DETERMINATION OF THE BAND OSCILLATOR STRENGTHS (0,1) AND (0,2) FOR THE $A^1\Pi - X^1\Sigma^+$ SYSTEM IN THE SiO MOLECULE

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The band oscillator strengths (0,1) and (0,2) for the $A^1\Pi - X^1\Sigma^+$ system in the SiO molecule have been determined by analysing the spectrum of plasma formed in an argon plasma-jet and protected against contact with the atmosphere. Silicon oxide SiO resulted from the reaction between $SiCl_4$ and O_2. The temperature of the plasma was defined by the one-line method basing on the ArI lines. Silicon concentration was determined spectrophotometrically using the SiI lines of known transition probabilities. The band oscillator strengths (0,1) and (0,2) calculated for the $A^1\Pi - X^1\Sigma^+$ system are 0.11 and 0.083, respectively, with an accuracy of about 35%.

Introduction

Knowledge of absolute oscillator strengths of diatomic molecular spectra is apart from the well known values of these magnitudes for atoms and ions, necessary for quantitative investigation of chemical and physical processes taking place at temperatures up to about 10 000 °K.

Among several spectral systems of the SiO molecule [1] the most important for analytical purposes is the $A^1\Pi - X^1\Sigma^+$ transition which gives the ultraviolet spectrum in the region of 2000–3000 Å thoroughly examined by Lagerquist and Uhler [2]. This system which may easily be observed both in emission and absorption, consists of several bands degraded towards the red part.

The studies on the determination of the SiO oscillator strengths have been initiated by two reports [3] and [4] and paper [5]. The result of these studies is the determination of absolute oscillator strengths with respect to the entire $A^1\Pi - X^1\Sigma^+$ system, without indicating the oscillator strength components for any particular rotation-vibration band. Report [3] gives a value of $f = 0.005$–0.002 obtained from the emission in a shock tube. The authors of report [4] found $f = 0.0144$ by examining the emission life of the SiO molecule excited in silicates exposed to laser radiation. The value $f = 0.023$–0.013 was obtained from the studies

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on absorption of light from a flash-lamp in a mixture of air and finely-powdered phenolic refrasil heated in a shock tube (3700–6000 °K) [5].

The results contained in papers [3], [4] and [5] which are very divergent, could not be used for diagnostic work since it would be necessary to make photometric measurements of the entire $A^1\Pi - X^1\Sigma^+$ spectrum of SiO over a range of about 1000 Å. This involves a large amount of work to be done and possible errors because of the common photorecording method used for measuring the spectra and the need for taking into account the varying spectral plate sensitivity.

Other objections against the f values given in papers [3], [4], [5] result from Tatum's work [6]. The calculations of the oscillator strength or transition probability with respect to the entire electron-vibration-rotation system which is usually expanded over a wide spectral region are so difficult and tedious that, according to Tatum's suggestions, they should not be used in molecular spectroscopy.

Apparatus and measuring method

A plasma-jet of our own design based upon the data given in Ref. [7] was used for excitation of the SiO spectrum. The burner operating in pure argon (99.98% and about 0.003% O_2) under a load of about 12 kilowatts, was adapted in the present work to introduce oxygen and $SiCl_4$ vapours by means of an additional adapter. The cell with $SiCl_4$ was thermostatted at 0°C. The flows of the main argon stream (7.5 Nl/min.), additional argon stream saturated with $SiCl_4$ vapours (1.5 Nl/min.) and oxygen (0.2 or 0.3 Nl/min.) were controlled by calibrated rotameters.

The plasma-jet was fed from a separately excited D. C. converter through resistance--induction elements. Electrode erosion was minimal and the compound was accurately and invariably in time fed into the plasma. The above conditions enabled the plasma-jet to operate for a long time with high stability and allowed even the laminar plasma stream to be exposed for a few minutes.

The plasma stream investigated was protected against any contact with the atmosphere by means of a cooled chamber with quartz windows.

The horizontal stream of plasma was represented by means of an achromatic quartz lens on the slit of a grating Zeiss PGS-2 spectrograph operating at a dispersion of 7.37 Å/mm. The conditions of representation provided a suitable depth of focus. The spectral slit was fixed at 0.110 mm what enabled to the execution of the paper measurement of the total spectral intensity over the range up to 4000 Å [8]. The spectra were recorded on Orwo UV-1 plates.

In order to reduce the obtained spectrum of the plasma to absolute values, the spectrum obtained from a Siemens-Edison tungsten ribbon lamp at 2800 °K and from a standard carbon arc at 3972°K were photographed on the same plate. The tungsten lamp was calibrated by means of a precision "Pyro-Werk" micropyrometer with account taken of the spectral--temperature dependence of the tungsten emission factor following to De Vos [9] and the lamp bulb transmittance determined with a Unicam SP-700 spectrophotometer. The source of light thus had a spectral range from 3000 to 20 000 Å and the absolute characteristics

with an accuracy of 12 to 2%, respectively. The plate calibration over 2200 Å was done by comparison with the spectrum of the crater of a carbon anode [10]. The standard arc was lit up by means of ELS-395 graphite which corresponded to the recommended standards. A D.C. arc between carbon electrodes placed at an angle of 120° permitted the calibration of the plate over the range 2100–8500 Å with an accuracy of 5 to 1.5%, respectively. It was experimentally found that both these sources of continuous spectrum agree each with other in the overlapping spectral ranges.

The photographed spectra were analysed by means of a Zeiss G II microphotometer with a recording G1B1 attachment. On the basis of a three-step filter fitted in the spectrograph and the Fe arc spectrum a calibration curve of the photographic emulsion was made each time for each particular spectral range of interest. By this method the recorded contours of lines or bands were converted from the optical density function into the intensity function depending on the wave number and, after integrating the area under the contours transformed in this way, a measure of intensity for a given line or band was obtained.

Such photometering of the spectrogram at various distances x from the symmetry axis of the photograph only provided information on the specific intensity sum $I(x)$ of a line or band towards the operator. In order to obtain the radiation intensity $I(r)$ at various distances r from the plasma stream of a cylindrical symmetry — the relation of $I(x)$ was converted into the $I(r)$ value by using the Abel integral solved numerically [11]. The values of $I(r)$ were thus obtained in relative units.

After taking into account the geometry of the systems: source-representing system-plate and spectrogram-microphotometer-optical density recording as well as the exposure times, the values of $I(r)$ were expressed in absolute units.

Qualitative analysis of the plasma stream

The spectral analysis of various sections of the plasma stream enabled us to find the following lines and bands of atoms, ions and molecules: ArI, OI, ClI, SiI, SiII and SiO and the strongest lines and bands of other plasma components resulting from contaminations contained in the SiCl$_4$, argon, oxygen and from minimal erosion of the plasmotron and shielding chamber: CuI, CuII, SnI, FeI, MgI, H$_\beta$, H$_\gamma$, VI, WI, NiI, CN, OH, NH, N$_2^+$ and NO.

Calculation and results

The absolute intensity of a given molecular band may be expressed by the relationship:

$$\int_{\lambda_{\text{head}}}^{\infty} I(\lambda)d\lambda = \frac{I}{4\pi} N \frac{g_e \cdot g_v}{Q_e \cdot Q_v} \exp\left(-\frac{E_e + E_v}{kT}\right) A \cdot h \frac{c}{\lambda_{\text{head}}} \qquad (1)$$

where $I(\lambda)$ is the band contour, that is the dependence of absolute intensity I on the wavelength λ, N is the number of the given molecules responsible for the emission discussed per unit volume, Q_e and Q_v are the sums of electronic and vibrational states of a molecule, $E_e + E_v$ are the excited levels of a given electron-vibration transition, g_e and g_v are their

statistical weights, T is absolute temperature, k is the Boltzmann constant, h is the Planck constant, c is the speed of light, and A is Einstein's spontaneous emission probability.

The use of a wavelength corresponding to the band head λ_{head} is very convenient for practical reasons.

The determination of the $\int\limits_{\lambda_{head}}^{\infty} I(\lambda)d\lambda$ value cannot be done by direct measurements. This expression may, however, be presented as follows:

$$\int\limits_{\lambda_{head}}^{\infty} I(\lambda)d\lambda = a \int\limits_{\lambda_{head}}^{\lambda'} I(\lambda)d\lambda \tag{2}$$

where a is a factor resulting from the radiation intensity distribution according to wavelength, while λ' is, in fact, the wavelength of the next vibration-rotation band head. The value of a was calculated on the basis of Herzberg's book [12] under the assumption that the molecule is a rigid rotator what is only an approximation in the case of SiO. The calculated factor depends on λ', that is on the number of single rotation lines taken into account during photometering. The values of quantum numbers J for particular branches P, R and Q became available thanks to an analysis of the SiO system under consideration made in [2]. Besides, the a factor depends on temperature T and rotation constant B' for the excited level.

After substituting the equilibrium constant of the reaction $Si + \frac{1}{2}O_2 = SiO$ into equation (1)

$$K_p = \frac{p_{SiO}}{p_{Si}(p_{O_2})^{1/2}} = \frac{N_{SiO}}{N_{Si}(p_{O_2})^{1/2}} \tag{3}$$

and transforming the equation thus obtained, the following equation results:

$$A_{SiO} = \frac{4\pi}{hc} \cdot \lambda_{head} \cdot \frac{Q_e \cdot Q_v}{g_e \cdot g_v} a \int\limits_{\lambda_{head}}^{\lambda'} I(\lambda)\, d\lambda \exp\left(\frac{E_e + E_v}{kT}\right) \cdot \frac{1}{(p_{O_2})^{1/2} N_{Si} \cdot K_p} \tag{4}$$

where p_{O_2} is the known oxygen pressure, and N_{Si} in the concentration of atomic silicon. K_p of the reaction is known over the temperature range up to $6000°K$ from two consistent reports [13], [14]. The values of K_p for higher temperatures were found after the linear extrapolation of the relation $\log K_p = f(1/T)$ was done.

The concentration of silicon N_{Si} has been experimentally determined by defining the absolute intensities of the lines SiI 2207.98 and 2216.67 Å on the same spectrogram from which the spectrum of SiO was photometered. Calculations were made by means of suitably transformed relationship (1) using the transition probability A for these lines as defined in [15].

The temperature was determined by a "one-line" method consisting in the determination of the absolute line intensity of ArI the concentration of which in the plasma was precisely known and A determined with adequate accuracy ($\pm 10\%$) [16]. The temperature defined also by using equation (1) were determined from the ArI lines 3554.31; 3567.66

and 3606.52 Å, found on the same spectrogram from which the SiI lines and SiO bands were taken. This excluded any error which might have resulted from changes in plasma conditions during the taking of the various photographs. In the peripheric areas of the plasma where the temperature was too low to excite the ArI lines the temperature was determined by measuring the relative intensities of the SiI lines whose relative transition probabilities were defined by the authors of the present work. The temperature of the plasma stream under examination oscillated from 6500 to 8200°K, depending on the place and section and the measurement error did not exceed 1.5%.

By using the above method of measurements and calculations, the following values of Einstein's spontaneous emission probabilities have been obtained for the $A^1\Pi - X^1\Sigma^+$ transition and bands (0,1) and (0,2) of the SiO molecule from 17 or 12 experimental points

$$(0,1) \quad A = 6.1 \times 10^7 \text{ sec}^{-1}$$

$$(0,2) \quad A = 4.5 \times 10^7 \text{ sec}^{-1}.$$

or, after recalculation, the following oscillator strengths:

$$(0,1) \quad f = 0.11$$

$$(0,2) \quad f = 0.083.$$

The respective average dispersion of the results obtained are 0.3 and 0.2×10^7 for A. and 0.005 and 0.003 for f.

The above values of A and f may possess systematic errors resulting from inaccurate determination of transition probabilities for the SiI line on which the present work was based. The measurement errors may reach up to a total of about 35%.

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