

receiver in the form of a sealed vessel (2) through the bottom of which four platinum electrodes passed, were ground flush, and were coated with a layer of molybdenum to protect them against the amalgamating properties of mercury. The entire instrument was immersed in liquid helium.

The experiment consisted of the following states:

1. The reflector temperature was set at  $0^{\circ}\text{C}$  (a temperature at which all the mercury atoms are fully reflected at the employed flux densities).
2. The evaporator heater was turned on, and after about  $\sim 2$  minutes the mercury temperature in the evaporator assumed the required value ( $T = 0 - +80^{\circ}\text{C}$ ).
3. The evaporator oven was turned off after a noticeable conductivity ( $R \sim 10^8$  ohm) appeared; the resistance variation ceased after  $\sim 20$  sec.
4. The reflector-surface temperature was set.
5. The evaporator heater was again turned on and the temperature raised to the working value and kept constant there for 3 - 5 minutes, after which the heater was again turned off. The dependence of the resistance on the time was plotted with the automatic recorder.

The  $R(t)$  dependence, which was investigated in detail in [2], was well reproducible under conditions of total particle reflection and had a sufficient rapid rise (from  $\sim 10^6$   $\Omega$ /atomic layer at  $R \sim 10^7$   $\Omega$  to  $\sim 10^{-2}$   $\Omega$ /atomic layer at  $R \sim 1$   $\Omega$ ). The character of the reflection of the mercury atoms from the glass surface was close to refuse, so that the  $R(t)$  plots obtained in the direct [2] and reflecting instruments (at  $\alpha = 0$ ) at the same flux density can be made congruent by changing the time scale by a factor 7 - 8. From the slopes of the curves obtained (a) under total-reflection conditions ( $T_{\text{ref}} = 0^{\circ}\text{C}$ ) and (b) under conditions of partial reflection (at the selected reflector temperature) determined the accommodation coefficient. The average attained accuracy was  $\sim 3\%$ .

To repeat the experiment, it was sufficient to heat the entire instrument, cooling only the stub containing the mercury, and to recondense all the mercury that had previously settled in the evaporator.

The results are shown in Fig. 2. The accommodation coefficient was estimated with particular care at  $4.2^{\circ}\text{K}$ , namely  $(1 - \alpha) < 3 \times 10^{-3}$ . The effective condensation temperature  $T_{\text{cr}}$  was arbitrarily chosen to be the temperature corresponding to reflection of 50% of the incident atoms. The figure shows also the dependence of  $T_{\text{cr}}$  on the intensity of the molecular beam incident on the surface. Naturally, the mercury already present on the reflector surface alters the accommodation coefficient. Thus, for example, if a thick mercury film ( $d_{\text{eff}} \sim 1 \mu$ ) is condensed on the reflector surface, then we get  $(1 - \alpha) < 0.01$  at  $T \leq 180^{\circ}\text{K}$ . One should expect the critical temperature to become higher when the condensation time is increased.

[1] M. Volmer and J. Estermann, *Zs. f. Phys.* **8**, 1 (1921).

[2] V. L. Tsybalenko and A. I. Shal'nikov, *Zh. Eksp. Teor. Fiz.* **65**, 2086 (1973) [*Sov. Phys.-JETP* **38**, No. 5 (1974)].

#### SUPEREQUILIBRIUM UV RADIATION IN SELF-IGNITION OF A $\text{CS}_2 + 4\text{O}_2$ MIXTURE AT ATMOSPHERIC PRESSURE

E. B. Gordon, M. S. Drozdov, Yu. L. Moskvina, and V. L. Tal'roze  
Institute of Chemical Physics, USSR Academy of Sciences  
Submitted 30 July 1973; resubmitted 21 September 1973  
*ZhETF Pis. Red.* **18**, No. 9, 560 - 563 (5 November 1973)

Anomalous emissivity was observed in self-ignition of a mixture of carbon disulfide with oxygen in the spectral band 350 - 420 nm. A mechanism explaining this effect is proposed on the basis of the kinetic features of the system.

Many spontaneous gas-chemical reactions are accompanied by nonequilibrium emission in the

visible and in the ultraviolet; this emission is due to electron excitation of the products of highly exoenergetic elementary acts in which atoms and radicals take part. In the cases investigated to date, the lack of equilibrium was due to the particles in excess of equilibrium, which are produced, for example, in the course of a branched chemical chain reaction. This was clearly demonstrated in the combustion of strongly diluted low-pressure mixtures, including low-temperature carbond-disulfide flames [1].

For ordinary self-maintaining flames and adiabatic explosions at atmospheric pressure in nondiluted mixtures, especially at large conversion rates, the main emission in the UV and in the visible bands is customarily assumed to be in equilibrium [2]. The reason is that when the temperature and density are increased the concentration of the chemically-active particles comes closer to equilibrium, the energy relaxation processes accelerate, and self-absorption of the radiation ultimately comes into play.

We have attempted to verify this general premise experimentally, using as an example just the  $CS_2 + O_2$  mixture for which Kondrat'ev observed a strong above-equilibrium emission at low temperatures and pressures [1]

Our experiments have shown that in self-ignition of the mixture  $[CS_2]:[O_2] = 1:4$  ( $P = 0.1 - 1.2$  atm) the UV emission is due to the radiative-recombination reaction  $SO + O \rightarrow SO_2 + hv$ , and its intensity can be described by the expression  $I = k_r[\hat{SO}][\hat{O}]$  photons/cm<sup>3</sup>/sec, where  $k_r$  is the rate constant of this reaction and  $[\hat{SO}]$  and  $[\hat{O}]$  are simply the equilibrium concentrations of the active particles under conditions of adiabatic combustion of the mixture [3].

Satisfaction of the indicated relations indicated that equilibrium has been established over all degrees of freedom and corresponds to an adiabatic mixture-combustion temperature  $T$ . This temperature was calculated with allowance for the dissociation of the end products, using the tabulated values of the equilibrium constants and of the specific heats of the components; the calculation accuracy is  $\Delta T \leq 100^\circ$  at a pressure  $P = 1$  atm and  $T = 3500^\circ K$ .

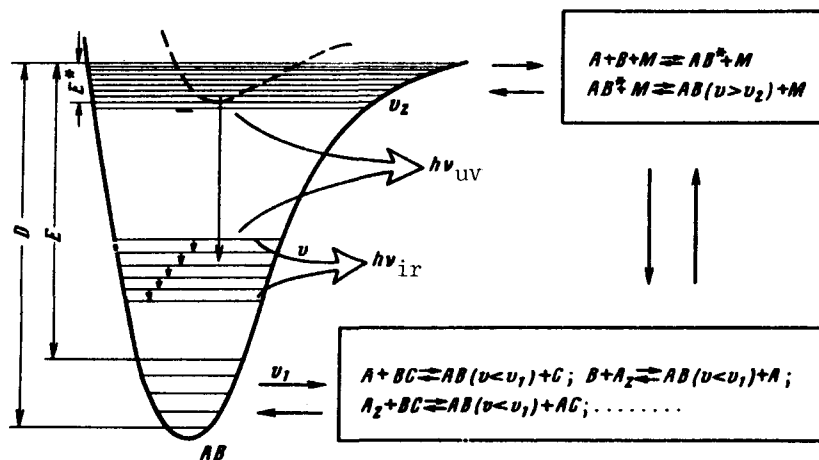
Under condition of full equilibrium, the spectral density of emission from a unit surface should not exceed the corresponding value for an absolutely black body with the same temperature,  $I_\lambda^0$ . The most convincing proof of the absence of equilibrium between the levels connected by the phototransition would therefore be obtained if the emissivity of the medium were to exceed unity.

To this end, we performed calorimetric and kinetic measurements of the radiation accompanying the self-ignition of the mixture. The main result, which in our opinion is unexpected, is that at wavelengths corresponding to maximum emission ( $\lambda_{max} \approx 370$  nm) the spectral emission density at 1 atm amounts to  $I = 1.2 - 1.5$  W/cm<sup>2</sup>nm, which is larger by an order of magnitude than the corresponding black-body value  $I^0(\lambda = 370 \text{ nm}) = 0.11$  W/cm<sup>2</sup>nm.<sup>1)</sup>

Particularly remarkable are the large lifetimes of this deviation from equilibrium,  $(4 - 5) \times 10^{-3}$  sec at such high pressures (it is assumed [2] that at the indicated  $P$  and  $T$  the deviation from equilibrium cannot last more than  $10^{-7}$  sec). Thus, our experiments show that under condition of steady-state product concentration, the populations of the levels connected by the investigated phototransition deviate strongly from equilibrium for quite a long time.

The cause of the effect is most likely the low population (in comparison with equilibrium) of the mean vibrational levels of the molecule  $AB$ , at which the phototransition terminates in the radiative recombination reaction. This situation can obtain under conditions of steady-state thermodynamic equilibrium over all the other levels and particle numbers, for the following reasons (see the figure):

1. In chemical reactions (radical and molecular, which are quite fast at  $T = 3500^\circ K$ ), the mean levels of the molecule  $AB$  are not populated. Indeed, the



recombination of the atoms and radicals leads to  $E_{AB}^V \approx D_{AB}$  ( $E_{AB}^V$  is the vibrational energy of the level  $v$  and  $D$  is the dissociation energy), but in reactions in which the molecules take part we have  $E_{AB}^V \ll D_{AB}$ , inasmuch as at such high temperature there are no noticeable amounts of compounds with binding energies  $E \leq 80$  kcal/mole, so that the thermal effect of such reactions is given by  $Q \approx D_{AB} - E \ll D_{AB}$ .

2. The anharmonicity of the vibrations causes the filling of the mean levels to proceed much more slowly than the relaxation of the lower levels (there is no fast  $v-v$  exchange<sup>2)</sup>).

3. The rather rapid non-equilibrium depletion of these levels via radiative vibrational transitions in the IR region, up to very large  $Pd$  ( $d$  is the linear dimension of the vessel) is not hindered by self-absorption, in view of the low concentration of the particles at these levels and the considerable spectral shift of these levels, which is due to the anharmonicity.

It can be shown that in this case the degree of non-equilibrium for levels  $v_1 < v < v_2$  ( $E^{v_1} \approx D - E$ ,  $E^{v_2} \approx D - E^*$ ) is described by the expression

$$N_v / \hat{N}_v = \exp(-S_v) + \exp\left(-\frac{E^{v_2} - E^v}{RT}\right) [1 - \exp(-S_v)] \gamma_v,$$

where  $\hat{N}_v$  is the population of the level  $v$  in thermodynamic equilibrium,

$$S_v = \sum_{u=v_1}^{v-1} \ln\{1 + [r_{u+1} k_{u+1} M]^{-1}\},$$

$M$  is the total concentration,  $k_v$  is the rate constant of the  $v-T$  exchange, and  $\tau_v$  is the radiative lifetime of the vibrational level  $v$ ; we have  $0 < \gamma_v < 1$  ( $\gamma_{v_1} = 1$ ;  $\gamma_{v_2} = 0$ ).

This yields a degree of non-equilibrium  $N_v / \hat{N}_v \approx 0.1 - 0.01$ . at  $k_v \approx 10^{-15}$  cm<sup>3</sup>/sec,  $\tau_v^2 \approx 10^{-4}$  sec, and  $P \approx 1$  atm for vibrational levels  $v - v_1 = 10 - 30$ .

Thus, the existence of irreversible IR emission from mean medium levels can make it possible to maintain in quasistationary fashion the non-equilibrium character of the phototransition  $AB^* \rightarrow AB(v) + h\nu_{IR}$ . This leads to a brightly pronounced anomalous emissivity of these systems. The question of the accompanying inverted population of the electron-vibrational transitions called for a special study.

1) The value of  $I_\lambda$  measured by us corresponds to an effective temperature  $T_{eff} = 4400^\circ K$ .

2) In our experiments the rate of the  $v-T$  processes exceeded the rate of filling of the medium  $v$  in UV transitions:  $I \approx 10^{20}$  quanta/cm sec and  $W_{v-T} \geq 10^{21}$  cm<sup>-3</sup>sec<sup>-1</sup>.

[1] V. N. Kondrat'ev, Zh. Fiz. Khim. **13**, 1260 (1939); **14**, 281, 287 (1940).

[2] A. G. Gaydon, Spectroscopy of Flames, Chapman and Hall, 1957.

[3] E. B. Gordon, M. S. Drozdov, Yu. L. Moskvina, and V. L. Tal'roze (Dokl. Akad. Nauk SSSR, in press (1974)).

#### TEMPERATURE DEPENDENCE OF THE RELAXATION RATE OF THE $\pi^+$ -MESON SPIN IN FERROMAGNETS

I. I. Gurevich, A. N. Klimov, V. N. Maiorov, E. A. Meleshko, B. A. Nikol'skii, V. S. Roganov, V. I. Selivanov, and V. A. Suetin

I. V. Kurchatov Institute of Atomic Energy

Submitted 2 October 1973

ZhETF Pis. Red. **18**, No. 9, 564 - 565 (5 November 1973)

Relaxation of the  $\pi^+$ -meson spin in iron and nickel was revealed by the attenuation of the muon precession in a transverse magnetic field. This precession can be the result of a number of processes, such as spin exchange between the muon and an electron of the metal in contact interaction, or the change in the spin-precession frequency of individual muon because of differences in the local magnetic fields at the muon locations (e.g., in the octa- and tetrapore of the unit cell). Another possible cause is the muon diffusion over the crystal. Of all the indicated processes, only the diffusion can depend on the temperature. When the temperature is increased, the rate at which the muon diffuses over the crystal increases, and an increase in the muon velocity can decrease the depolarizing action of the local magnetic fields, since these fields begin to vary with time when the muon moves. A decrease in the rate of depolari-