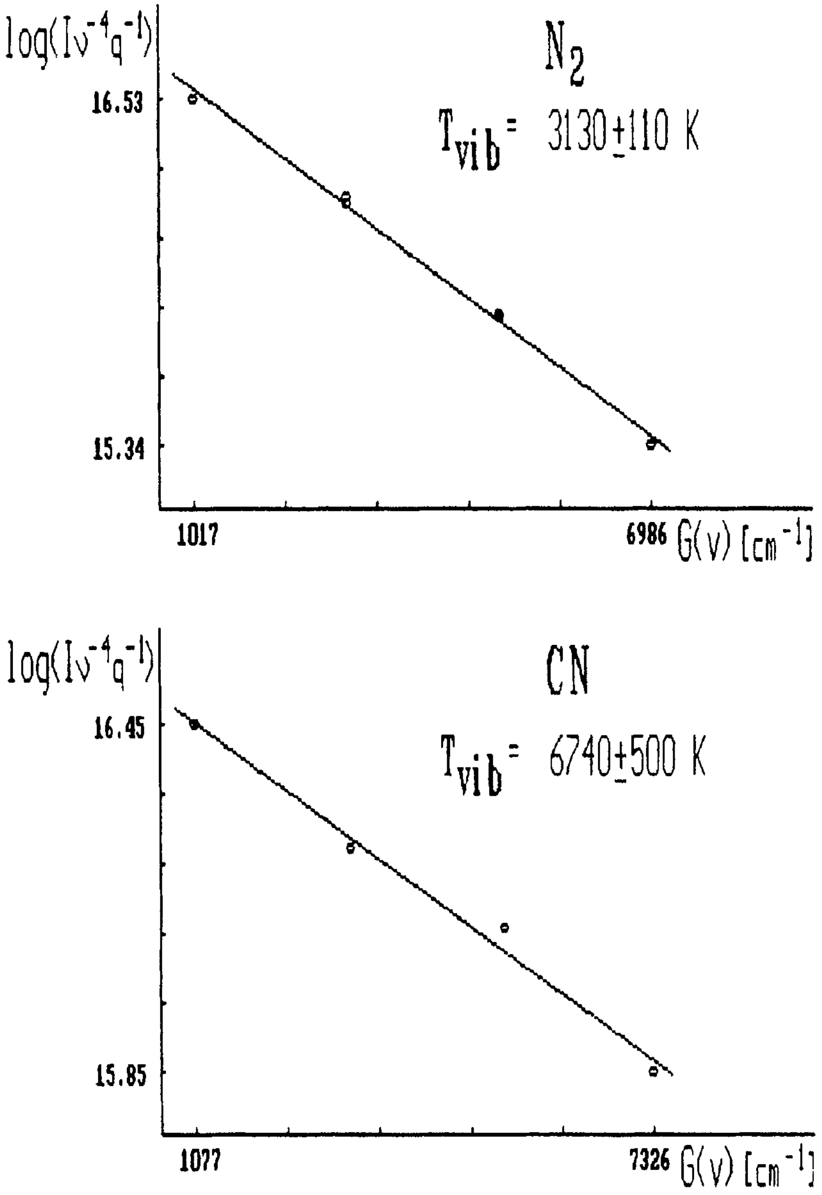

FIG. 2. The Boltzmann plots for the N_2 and CN vibrational levels.

temperature of N_2 obtained here is very well consistent with that derived in glow discharge (Grimm lamp) by Büger (3000 K from 380.5, 375.5 and 371.1 nm bands).[15]

DISCUSSION

Lower values of the vibrational temperature of the N_2 molecule, in comparison with the CN and N_2^+ temperatures are very likely related to spectroscopic properties of N_2 (i.e. existence of metastable states).

The vibrational temperatures of molecules (CN, N_2^+) in the hollow cathode discharge, have been found here to be similar to the excitation temperatures of atoms ($T_{vib} \simeq T_{ex}$). The rotational temperature is as a rule, very close to the translation temperature ($T_{rot} \simeq T_{trans}$). It suggests that not only atom-electron and molecule-electron collisions but also atom-molecule collisions may play an important role in achievement of an equilibrium in energy distributions. The energy exchange processes dominating in the atom-molecule collisions should be :

$$\Delta E_{vib}(\text{molecule}) = \Delta E_{el}(\text{atom}) \quad \text{(i)}$$
$$\Delta E_{el-vib}(\text{molecule}) = \Delta E_{el}(\text{atom}) \quad \text{(ii)}$$
$$\Delta E_{rot}(\text{molecule}) = \Delta E_{kin}(\text{atom}). \quad \text{(iii)}$$

The example for the second case (ii) may be the reaction of the charge transfer :

$$Ar^+ \, (^2P) + N_2 \, (X^1\Sigma^+, 0) = Ar \, (^1S) + N_2^+ \, (X^2\Sigma^+, v)$$

No clear dependence of the vibrational temperature on experimental conditions has been observed here.

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REFERENCES

1. B. M. Patel and J. D. Winefordner, Can. J. Spectrosc. **1987**; **32** : 138.
2. C. L. Chakrabarti, K. L. Headrick, J. C. Hutton, B. Marchand, M. H. Back, Spectrochim. Acta **1989** ; **44B** ; 385.
3. R. Mavrodineanu, J. Res. Nat. Bur. Standards **1984** ; **89** : 143.
4. R. De Marco and D. Kew, Spectrochim. Acta **1985** ; **41B** : 591.
5. S. Caroli, J. Anal. Atom. Spectrosc. **1987** ; **2** : 661.
6. K. Tsunoda, H. Haraguchi and K. Fuwa, Spectrochim. Acta **1980** ; **35** : 715.
7. J. Borkowska-Burnecka, W. Zyrnicki, Anal. Lett. **1985** ; **18** : 1539.
8. J.S. Dobrosavljevic and M. Marinkovic, Spectrochim. Acta **1974** ; **29B** : 87.
9. D.M. Mehs and T.M. Niemczyk, Appl. Spectrosc. **1981** ; **35** : 66.
10. W. Żyrnicki and J. Poślednik, Spectrochim. Acta **1985** ; **40B** : 995.
11. J.A.C. Broekaert, Bull. Soc. Chim. Belg. **1977** ; **86** : 395.

12. W. Zyrnicki, Z. Tomasik, I. Nowicka, Spectrosc. Lett. **1984** ; **17** : 207.

13. G. Marr, "Plasma Spectroscopy", Elsevier Pub. Co., London 1968.

14. K.P. Huber, G. Herzberg, "Molecular Spectra and Molecular Structure" (IV. Constants of Diatomic Molecules). D. Van Nostrand Co., Inc., N.York 1957.

15. P.A. Bürger, Z. Naturforsch. **1975** ; **30A** : 216.

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