

# On reasons for strong absorption of light in an optical fibre at high temperature

S.I. Yakovlenko

**Abstract.** A hypothesis is proposed that explains qualitatively a strong absorption of light in quartz. The hypothesis is based on an analogy with the so-called chemical radiative collisions (RC reactions), which were extensively studied in the 1970–1980s. In these reactions, individual chemical bonds dissociate and new bonds are formed. An estimate is made for a reaction in which a free (non-bridge) oxygen atom bounds with a bridge atom, while another oxygen atom undergoes a reverse transition. The estimates show that the limiting absorption coefficient can achieve ten hundreds inverse centimetres.

**Keywords:** optical fibre, photosubstitution reaction, radiative collisions.

The absorption coefficient of light in the visible and near-IR regions in quartz can be as high as  $\sim 1000 \text{ cm}^{-1}$  at 2000 K [1–5]. This leads to the generation of a damage wave propagating toward laser radiation in optical fibres [1–11]. The wave is usually initiated by a local external heating or by touching a surface absorbing laser radiation by the fibre end.

The mechanism of generation and propagation of a damage wave is clear in principle [1–5, 12, 13]: If the absorption coefficient is increased in some part of the fibre, this part is heated, resulting in a further increase in absorption. The heat conduction provides the propagation of such a heat absorption wave toward laser radiation.

However, the mechanism of the absorption enhancement is not quite clear so far. It is known that the absorption coefficient increases exponentially with temperature and exhibits an additional jump at the quartz melting temperature ( $\sim 2000 \text{ K}$ ). It was shown in [14] that free electrons induced by heating cannot provide the required absorption and there are grounds to believe that strong absorption is related to the interaction of the electron shells in  $\text{SiO}_4$ ,  $\text{SiO} + \text{O}$  complexes.

Below, we propose a hypothesis that explains qualitatively strong absorption at high temperatures. The hypothesis is based on the analogy with so-called radiative

collisions (RC reactions), which were extensively studied in the 1970–1980s (see review [15] and book [16]).

**On radiative-collision reactions.** RC reactions are optical transitions between the electron shells of colliding atoms and molecules. They are of interest, in particular, because transitions can occur simultaneously in two colliding particles, resulting in the appearance of new absorption bands in a gas mixture, which are absent in each of the individual gases. Of most interest for our study are chemical RC reactions [17–20] in which individual chemical bonds dissociate and new bonds are formed. An example of such reactions is the photosubstitution reaction



The possibility of proceeding chemical RC reactions is strongly restricted by the Franck–Condon principle. For example, to realise reaction (1), the atom A should approach the molecule BC so that the configuration of the quasi-molecule\* ABC would simultaneously correspond to the B–C bond and the repulsion of the atom A in the initial state  $|i\rangle$  and also to the A–B bond and the repulsion of the atom C in the final state  $|f\rangle$ . If the substitution reaction does not proceed in the absence of a light field, then the repulsion force at moderate gas temperatures does not allow, as a rule, the atom A to come sufficiently close to the atom B to form a stable AB bond. In this case, the probability of events (1) in the A + BC mixture is very low.

Earlier, important exceptions from this quite common situation were found [17–19]. They take place when a quasi-molecule ABC has a comparatively low-lying ion term. An example is the replacement of one of the fluorine atoms by the xenon atom after absorption of a photon stimulating a transition from the covalent to the ion term of the  $\text{Xe} + \text{F}_2$  system. The results of these studies were registered as a discovery [21], and papers [15, 19] were mentioned in the Nobel lecture [22].

Below, we consider the possibility of a similar reaction in the symmetrical A = C system without the involvement of an ion term.

**On the mechanism of photosubstitution reaction in quartz.**

A stoichiometric quartz has the structure  $\text{SiO}_2$ , but it forms molecular  $\text{SiO}_4$  configurations in a cell. The  $\text{SiO}_2$  quasi-

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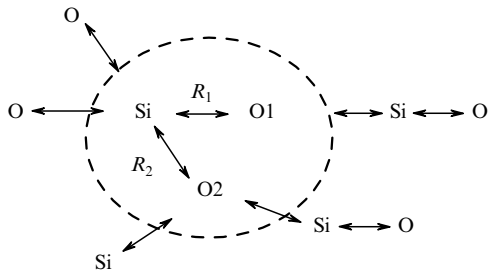
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\* It is accepted to call a quasi-molecule the interacting atomic particles colliding or flying apart at the relative velocity  $v$  which is much lower than the characteristic velocity of electrons in the atom,  $v \ll v_a \approx 2.2 \times 10^8 \text{ cm s}^{-1}$ , so that the concept of an electronic term can be used for such temporal complexes.

molecule is unstable and it does not exist in a stable state in gases. At the same time, the SiO molecule is rather stable (the binding energy is 8.25 eV [23]). This suggests that the electron surfaces of the O + SiO system have both bound and repulsive states for the same nuclear configuration.

Consider for simplicity the O2 – Si – O1 configuration, which is shown inside the dashed ellipse in Fig. 1. Here, O1 and O2 are the oxygen atoms under study. We assume that the O2 atom is first bound with the Si atoms, while the O1 atom is in a quasi-free state, which means that the O2 atom in the initial state is a bridge atom, while the O1 atom is a non-bridge atom. Then, when the rest of the atoms are fixed, the dependence of the interaction energy of the O1 atom with the SiO complex on the distance  $R_1$  between the nuclei of Si and O1 is described by the repulsion curve ( $U_{i,rep}$ ) (Fig. 2). The dependence of the interaction energy of O2 on the distance  $R_2$  between nuclei Si and O2, when the rest of the atoms are fixed, is described in the initial state by the attraction curve ( $U_{i,att}$ ).



**Figure 1.** Scheme of the quartz structure. The dashed curve indicates the O2 – Si – O1 complex.

A photon can simulate the reaction



which is similar to (1). In this reaction, the O1 atom undergoes a transition to the bound state, while the O2 atom passes to a free state. In this case, the O2 atom becomes non-bridged, and the dependence of the interaction energy of O2 with SiO1 on the distance  $R_2$  becomes repulsive ( $U_{f,rep}$ ). At the same time, the O1 atom becomes a bridge atom, and the dependence of the interaction energy of O1 with SiO<sub>2</sub> on the distance  $R_1$  is attractive ( $U_{f,att}$ ) (Fig. 2).

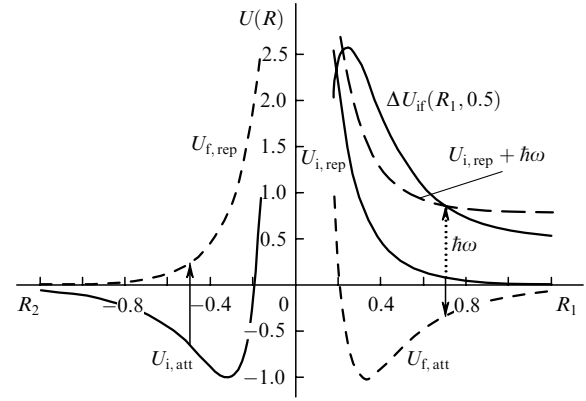
The difference of transition energies

$$\Delta U \equiv U_{f,att} - U_{i,rep} + U_{f,rep} - U_{i,att}$$

of the RC reaction can be reasonably treated as optical transitions in a compound (atom + field) system (see details in [15, 16]). In this case, the terms of the compound system are intersected when  $\hbar\omega = \Delta U$ .

A photon is absorbed when  $\Delta U > 0$ , and it is emitted when  $\Delta U < 0$ . The quantity  $\Delta U$  determines a conditional energy surface to which the system should undergo the photoinduced transition in reaction (2).

**Phototransition probability.** According to the reference data, a phase transition occurs in quartz at  $T \sim 2000$  K. It is reasonable to assume that many non-bridge atoms are formed in this case. As a result, the efficiency of reaction (2) drastically increases.



**Figure 2.** Qualitative dependence of the interaction energy of the oxygen atom with the SiO complex on the distance between the nuclei of O and Si. The solid arrows indicate transitions of the SiO system, the dashed arrow shows the transition corresponding to absorption of a photon. All the quantities are expressed in relative units.

We will use the so-called quasi-static approximation, which was described in detail in [15, 16]. Within the framework of this approximation, the spontaneous emission spectrum can be written in the form

$$A_{fi}(\omega) = A_{fi} \delta(\Delta U_{if} - \hbar\omega). \quad (3)$$

Here,  $A_{fi}$  is the integrated probability of a spontaneous transition for a given configuration, which is proportional to the square of the transition dipole moment in a quasi-molecule, and  $\delta(x)$  is the delta function.

For the Maxwell velocity distribution (Boltzmann energy distribution), the number of SiO + O quasi-molecules in the unit volume with the distances  $R_1$  and  $R_1 + dR_1$  between atoms is determined by the density of nearest-neighbour distribution

$$dN_i^{\text{SiO}} = N_i^{\text{SiO}} N_i^{\text{O}} \exp \left\{ - \left[ \frac{U_{i,rep}(R_1)}{T} \right] \right\} dp(R_1),$$

where  $N_i^{\text{SiO}}$  and  $N_i^{\text{O}}$  are the densities of SiO and O;  $T$  is the gas temperature measured in the energy units; and  $dp = 4\pi R_1^2 \times \exp[-(4\pi R_1^3/3)(N_{\text{SiO}} + N_{\text{O}})] dR_1$ .

By multiplying  $dN_i^{\text{SiO}}$  by the photon energy and integrating over  $R_1$ , we obtain the expression for the power of spontaneous RC emission from the unit volume

$$Q_{sp}(\omega) = \hbar\omega A_{fi} \frac{4\pi R_{1\omega}^2}{F(\omega)} \exp \left[ - \frac{U_{i,rep}(R_{1\omega})}{T} \right] \times \exp \left[ - \frac{4\pi R_{1\omega}}{3} (N_{\text{SiO}} + N_{\text{O}}) \right] N_i^{\text{SiO}} N_i^{\text{O}}.$$

Here,  $F(\omega) = (d\Delta U/dr)_{r=R_1}$  is the difference of the slopes of the terms at points  $R_1 = R_{1\omega}$ , where  $\hbar\omega = \Delta U$ .

By using the relation between the emission power and the absorption coefficient  $\kappa_{if}(\omega)$ , we obtain

$$\kappa_{if}(\omega) = q_{if}^0(\omega) N_i^{\text{SiO}} N_i^{\text{O}} \exp \left[ - \frac{U_{i,rep}(R_{1\omega})}{T} \right]. \quad (4)$$

Here,

$$q_{if}^0(\omega) = \frac{\lambda^2}{4} A_{fi} \frac{4\pi\hbar R_{1\omega}^2}{F(\omega)} \exp\left[-\frac{U_{i,rep}(R_{1\omega})}{T}\right] \times \exp\left[-\frac{4\pi R_{1\omega}^3}{3}(N_{SiO} + N_O)\right] N_i^{SiO} N_i^O. \quad (5)$$

The quantity  $q_{if}^0$  ( $\text{cm}^5$ ) is the absorption coefficient per pair of particles, being similar to phototransition cross sections in atoms.

Because the shape of potential surfaces is unknown, we will estimate only the limiting value of  $q_{if}^0(T \rightarrow \infty)$ . Assuming that  $\lambda \sim 1.06 \mu\text{m}$ ,  $A_{fi} \sim 10^6 \text{ s}^{-1}$ ,  $R_{1\omega} \sim 0.2 \text{ nm}$ ,  $F(\omega) \sim 2 \text{ eV}/R_{1\omega}$ ,  $N^{SiO} \sim N^O \sim 10^{22} \text{ cm}^{-3}$ , we obtain  $q_{if}^0(T \rightarrow \infty) \sim 3 \times 10^{-40} \text{ cm}^5$ , and  $\kappa_{if} \sim 3 \times 10^4 \text{ cm}^{-1}$ .

This value is greater approximately by a factor of forty than the absorption coefficient ( $760 \text{ cm}^{-1}$ ) required for explaining the observed velocity of heat absorption waves [3, 4, 12, 13]. To obtain more accurate results, it is necessary to calculate the energies of excited electronic states for a system containing five atoms.

Note that the drastic temperature dependence of the absorption coefficient is observed for two reasons. First, the rate of reaction (5) increases exponentially because a greater number of atoms can 'get in on a potential hill', i.e., approach the distance at which a photon can be absorbed. Second, the number of non-bridge O atoms increases drastically at the quartz melting temperature. As quartz is cooled, the non-bridge atoms undergo transitions to the bound states and quartz becomes transparent again.

Therefore, the mechanism of photosubstitution proposed in the paper can explain qualitatively the high absorption coefficients of quartz at high temperatures.

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