SPECTROSCOPIC STUDY OF CHEMILUMINESCENCE

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A b s t r a c t. Chemiluminescent low-pressure flame has been found to be an excellent source to excite spectra of molecules hardly to be produced at other experimental conditions. Spectroscopic diagnostics of plasma usually employs easily resolved spectra of light molecules such as N_2, N_2^+, OH, CN or CH. In the present study, spectra of the $a^3\Sigma_u^+$ $(a_1 1_u)$ − $X^1\Sigma_g^+$ $(X0_g^+)$ transition of the Bi_2 molecule produced in chemiluminescence from the $Bi_x/O_2(a^1\Delta, b^1\Sigma^+)$ system were used to determine rotational and vibrational temperatures. Spectra were recorded using a high-resolution Fourier-transform spectrometer (Bruker IFS 120 HR) in the spectral range from 3000 to 7000 cm^{-1}. The R, Q and P branches of the 2-3 and 6-0 bands served for the rotational temperature measurements. The vibrational temperature was derived from $\Delta\upsilon=-3$ sequence bands of the a-X transition. The both temperatures were close together and near 330 K. It indicates that for the chemiluminescent flame occurs complete rotational and vibrational relaxation.

K e y w o r d s: chemiluminescent flame, bismuth dimer, temperature measurements, rotational temperature, vibrational temperature, FTIR spectra.

INTRODUCTION

Temperature of a cold plasma can be determined by means of thermocouple or using pyrometric measurements. Thermocouple can introduce some disturbances of the plasma flow and a disadvantage of the pyrometric measurements is the strong dependence of the monochromatic radiation of the emitting surface on observation geometry. A very suitable and not disturbing method of plasma diagnostics is emission spectroscopy. Spectroscopic diagnostics of plasma employs spectra of atoms, ions and diatomic molecules. The determination the plasma temperature has been the object of many papers. Excitation (or ionisation) temperature has been determined for different plasmas generated both in glow and hollow cathode discharges [1], microwave torch [2,3], dielectric barrier discharge [4,5] and inductively coupled discharge [6,7]. Such parameters as temperature values

provide some information about plasma equilibrium, ionisation, excitation processes and chemical reactions. For determining the gas kinetic temperature in different plasmas methods based on optical emission spectroscopy are widely used. The excellent diagnostics tools are methods based on spectra of diatomic molecules formed in plasma. The rotational plasma temperature (T_r) is close to gas kinetic temperature (T_g) at an assumption that rotational-translational relaxation is sufficiently fast to equilibrate T_r and T_g. Commonly used molecules serving for rotational temperature measurements are light molecules such as N_2, O_2, H_2, CN, CH, C_2, OH, SiH (see e.g. [8-10]). Heavy molecules have not been used for spectral diagnostics, mainly due to their spectra rotationally resolved are hardly to be recorded. In many experimental cases, it is difficult to obtained well-resolved rotational spectra mainly due to low resolving power of spectral equipment used. In the case of plasma with very weak light emission or plasma with turbulent flow a large entrance slit must be applied and/or time resolved intensity measurements are necessary in order to have a sufficiently strong signal recorded by the photo-detector. Some workers used partially resolved molecular spectra for evaluation of gas temperature through comparison of simulated and experimentally obtained spectra [11,12]. However, such an approach does not seem to be very reliable.

For heavy molecules, the spectral resolution must be especially high due to very small energy differences between the rotational levels. Application of the high resolution Fourier-transform spectrometer to record rotational spectra is very helpful to obtain satisfactory resolution even for heavy particles.

For the first time in the present work, heavy molecule spectra have been used for plasma diagnostics. The well resolved spectrum of bismuth dimer, the heaviest stable diatomic molecule, produced in the chemiluminescence reaction between Bi_x vapour and metastable oxygen has been applied for rotational and vibrational temperature measurements.

EXPERIMENTAL SETUP

The near-infrared spectra of the Bi_2 molecule were obtained in a low-pressure chemiluminescent flame generated by reaction of Bi_x vapour with microwave discharged oxygen. The detailed description of experimental set-up one can find in [13]. Chemiluminescence spectra were recorded by high resolution Fourier-transform spectrometer (Bruker IFS 120HR) in the spectral range from 3500 to 7000 cm^{-1} using InSb and Ge detectors. The spectral resolution was 0.02 cm^{-1}. The final spectrum was derived from 10 to 30 interferometer scans. The accuracy of the line wavenumber measurements were better than ± 0.005 cm^{-1}. Some spectra in the Ge detector range were measured using narrow-or broad-band interference filters to suppress the extremely strong BiO band near 7000 cm^{-1}.

CHEMILUMINESCENCE FLAME AND SPECTRA

Low-pressure chemiluminescence has been found to be an excellent method to excite developed spectra of molecules not observed at other experimental conditions. Some molecules such as NaPb, KBi, NaSb were synthesized for the first time in the chemiluminescent flame. Electrodeless chemiluminescent discharge is substantially different from low-pressure plasma sources. The chemiluminescence spectra are rich in molecular bands and show a limited number of neutral atomic lines.

In molecules, containing heavy atom, the electronically excited states usually come down in energy. Also, due to large spin-orbit coupling and mixing of the states angular momentum coupling approaches Hund's case (c) and many transitions which are forbidden in the case (a) (e.g., spin-forbidden) show subtransitions with reasonably high transition probabilities. As a result, the molecules show rich spectra in the NIR range. The spectra are expected to show bands and band systems with rotational and vibrational temperatures close to the translational temperatures in the reaction system. The NIR range is quite suitable for sensitive emission measurements with modern FT spectrometers.

BI_2 $A^3\Sigma^+_U(A_1 1_U) - X^1\Sigma^+_G$ ($X0^+_G$) SPECTRUM

A number of electronic transitions of bismuth dimer have been investigated since 1933 [14]. The best characterized system is the $A(0^+_u) - X^1\Sigma^+_g$ ($X0^+_g$) transition with the bands in the 450 – 790 nm region. The bands of the $a^3\Sigma^+_u(a_1 1_u) - X^1\Sigma^+_g$ ($X0^+_g$) transition lying in the near-infrared were used here for rotational and vibrational temperature measurements. The spectrum consisted of several short sequences of red degraded bands. The highest observed vibrational numbers of upper and lower electronic states were v'=13 and v''=10, respectively. The most prominent and well developed were the v'=0 and v'=0 progressions. The rotational structure of the bands was well resolved and in the each band, according to the nature of the $\Delta\Lambda=1$ electronic transition, R (forming a head), P and Q branches can be identified. The intensity of the R and P branches were comparable, while the lines of the Q branch were approximately two times more intensive. The odd-numbered R, P and Q-lines had lower intensity as even numbered.

TEMPERATURE MEASUREMENTS

The emission intensity for a vibrational-rotational line in an electronic transition can be given by

$$I_{\upsilon'J';\upsilon''J''} = \alpha[N_{\upsilon'J'}/(2J'+1)]v^4_{\upsilon'J',\upsilon''J''}R^2_e\, q_{\upsilon'\upsilon''}S_{J'J''} \qquad (1)$$

where $N_{\upsilon'J'}$ is the population of the $(\upsilon'J')$ level, $\nu_{\upsilon'J',\upsilon''J''}$ is the transition frequency, R^2_e is the electronic transition moment, $q_{\upsilon'\upsilon''}$ is the Franck-Condon factor of the $(\upsilon'J', \upsilon''J'')$ transition, $S_{J'J''}$ is the line strength (Hönl-London factor), J' is the rotational quantum number of the upper level and α is a proportionality constant.

If the population densities of the rotational levels are close to the Boltzmann law, the rotational temperature (T_{rot}) can be deduced from the slope of the plot

$$\ln (I_{J'J''} \nu_{J'J''}^{-4} S_{J'J''}^{-1}) = \text{constant} - F'(J) k^{-1} T_{rot}^{-1} \qquad (2)$$

where $\nu_{J'J''}$ is the frequency of the rotational line, $F'(J)$ is the rotational energy of the upper level and k is the Boltzmann constant.

For determination of the rotational temperature of the chemiluminescent flame the intensities of rotational lines of the 6-0 and 2-3 bands of the a-X transition of Bi_2 were used. The rotational and vibrational assignments and spectroscopic constants were taken from [13]. Hönl-London factors were calculated using commonly known relations [15]. Considering spectral line overlapping a careful selection of rotational lines used for the temperature measurement was carried out. The emission intensities of the R, P and Q lines were first fitted to the relation (2) individually for each branch and the linear regression was employed for temperature determination. In the next step a global fit was attempted for each band analysed. The obtained temperature values with their standard deviation (SD) uncertainties are listed in Table 1.

Table 1. Rotational temperatures from individual and global fits, in K.

	2-3 band	6-0 band
R branch	325±12	332±25
P branch	343±14	353±54
Q branch	348±11	332±62
All branches	341±7	331±16
(the J range)	(57 – 175)	(76 – 137)

The Boltzmann plots for the 2-3 and 6-0 bands were presented in Fig. 1. The temperature values for the bands with different vibrational quantum number of the upper state are approximately equal to each other in the frame of their SD uncertainties. It indicates that the population distributions of the rotational levels in the upper state are completely thermalised in the chemiluminescent flame.

The vibration temperature (T_{vib}) can be determined on the base of band head intensity measurements by means of the relation

$$\ln (I_{\upsilon'\upsilon''} \, \nu_{\upsilon'\upsilon''}^{-4} \, q_{\upsilon'\upsilon''}^{-1}) = \text{constant} - G'(\upsilon) \, k^{-1} \, T_{vib}^{-1} \qquad (3)$$

where : $I_{\upsilon'\upsilon''}$ is the band intensity, $\nu_{\upsilon'\upsilon''}$ is the frequency of the band head, $q_{\upsilon'\upsilon''}$ is the Franck-Condon factor, $G'(\upsilon)$ is the vibrational energy of the upper state.

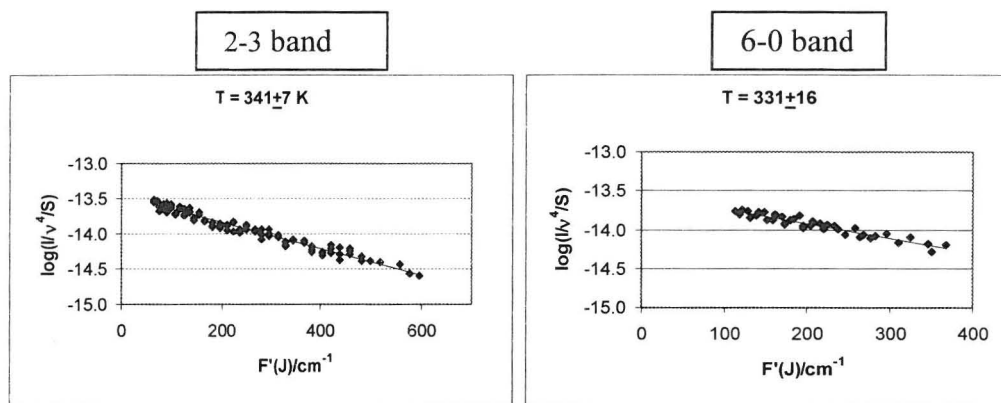Fig. 1. Rotational Boltzmann plots for the bands of the a-X transition of the Bi$_2$ molecule.

The band intensities were measured here as the band head intensities with a special attention paid to a background correction for each band. For vibrational temperature measurements the bands of the sequence $\Delta\upsilon = -3$ were employed. The Franck-Condon factors calculated using program based on RKR potential and intensities of the bands were fitted to the expression (3). The vibrational Boltzmann plot is presented in Fig. 2. As it can be seen the population distributions of the vibrational levels are in agreement with the Boltzmann distribution. The vibrational levels of the upper electronic state of Bi$_2$ may be also considered as thermalised, as in the case of rotational levels.
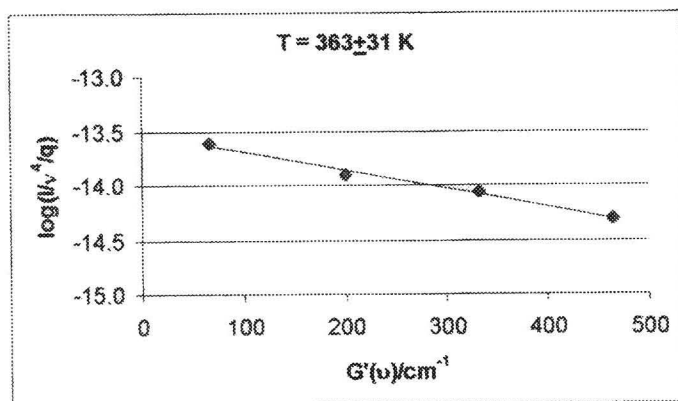
Fig. 2. Vibrational Boltzmann plot for the a-X transition (sequence $\Delta\upsilon = -3$) of the Bi$_2$ molecule.

The chemiluminescent flame represents a non equilibrium state despite of a consistence between the rotational and vibrational temperatures. There are very prominent differences between the chemiluminescent flame investigated here and other low pressure plasma sources as e.g., electrodeless discharges or hollow cathode lamps. In the low pressure plasma generated in the electric discharges $T_{rot} < T_{vib} \le T_{ex}$, while for the chemiluminescence flame studied here, T_{rot} and T_{vib} are well comparable. Various excitation mechanisms in a low pressure plasma and a chemiluminescent flame are responsible for the different relations between the temperatures.

CONCLUSIONS

Heavy molecules can serve very well as thermometric species for spectroscopic diagnostics of plasma as it was shown here for the first time using the Bi$_2$ molecular spectra. Heavy-atom containing molecules such as e.g., Bi$_2$ have lower constants B and ω_e than light molecules. Lines with much more higher J_{max} quantum numbers (for intensity measurements) are available for heavy molecules. As a result, the bands show many lines up to high J values but still are narrow so no correction of the relative intensities for changes of the sensitivity of the spectrometer is necessary. The $\Delta\upsilon = -3$ sequence bands are also extended over a relatively small wavenumber range, so the correction for changes of the sensitivity of the detection system is not important.

Temperature measurements have shown that the vibrational and rotational temperatures of Bi$_2$ in the chemiluminescent flame are quite well consistent.

Populations of the rotational and vibrational levels of the upper electronic state of bismuth dimer (a $^3\Sigma^+(1)$) can be described by the Boltzmann distribution law.

The high resolution FT spectrometry is an excellent tool for studying rotational intensity distributions even for very heavy molecules. Nevertheless a careful selection of rotational lines (free from interferences) for the temperature determination is of great importance.

The present work is the first step of studies undertaken for spectroscopic characteristics of the chemiluminescent flame.

REFERENCES

1. **Borkowska-Burnecka J., Żyrnicki, Spectrosc W.** Let. 30, 701-716, 1997
2. **Engel U., Prokisch C., Voges E., Hieftje G.M., Broekaert J.A.C.**, J. Anal. At. Spectrom. 13, 955-961, 1998.
3. **Osiac M., Lavrov B.P., Röpcke J., Quant J.** Spectrosc. Radiat. Transfer 74, 471-491, 2002.
4. **Nozaki T., Miyazaki Y., Unno Y., Okazaki K.**, J. Phys. D: Appl. Phys. 34, 3383-3390, 2001.
5. **Pellerin S., Musiol K., Motret O., Pokrzywka B., Chapelle J.**, J. Phys. D: Appl. Phys. 29, 2850-2865, 1996.
6. **Laux C.O., Gessman R.J., Kruger C.H., Roux F., Michaud F., Davis S.P.**, J. Quant. Spectrosc. Radiat. Transfer 68, 473-482, 2001.
7. **Iacone L.A., Masamba W.R.L., Nam S-H., Zhang H., Minnich M.G., Okino A., Monraser A.**, J. Anal. At. Spectrom. 15, 491-498, 2000.
8. **de Izarra C.**, J. Phys. D: Appl. Phys. 33, 1697-1704, 2000.
9. **Zyrnicki W.**, Spectrosc. Let. 25, 175-188, 1992.
10. **Ishii I., Montaser A.**, Spectrochim. Acta 46B, 1197-1206, 1991.
11. **Hermann J., Coursimault F., Motret O., Acquaviva S., Perrone A.**, J. Phys. B: At. Mol. Opt. Phys. 34, 1917-1927, 2001.
12. **Stamou S., Mataras D., Rapakoulias D.**, J. Phys. D: Appl. Phys. 31, 2513-2520, 1998.
13. **Breidohr R., Setzer K.D., Shestakov O., Fink E.H., Zyrnicki W.**, J. Mol. Spectrosc. 166, 251-2520, 1994.
14. **Huber K.P., Herzbeg G.**, Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules. Van Nostrand Reinhold Co., New York, 1979.
15. **Herzberg G.**, Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules. Van Nostrand Co., Princeton, 1950.

BADANIA SPEKTROSKOPOWE CHEMILUMINESCENCJI

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S t r e s z c z e n i e. Niskociśnieniowa plazma chemiluminescencyjna jest doskonałym źródłem wzbudzenia cząstek, które trudno jest uzyskać w innych warunkach eksperymentalnych. W prezentowanej pracy badano plazmę chemiluminescencyjną otrzymaną w układzie Bi_x/O_2 dla określania temperatur rotacyjnych i oscylacyjnej. Widma rejestrowano za pomocą spektrometru fourierowskiego wysokiej rozdzielczości (Bruker IFS 120 HR) w zakresie od 3000 do 7000 cm^{-1}. Obie temperatury były zbliżone i wynosiły ok. 330 K.

S ł o w a k l u c z o w e: chemiluminescencja, dimer bizmutu, pomiar temperatury, temperatura rotacyjna, temperatura oscylacyjna, widma FTIR.