LIMIT YIELD OF PHOTOLUMINESCENCE FROM THE POINT OF VIEW OF THERMODYNAMICS OF IRREVERSIBLE PROCESSES

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The methods of irreversible thermodynamics have been applied to yield of photoluminescence. It has been shown that the limit yield of luminescent system interacting with surroundings is not greater than one only in Stokes region of excitation.

Introduction

The problem of photoluminescence yield and possibility of heat conversion into radiation energy was discussed by Pringsheim (1946) and Vavilov (1946). Then Landau (1946) on the basis of the second law of classical thermodynamics, has shown that in general a limit yield of photoluminescence greater then one is not impossible. Recently Mazurenko (1965) has applied the methods of thermodynamics of irreversible processes to some problems of photoluminescence, but the important question of luminescence yield has not been finally solved. Up to the present time the anti-Stokes drop of photoluminescence yield was also thermodynamically considered by Budó and Ketskeméty (1964).

Landau considered a system consisting of two parts: a luminescent molecules and an enclosure with perfectly reflecting walls. The enclosure contains excitation radiation. By the withdrawal of a partition the parts are brought into contact and the final internal energy is established. In this case the energy yield of photoluminescence in Stokes region is

$$\eta \leqslant 1 + \frac{T}{T_0},\tag{1}$$

where T_0 is interpreted as an effective temperature of the radiation. Landau's result states that the limit energy yield of photoluminescence can in principle be greater than one. The relationship (1) is a good approximation if only the radiation is confined to a small frequency band, *i.e.* if the entropy of the emitted radiation is small. Thus the ratio T/T_0 can only

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be a correction in (1) and one must therefore expect $T \ll T_0$. For wide bands of radiation its entropy is increased and also the expression T/T_0 is greater.

The aim of the present paper is to show that the methods of irreversible thermodynamics applied to the solution of the problem of photoluminescence yield give a result corroborated by the experimental data.

It is known that the second law of thermodynamics of irreversible processes is locally valid. It requires that a certain minimum of entropy must be created by internal processes in every element of a considered system. Therefore, in contradiction to the classical thermodynamics, the phenomena in non-closed system can be studied.

Energy yield of Stokes luminescene

Consider now a system of luminescent molecules in a heat reservoir. The system is optically homogeneous and isotropic. Non-excited molecules are in thermal equilibrium with the heat reservoir (the surrounding medium) at the temperature T. For simplicity we suppose that the excited molecules are in equilibrium with unpolarized, uniform in every direction and nearly monochromatic exciting radiation characterized by the temperature T^*. According to Prigogine (1955) the time rate of change of the entropy of the system is $\dot{S} = \dot{S}_i + \dot{S}_e$, where $\dot{S}_i$ is the amount of entropy created by the radiation processes and $\dot{S}_e$ — the time rate of change of entropy as a result of interaction of the excited molecules with surroundings. In steady processes, when the system is continuously excited by light of constant intensity, $\dot{S} = 0$. According to the second law of thermodynamics $\dot{S}_i \gg 0$, thus $\dot{S}_e \leqslant 0$. Assume that the luminescent system has a large heat capacity, so that its temperature remains constant during the process.

For Stokes luminescence, some of the absorbed energy must be reradiated, some may have leaked to the surroundings. Let $\dot{S}_{ea}$ be the time rate of change of entropy of the system associated with the energy absorption and $\dot{S}_{es}$ — the time rate of entropy associated with the energy exchange with the surroundings. If $\dot{W}_a$ is the absorbed power of energy and $\dot{W}_s$ — the power of energy transferred to the surroundings, then

$$\dot{S}_e = \dot{S}_{ea} + \dot{S}_{es} = \frac{\dot{W}_a}{T^*} - \frac{\dot{W}_s}{T}. \tag{2}$$

$\dot{W}_s$ is negative, when energy is given up by the system of luminescent molecules. The power of emitted photoluminescence is

$$\dot{W}_l = \dot{W}_a - W_s. \tag{3}$$

Since $\dot{S}_e \leqslant 0$, the energy yield of photoluminescence is

$$\eta = \frac{\dot{W}_l}{\dot{W}_a} \leqslant 1 - \frac{T}{T^*}. \tag{4}$$

This inequality shows that the energy yield of photoluminescence of molecules interacting with the surroundings must be not greater than one.

It is known that the energy yield of photoluminescence is proportional to the quantum yield Q. For $T < T^*$ we have

$$\eta = Q\,\frac{\bar{\nu}_l}{\nu_a} \leqslant 1, \tag{5}$$

where $\bar{\nu}_l$ is the centre of gravity of the luminescence spectrum, ν_a — the frequency of absorbing energy. The inequality (5) is in agreement with experience. In the Stokes region of excitation the quantum yield is independent of the absorption frequency ν_a. In other words, the energy yield of photoluminescence increases with decreasing of ν_a. As shown by experiments the energy yield decreases in the anti-Stokes region of luminescence. This is associated with a still greater drop of the quantum yield. Therefore the thermodynamic proof of (5) for the anti-Stokes region of excitation is synonymous with a proof of the steep drop of the quantum yield in this luminescence region.

Anti-Stokes luminescence

For anti-Stokes luminescence, where $\bar{\nu}_l > \nu_a$, part of the excitation energy is supplied by heat of the surrounding medium. It is the case where the elementary process of absorption and then emission of light for anti-Stokes excitation is associated with transformation of thermal energy into light. Suppose that the considered luminescent molecules are poly-atomic. The thermal vibrations of nuclei of the luminescent molecules are in equilibrium with thermal radiation of the surroundings, whose absolute temperature is T. The amplitudes of the nuclei vibrations oscillate around an equilibrium state. This departures from equilibrium state are fluctuations of energy modulating the excitation radiation. The theory shows (Prigogine, 1955) that the fluctuations decrease the mean entropy of the system. Therefore the time rate of entropy $\dot{S}_f = -\dfrac{\dot{W}_f}{2T}$ (where $\dot{W}_f$ is the power of fluctuation energy) is negative. For this case

$$\dot{S}_e = \frac{\dot{W}_a}{T^*} - \frac{\dot{W}_f}{2T} \leqslant 0, \tag{6}$$

where $\dot{W}_a$ is the power of absorbed radiation.

According to the conservation law of energy, the power of emitted radiation in anti-Stokes region of luminescence is

$$\dot{W}_l = \dot{W}_a + \dot{W}_f. \tag{7}$$

Thus the energy yield is

$$\eta = \frac{\dot{W}_l}{\dot{W}_a} \geqslant 1 + 2\,\frac{T}{T^*}. \tag{8}$$

For real systems we also have $T \ll T^*$, which guarantees that in general the limit yield of anti-Stokes luminescence can be not greater than one. It can be seen that the condition $\eta = 1$ is strictly fulfilled at the temperature $T = 0$ of the surroundings. The result (8)

was possible to obtain owing to our assumption that the fluctuation of vibrations of the nuclei of luminescent molecules lower the entropy of absorbed energy. This can be interpreted from the point of view of interaction of the system of luminescent molecules with surroundings. In the intramolecular processes of interaction an increment of energy is supplied by the surroundings to luminescent molecules but not to the excitation radiation (source of the radiation) at temperature $T^* > T$. The heat transfer from molecules at temperature T to molecules at temperature T^* is thermodynamically impossible. Our considerations indicate that the thermodynamic interpretation of the anti-Stokes drop of photoluminescence yield observed experimentally is not possible by taking into acount processes within the excited molecules and the energy fluctuation of exciting radiation.

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