

The Effect of Light Intensity on the Efficiency of Photochemical Energy Conversion through Electron Transfer**

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The thermodynamic properties of light have been the subject of debate for many years. The fundamental question of whether light has a thermodynamic entropy has been discussed of theoretical grounds but so far no experimental data have been available to settle the argument one way or the other. Yet the implications of an entropy content of light are far-reaching from the point of view of practical applications (energy conversion) as well as from that of fundamental knowledge: If light has a thermodynamic entropy, then it cannot be converted entirely into electrical or mechanical energy and the conversion efficiency decreases with the intensity of light. – In this paper the basic assumptions of the entropic and non-entropic models of light are briefly reviewed. It is then shown that the photochemical electron transfer reaction which is involved in the quenching of the fluorescence of some oxonine dyes by electron donor aromatic molecules supports the non-entropic model, which means that the entire energy of light is in principle available in the form of chemical free energy (or electrical or mechanical energy) independently of light intensity.

1. The Nature of Light in Thermodynamics

In any process of transformation of the energy of light into other forms of energy – electrical energy in particular – the effi-

ciency which can be attained is of prime importance. Among the various factors which can limit the conversion efficiency the most general is thought to be the thermodynamic limitation linked to the entropy of light.

In its simplest form this entropy of light is that lost by the source of temperature T_r which has radiated an energy E , $\Delta S = E/T_r$. The temperature T_r is then also a temperature of the light⁽¹⁾, and this can be expressed according to the Planck radiation law as

$$T_r = \frac{hc}{k\lambda \ln \left(1 + \frac{2hc^2\Omega}{\lambda^5 E_\lambda} \right)}$$

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It is further held that the temperature of a directional beam of light (concentrated in a solid angle Ω) is lowered when it is absorbed since its entropy increases as the directionality is lost; the relevant solid angle increases from Ω to 4π and the temperature of the absorbed or scattered light becomes simply

$$T_{rs} = \frac{hc}{k\lambda} \cdot \frac{1}{\ln \left(1 + \frac{8\pi hc^2}{\lambda^5 E_\lambda} \right)}$$

For a fixed narrow frequency range the temperature of light depends then only on the irradiance E_λ , that is on the intensity expressed for instance in watt per square metre. The calculation shows that the maximum energy conversion efficiency

$$\eta = (T_r - T_s)/T_r$$

is of the order of 0.7–0.8 for sunlight if the temperature T_s of the absorbing sample is of around 300 K. As the intensity of the light decreases the maximum conversion efficiency decreases very slowly on account of the logarithmic dependence of T_r on irradiance.

This model of light as a form of heat, that is a form of energy endowed with entropy, suggests that the population N^* of excited molecules must be related to the population N^0 of ground state molecules through a Boltzmann distribution:

$$N_d^* = N^0 \exp(E/kT_s)$$

in the dark, and

$$N_l^* = N^0 \exp(E/kT_r)$$

in the light, for an excited state energy E . This is a clear analogy between the effects of light and of heat on a chemical sample.

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This requirement for the relative excited state population N^*/N^0 to be determined solely by the intensity of the incident light appears however to be unrealistic. The excited state population N^* is determined by the number of photons absorbed, not by the number of photons incident; for any given irradiance this depends on the absorbance of the sample, that is on the extinction coefficient of the light absorbing species as well as on the concentration of ground state species. The relative excited state population N^*/N^0 cannot therefore be determined solely by the «temperature» of light, whereas for a sample in the dark the Boltzmann distribution $N^*/N^0 = \exp(E/kT)$ undoubtedly applies.

This leads us to reconsider the basic assumptions of the «light as heat» model^[2]. Indeed, there is a fundamental difference between the actions of heat and of light of frequencies corresponding to electronic excitations of molecules: the heat energy is necessarily distributed among all the particles of the sample, and it is not possible to pick out certain species as being energy rich while other species remain unaffected; but the energy of light can be channelled into one specific type of molecule, all others remaining unchanged. Similarly, heat energy distributes itself among all the different energy levels, translational, rotational, vibrational as well as electronic, whereas the energy of light produces in the first place only electronically excited molecules. Thus the statistical basis of the Second Law of thermodynamics is not fulfilled for an illuminated sample which contains electronically excited molecules.

Indeed, if the illuminated sample differs from the dark sample only by the presence of a new chemical species (the excited molecules) without any change in the translational, rotational, and vibrational motions of the molecules, it seems logical to consider that the thermodynamic entropy of the system also remains unchanged.

If this is true, then light has no thermodynamic entropy and it must be a form of «high-grade» energy akin to electrical or mechanical energy; it follows then that there is no thermodynamic limitation to the conversion efficiency of light in photochemical systems.

However, if light is a form of energy without thermodynamic entropy the question does arise of the fate of the entropy of a radiating hot body: the energy of the hot (e.g. incandescent) body is in the form of heat, so that an entropy dQ/T is lost as heat dQ is transformed into light $dE = dQ$. The following answer can be suggested to this problem:

An incandescent body does not bring heat directly to the absorbing sample; in the first place it forms radiation (light) in the empty space which surrounds it, and this radiation may be absorbed at some later stage by a distant sample. The pro-

cess of production of radiation is therefore a transfer of heat energy at a temperature T to empty space at 0 K, and this is equivalent to a heat engine which works between a hot source at a temperature T and a cold source at 0 K: according to the Carnot theorem heat can be transformed completely into «work» (high-grade energy) since the conversion efficiency is

$$\eta = (T_r - 0)/T_r = 1$$

2. Photochemical Electron Transfer and the Rehm-Weller Equation

Electron transfer processes are probably the most suitable types of photochemical reactions for energy storage, the stored energy then being in the form of electricity or hydrogen gas for example. In addition, absorbers can be used to cover a wide spectral range of sunlight, such as the porphyrins on which many natural pigments are based.

The energy balance of a photoinduced electron transfer reaction is given by the Rehm-Weller equation in the usual form^[3]

$$\Delta G = E_{\text{ox}}(\text{D}) - E_{\text{red}}(\text{A}) - E^* + C$$

Here ΔG is the free energy of the reaction, $E_{\text{ox}}(\text{D})$ being the oxidation potential of the donor molecule D and $E_{\text{red}}(\text{A})$ the reduction potential of the acceptor molecule A; these potentials must be measured against a common reference potential, and a correction C must be applied to them if the resulting particles are charged and if the distance at which electron transfer takes place is of the order of molecular dimensions. The energy of E^* is that of the electronically excited state involved in the reaction.

Although the final result is meant to be the reaction free energy (ΔG), this is expressed in terms of a mixture of macroscopic (E_{ox} , E_{red}) and molecular (E^*) quantities. The implication is that the entire energy E^* of the electronically excited molecules is available in the form of free energy, and this is in contradiction with the «light as heat» model (but in agreement with the «light as high-grade energy» model).

In terms of macroscopic quantities the Rehm-Weller equation can be written as

$$\Delta G = E_{\text{ox}}(\text{D}) - E_{\text{red}}(\text{A}) + C - \eta E_{\text{hv}}$$

if E_{hv} is the total energy of light absorbed and η is the conversion efficiency of this light into chemical free energy. This conversion efficiency is itself the product of factors which represent:

η_s , the spectral overlap of the absorption spectrum of the absorber with the spectrum of the incident light (e.g. sunlight); η_d , the loss of energy through radiationless

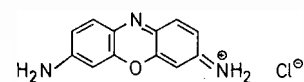
transition from the state reached through absorption to the reactive state; η_T , the entropic limitation in the light-as-heat model.

The first two conversion efficiency factors apply to both models of the thermodynamic properties of light. In principle these two factors η_s and η_d can be made to be ideally close to unity if the excitation light is highly monochromatic and if the electron transfer step originates from the state reached through absorption: the factor η_T of around 0.75 is on the other hand inherent to the light-as-heat model. It now appears that the Rehm-Weller equation is based implicitly on the light-as-high-grade-energy model, since only then can E^* be used as free energy (in the light-as-heat model only $\eta_T E^*$ can be used). Since η_T can be as low as 0.7 when the light intensity is low, a number of photoinduced electron transfer processes are predicted to be exergonic if light is a form of high-grade energy but endergonic if light is a form of heat.

3. Fluorescence Quenching of Oxonine Dyes by Electron Donors

For a test of the two thermodynamic models of light the quenching of some oxonine dyes through electron transfer from amines and methoxy compounds has been chosen, largely because the reaction free energy can be obtained accurately from electrochemical and spectroscopic data. Both the reactants and the products include one singly charged species and one uncharged species, so that the Coulomb term C is zero; this is an important condition since the estimation of this term is still open to doubt.

It has been found that the quenching of the fluorescence of the oxonine dye



by various electron donors is close to the diffusion-controlled limit even when the calculated free energy is as small as -0.12 eV^[4]. Since the energy of the reactive state is 2.07 eV, such a process would be endothermic by up to 0.4 eV according to the light-as-heat model (the available energy would then be $\eta E^* = 0.77 \times 2.07$ eV, taking a thermodynamic efficiency close to that of sunlight. If the intensity of light is much lower, the endothermicity becomes even greater.

The fluorescence quenching of oxonine can be monitored in conditions of extremely low light intensities by means of the single photon counting technique. The electron transfer process still proceeds at a nearly diffusion-controlled rate independently of light intensity, and this is not expected according to the light-as-heat model; a reaction which is endergonic to some 0.5 eV would not be able to com-

pete with fluorescence emission of a rate constant of around 10^9 s^{-1} . The experimental evidence based on the energetics of photoinduced electron transfer is therefore firmly in favour of the model of light as a form of high-grade energy.

4. Conclusion

We have started with a theoretical discussion of the thermodynamic properties of light, the fundamental question being whether light (or electromagnetic radiation in general) contains a thermodynamic entropy related to light intensity. If this were the case, then the maximum attainable efficiency of conversion of the energy of light into chemical free energy would

be limited and would depend on light intensity.

The actual conversion efficiency can be measured through the energy balance of photoinduced electron transfer reactions. These reactions take place with high efficiency even in conditions in which the entropic model of light implies that they should be highly endergonic, thus giving firm support to the non-entropic model of light (light as a form of high-grade energy, against light as a form of heat energy).

This conclusion reinforces the justification for the development of photo-physical/photochemical methods for the conversion of solar energy into other forms of high-grade energy anywhere in

the world; the conversion efficiency would be quite as high on a rainy day in Switzerland as on a blistering day in the Sahara.

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