THE VIBRATIONAL TEMPERATURE OF ORGANIC MOLECULES AND THE RELATIONSHIP BETWEEN ABSORPTION AND FLUORESCENCE SPECTRA IN SOLUTIONS

By

A. RINGLER and L. SZALAY

Institute of Biophysics, Attila József University, Szeged

The vibrational temperature as a function of the band widths and the Stokes-shift was determined for electron exitation spectra of Gaussian distribution in case of mirror simmetry of different kinds and of asimmetry of absorption and fluorescence. An approximate formula is given for the rapid determination of the vibrational temperature from the spectrum characteristics.

Introduction

If complicated molecules are optically excited with frequencies greater than those of the pure electronic transition, the excess energy is degraded by radiationless processes and may appear as local heat; this can cause translational diffusion of the photodissociation products [1], rotational diffusion in condensed systems [2], change in the "photoorientation" of molecules excited by polarized light [3] and the depolarization of fluorescence in solutions [4]. ALBRECHT [5] suggested a very quick dissipation of the local heat while JABŁOŃSKI [6] assumed a quick and a slow mechanism of dissipation, in the picosecond and the nanosecond range, respectively. KOZMA et. al. [7] offered a thermodynamical interpretation of the dissipation of heat, assuming a weak thermal interaction between the "hot", excited molecule and its environment. This approach has been corroborated by studying the dependence of the local heat on temperature [8] and solvent [9].

The problem of local heat around a "hot", excited molecule in solution is closely connected with a relationship between the absorption $k(v)$ and fluorescence energy spectra $f_e(v)$ already studied several decades ago [10]. The following form of this relationship was proposed by STEPANOV [11]:

$$f_e(v)/k(v) = D(T) v^3 \exp(-hv/kT) \tag{1}$$

where $D(T)$ is a constant independent of the frequency of light v, T is the temperature of the solution, and h and k are the Planck and Boltzmann constants, respectively. KETSKEMÉTY et. al. [12] gave a more generally valid formula containing also the frequency-dependent relative yield of fluorescence and the refractive index of the solution. The relationship was studied by several authors [13], and found to be valid. However, in the majority of cases, the temperature T^* calculated from equation (1) in the knowledge of the other quantities was higher than the ambient tempera-

ture T originally introduced into (1). The higher temperature was explained by assuming that a part of the excess electronic excitation energy is not transferred to the environment within the mean life-time of the excited state. In vapours this occurs very easily and permits the vibrational specific heat to be determined experimentally [14]. Since a T^* higher than T is obtained from (1) in many cases, the distribution of the molecules among the different vibrational levels in these cases corresponds to a local or vibrational temperature T^*. Therefore, the excited molecules act as "thermometers", revealing the vibrational temperature at the instant of emission. The reading of this molecular temperature indicator is given in (1) through the shapes, the overlap and the relative intensity distributions of the fluorescence and absorption spectra.

In this paper the influence of the band widths and the Stokes-shifts of the fluorescence and absorption spectra on the local temperature was studied for different model systems.

Methods

The calculations were based on the linearized form of (1):

$$F(v) \equiv \ln\left[D(T)v^3 \frac{k(v)}{f_e(v)}\right] = \frac{h}{kT}v. \tag{2}$$

From the slope of the straight line $F(v)$, $T \equiv T^*$ was calculated. For $k(v)$ and $f_e(v)$ different distributions were taken, assuming different symmetries (and also asymmetries) between these distributions. This is an allowed procedure, since the slope of the function $F(v)$ depends only on the relative spectra. The calculation of T^* was performed easily and quickly with a Minsk-22 computer by means of a simple computer program.

The local temperature and the shapes and locations of the absorption and fluorescence spectra

1. Gaussian distribution of spectra

(a) *The case of Levshin mirror symmetry* [15]. The relationship (2) should be written for the fluorescence quantum spectrum $f_q(v)$, by using the relationship $f_e(v) = hvf_q(v)$:

$$2\ln v + \ln \frac{k(v)_{rel}}{f_q(v)_{rel}} + \text{const} = \frac{h}{kT}v. \tag{3}$$

In the case of Gaussian distribution

$$k(v)_{rel} = \exp\left[-(v-m)^2/2\sigma_a^2\right] \tag{4}$$

and

$$f_q(v)_{rel} = \exp\left[-(v-n)^2/2\sigma_e^2\right] \tag{5}$$

where m, n and σ_a, σ_e are the locations and standard deviations of the absorption and fluorescence spectra, respectively. (Further, the band width will be given in

terms of standard deviations.) If these representations with $\sigma_a = \sigma_e = \sigma$ are substituted into (3) and the values of the constants are considered, we obtain

$$2 \ln v + \frac{m-n}{\sigma^2} v + \text{const} = \frac{4800}{T} v. \qquad (6)$$

The function $G(v) = 2 \ln v + \dfrac{m-n}{\sigma^2} v$ is used now for the determination of $T^* \equiv T$ (linearity dues not hold over a greater interval of v due to the presence of $\ln v$). With $m = 4.5 \cdot 10^{14}$ Hz (666.7 nm) and $\sigma = 0.1 \cdot 10^{14}$ Hz ($\cong 15$ nm), the dependence of T^* on the Stokes-shift $m-n$ and on σ is shown in Fig. 1.
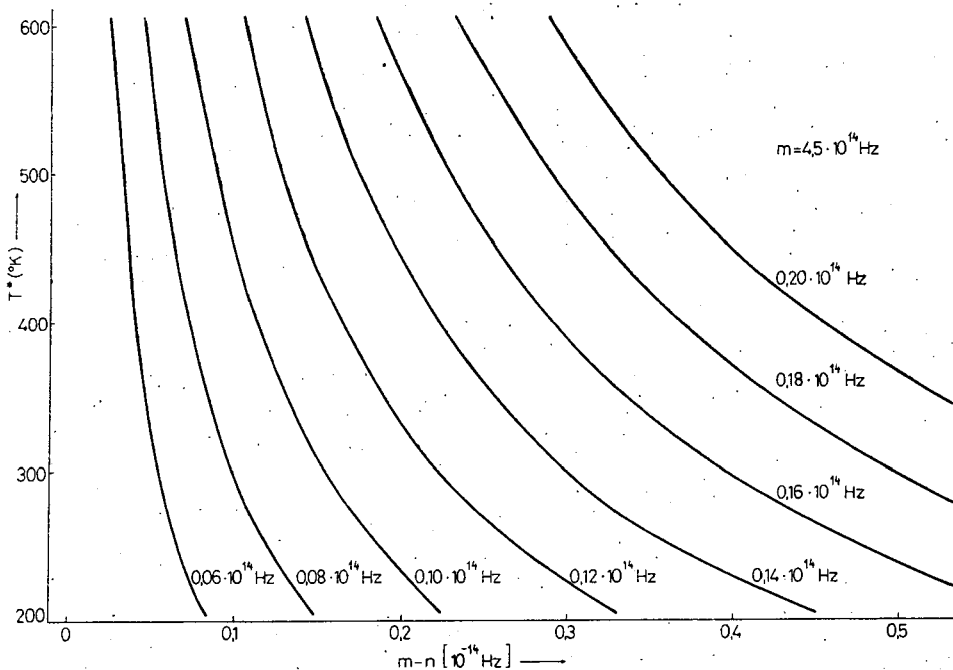

Fig. 1. Dependence of the vibrational temperature T^* on the Stokes-shift m—n at different standard deviations σ of the absorption and fluorescence bands of Gaussian distribution

(b) *The case of Blohintsev mirror symmetry* (16).

$$k(v)_{\text{rel}} = \exp\left[-(v-m)^2/2\sigma^2\right]$$

and

$$f_q(v)_{\text{rel}} = \text{const} \frac{v^3}{2v_0 - v} \exp\left[-(2v_0 - m)^2/2\sigma^2\right]$$

should be substituted into (3). v_0 is the mirror frequency. The result is

$$\ln \frac{2v_0 - v}{v} - \frac{2(v_0 - m)}{\sigma^2} v + \text{const} = \frac{4800}{T} v. \tag{7}$$

The function $G(v) \equiv \ln (2v_0 - v)/v - 2(v_0 - m)v/\sigma^2$ is used for the determination of T^*. The result of the calculations is in accordance with that obtained for Levshin mirror symmetry; only small quantitative deviations were observed.

(c) *The case of non-symmetry.* In this case the representations (4) and (5) should be substituted into (3); the result is:

$$2 \ln v + \frac{(v - n)^2}{2\sigma_e^2} - \frac{(v - m)^2}{2\sigma_a^2} + \text{const} = \frac{4800}{T} v. \tag{8}$$

With $m = 4.5 \cdot 10^{14}$ Hz (666,7 nm), $\sigma_a = 0.2 \cdot 10^{14}$ Hz ($\cong 31$ nm) and $n = 4.1 \cdot 10^{14}$ Hz (731.7 nm) and different values of σ_e, T^* was calculated and plotted as a function
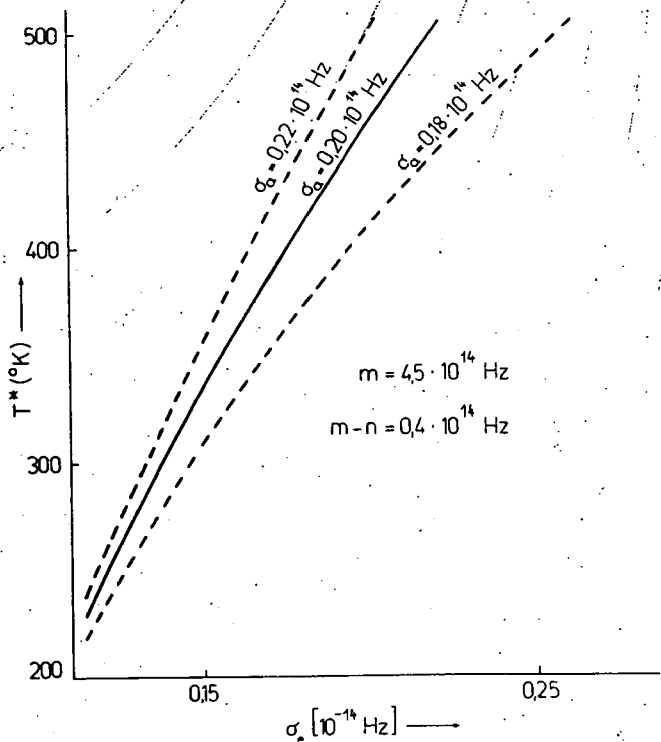

Fig. 2. Dependence of the vibrational temperature T^* on the standard deviation σ_e of the fluorescence band of Gaussian distribution with absorption maximum at $m = 4.5 \cdot 10^{14}$ Hz and Stokes-shift $m - n = 0.4 \cdot 10^{14}$ Hz at different standard deviations σ_a of the absorption band

of σ_e (Fig. 2, solid line). With $\sigma_a = 0.18 \cdot 10^{14}$ Hz (28 nm) and $0.22 \cdot 10^{14}$ Hz (34 nm) the dependence of T^* on σ_e is somewhat different (Fig. 2, broken lines). If $m = 5.5 \cdot 10^{14}$ Hz (545.5 nm), the functions $T^*(\sigma_e)$ $(\sigma_a = \text{const})$ will be enhanced by a maximum of only 1%. If $m = 4.5 \cdot 10^{14}$ Hz and $\sigma_a = 0.2 \cdot 10^{14}$ Hz, the dependence of T^* on σ_e at different locations of the fluorescence maximum is shown in Fig. 3.
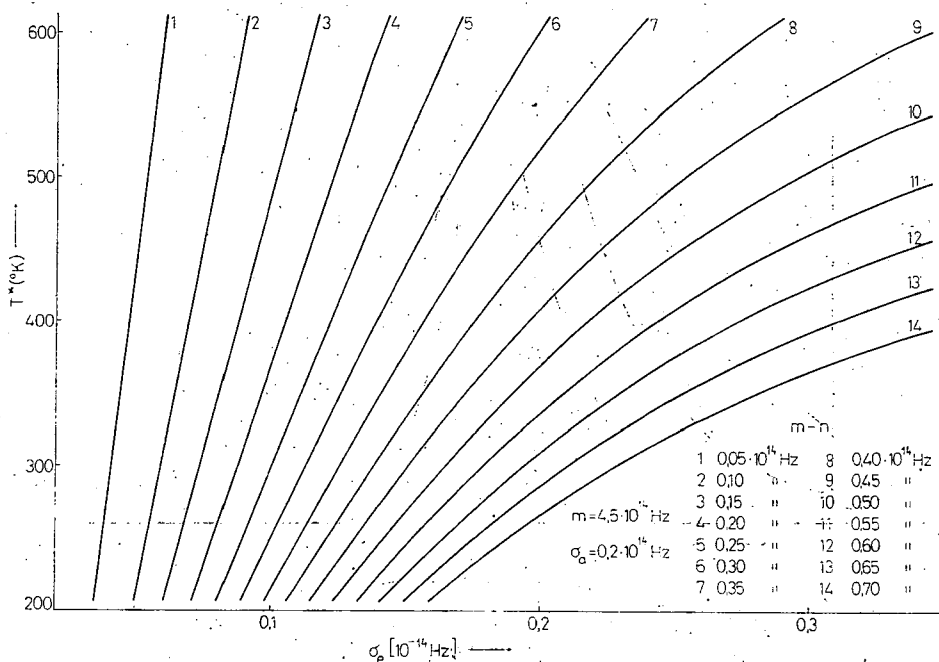

Fig. 3. Dependence of the vibrational temperature T^* on the standard deviation σ_a of the fluorescence band of Gaussian distribution with absorption maxiumum at $m = 4.5 \cdot 10^{14}$ and a standard deviation σ_a of the absorption band at different Stokes-shifts $m - n$ of the fluorescence and absorption bands

2. *Analytical forms of absorption and fluorescence.* DOMBI et. al. [17] derived analytical expressions for the active absorption and fluorescence spectra. According to their results

$$f_q(v) = Bv^3 \operatorname{ch}^{-1}[a(v - v_0)] \exp(-bv) \qquad (9)$$

$$k(v) = Av \operatorname{ch}^{-1}[a(v - v_0)] \exp(bv) \qquad (10)$$

With proper choice of the parameters a and b, the analytical and experimental fluorescence spectra coincide. If the analytical spectra are substituted into (1), we obtain $b = \text{const } h/2kT$. According to SZALAY etal. [13], $a = \text{const } h/2kT$, too. Using this dependence of the parameters on the temperature, the temperature-

dependence of the absorption and fluorescence spectra can be established. For 300 and 500°K at $v_0 = 5.33 \cdot 10^{14}$ Hz ($= 563$ nm), this dependence is shown in Fig. 4. In the anti-Stokes region the spectra can be well approximated with Gaussian distributions.
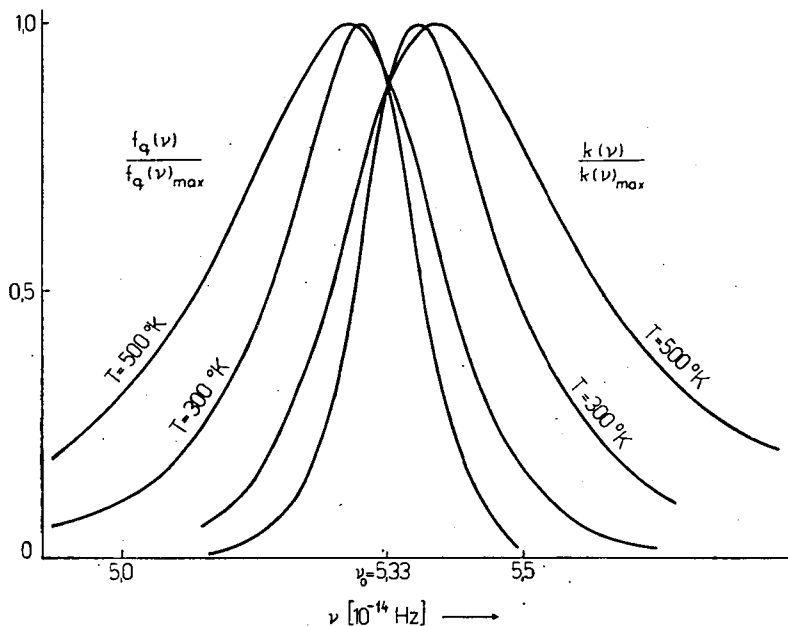

Fig. 4. Relative absorption and fluorescence spectra calculated with the analytical expressions (9) and (10) for 300 and 500°K

Approximate relationship between the vibrational temperature and the spectral characteristics

Figs 1—4. show that the vibrational temperature T^* depends on the widths of absorption and fluorescence (σ_a and σ_e), the distance of absorption and fluorescence peaks ($m-n$, Stokes-shift) and (to a smaller extent) on the location of the absorption maximum. According to Figs 1—3. it can be supposed that $T^* \sim \sigma_a$ and $\sim \sigma_e$, and further $\sim 1/(m-n)$, so that finally $T^* \sim \sigma_a \sigma_e/(m-n)$.

For the values of our parameters, the proportionality factor is approximately $h/k \cdot 1.04$. Therefore

$$T^* \cong \frac{1}{1\cdot 04} \frac{h}{k} \frac{\sigma_a \sigma_e}{m-n} = 4615 \frac{\sigma_a \sigma_e}{m-n} °K. \tag{11}$$

(Here the quantities σ_a, σ_e and $m-n$ are considered without the factor 10^{14}.) If the standard deviations of the Gaussian distributions are replaced by half band widths, this expression can easily be rewritten in a form reminiscent of equation (6) of KAZACHENKO's paper [18]. With equation (11) T^* is easily calculated, but a high precision of the quantities is necessary.

If the spectra are plotted as functions of the wavelength λ, and the accuracy of the wavelength λ, and the accuracy of the determination of the locations of maxima is 0.5 nm, the value of T^* can be given as $T^* \pm 16° K$ (with an accuracy of 1 nm, $T^* \pm 28° K$ is obtained). Fig. 5 shows the accuracy of the approximation of T^* calculated with (11).
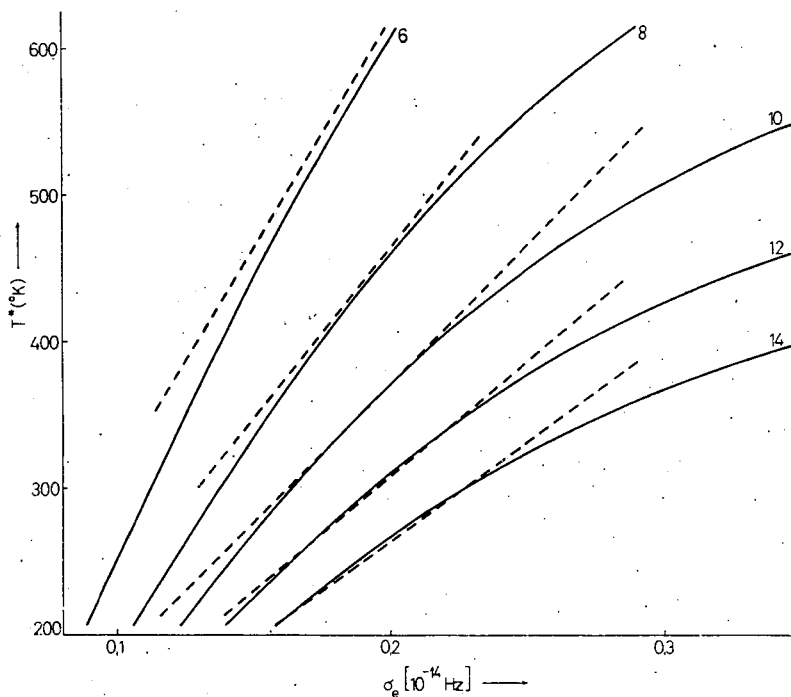

Fig. 5. Selected curves from Fig. 3 approximated by curves (broken lines) calculated with (11)

The deviation from symmetry of the absorption and fluorescence bands

In the case of Levshin symmetry [15] $v_a - v_e = 2(v_0 - v_e)$. If both the absorption and the fluorescence bands are of Gaussian distribution, the difference $v_a - v_e$ as a function of $v_0 - v_e$ yields a straight line with a slope k different from 2; it is defined in $v_a - v_0 = k(v_0 - v_e)$. The dependence of k on the standard deviations σ_e and σ_a is shown in Fig. 6. If the fluorescence band is narrower than the absorption band, k is smaller than 2; in the reverse case k is greater than 2. In all cases the intercept of the straight lines is found at 1. All straight lines in Fig. 6 can therefore be given by the equation

$$v_a - v_0 = \left(\frac{\sigma_e}{\sigma_a} + 1\right)(v_0 - v_e) \qquad (12)$$

A. RINGLER AND L. SZALAY

(otherwise in the case of $\sigma_a=\sigma_e$, k could not have the value 2). This means that of course, the slopes of the straight lines in Fig. 6 can be determined by means of the standard deviations only for spectra of Gaussian distribution. If $k(v)$ and
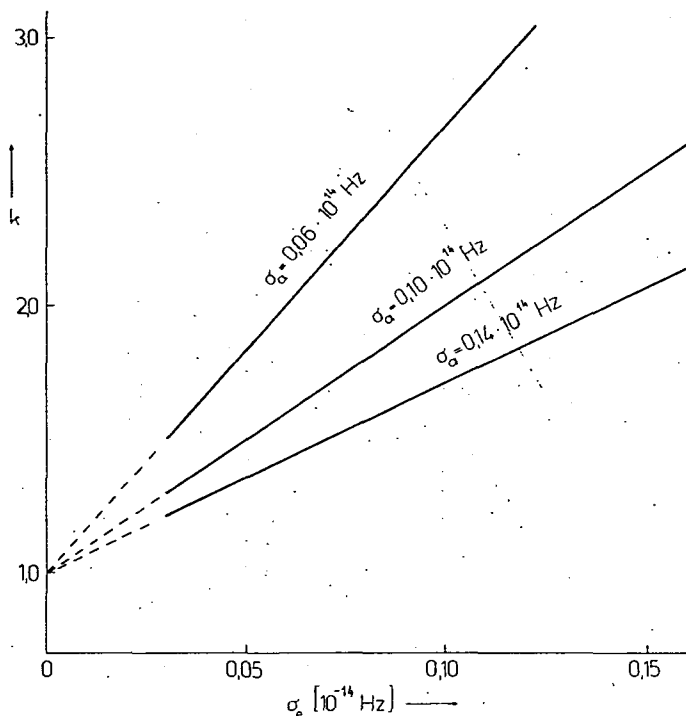

Fig. 6. Slope k of the mirror symmetry relation $v_a - v_0 = k(v_0 - v_e)$ as a function of the standard deviations of the fluorescence and absorption bands (σ_e and σ_a) of Gaussian distribution

$f_q(v)$ have Gaussian distributions with different standard deviations σ_a and σ_e, and v_0 is in the interval $n < v_0 < m$, while further the condition

$$\exp\left[-(v_0-n)^2/2\sigma_e^2\right] = \exp\left[-(v_0-m)^2/2\sigma_a^2\right]$$

is fulfilled, the following relationship is valid:

$$\frac{\sigma_e}{\sigma_a} = \frac{v_0-n}{m-v_0}. \qquad (13)$$

Introducing this into (12)

$$k = \frac{v_0-n}{m-v_0}+1 = \frac{m-n}{m-v_0} \qquad (14)$$

This is another possibility for the determination of the slopes of the straight lines in Fig. 6.

References

[1] *Normann, I., G. Porter:* Proc. Roy. Soc. London A **230**, 399 (1955).

[2] *Albrecht, A. C., W. T. Simpson:* J. Amer. Chem. Sec. **77**, 4454 (1955).

[3] *Albrecht, A. C. :* J. Chem. Phys. **27**, 1413 (1957).

[4] *Jablonski, A.:* Bull. Acad. Polon. **8**, 655 (1960).
        Lisicki, E.: Bull. Acad. Polon. **11**, 665 (1963).

[5] *Albrecht, A. C.:* J. Mol. Spectr. **6**, 84 (1961).

[6] *Jabloński, A.:* Int. Conf. on Luminescence, Torun (1963).

[7] *Kozma, L., L. Szalay, J. Hevesi:* Acta Phys. et Chem. Szeged **10**, 67 (1964).

[8] *Hevesi, J. Kozma L., L. Szalay:* Acta Phys. Polon. **29**, 57 (1966).

[9] *Ketskeméty, I., L. Szalay, Z. Várkonyi:* Acty Phys, et Chem. Szeged. **11** 15 (1956).

[10] *Kennard, E. H.:* Phys. Rev. **11**. 29 (1918); **28**, 672 (1926).

[11] *Stepanov, B. I.:* Dokl. Akad. Nauk SSSR **112**, 839 (1957); Soviet Phys. **2**, 81 (1957);
        Kazachenko, L. P., B. I. Stepanov: Opt. Spektr. **2**, 339 (1957).

[12] *Ketskeméty, I., J. Dombi, R. Horvai:* Ahn. Phys. **7**, 342 (1961); Acta Phys. Hung. **12**, 263
        (1960); **14**, 165 (1962);

[13] *Alentsev, M. N.:* Opt. Spektr. **4**, 690 (1958);
        Alentsev, M. N.: L. A. Pahomitcheva: Izv. Akad. Nauk SSSR Fiz. Ser. **22**, 1377
        (1958); **24**, 734 (1960;
        Kravtsov, L. A., A. N. Rubinov: Opt. Spektr. **12**, 636 (1962);
        Hevesi, J., L. Kozma: Acta Phys. et Chem. Szeged **8**, 103 (1962);
        Razhanova, E. F., M. S. Fadeeva, T. S. Pavlina: Izv. Akad. Nauk SSSR Fiz. Ser. **24**,
        769 (1960);
    Mazurenko, Yu. T., B. S. Neporent: Opt. Spektr. **12**, 317 (1962);
    Klochkov, V. P., S. M. Korotkov: Opt. Spektr. **22**, 189 (1967);
    Bálint, E., E. Lehoczki, J. Hevesi: Acta Phys. et Chem. Szeged **17**, 1 (1971);
    Szalay L., J. Hevesi, L. Kozma: Magyar Fizikai Folyóirat **13**, 170 (1965).

[14] *Borisevich, N. A., V. V. Gruzinski:* Opt. Spektr. **14**, 39 and 457 (1963);
    Hevesi, J., G. S. Singhal: Spectrochim. Acta **25** A, 1751 (1969);
    Borisevich, N. A.: Acta Phys. et Chem. Szeged. **10**, 9 (1964).

[15] *Levshin, V. L.:* Fotoluminescencia zhidkih i trovrduch veshtchestv, Moscow—Leningrád, 1951.

[16] *Blohintsev, D. I.:* J. Phys. SSSR **1**, 127 (1959).

[17] *Dombi, J., I. Ketskeméty, L. Kozma:* Acta Phys. et Chem. Szeged **10**, 15 (1964).

[18] *Kazachenko, L. P.:* Opt. Spektr. **18**, 703 (1965).

СВЯЗЬ КОЛЕБАТЕЛЬНОЙ ТЕМПЕРАТУРЫ ОРГАНИЧЕСКИХ МОЛЕКУЛ С АБСОРБЦИОННЫМИ И ЭМИСИОННЫМИ СПЕКТРАМИ РАСТВОРОВ

А. Ринглер, Л. Салаи

Определены колебателная температура в зависимости от щирины полосы и смещения Стокса для разных случаев зеркальной симметрии, и для несимметрического случая на основании секторов электронного возбуждения, обладающих распределением по Гауссу. Предложено приближенное уравнение для быстрого расчета вибрационной температуры на основе спектральных характеристик.