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[1] S.A. Volobuev et al. Acta Phys. Acad. Scient. Hungar. 29, Suppl. 1, 127 (1970).
[2] S.A. Volobuev, et al., Izv. AN SSSR, ser. fiz. 34, 2259 (1970).
[3] Pravda, 24 January 1969.
[4] R. Browning et al., Nature 238, 138 (1972).
[5] G.M. Frye et al., Reported at IAU Symposium No. 55 on X-ray and γ-ray Astronomy, 1972.
[6] D.R. Hearn, Nucl. Instrum. Meth. 70, 200 (1969).
[7] E.O'Mongain, Preprint of Smithsonian Institute, Sept. 1972.
[8] G.M. Frye et al., Nature 233, 466 (1971).
[9] S.A. Volobuev et al., Astron. zh. 48, 1105 (1971) [Sov. Astron.-AJ 15, 879 (1972)].
[10] B.M. Vladimirskii et al., ibid. 49, 3 (1972) [16, 1 (1972)].
[11] F. Biraud, Nature 232, 178 (1971).

ELECTRON-VIBRATIONAL INVERSION IN THE REACTION OF OXIDATION OF CARBON DISULFIDE

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As is well known, chemical reactions are widely used to produce inverted population of the vibrational degrees of freedom of molecules [1]. It has been suggested many times that chemical excitation of the electronic levels would be desirable [2], since a rise in the temperature of the reacting mixture does not influence strongly the deactivation of the electronically excited molecules, so that the rate of such a chemical reaction can be made very large (e.g., limited only by the rate at which the reacting substances explode) without loss of inversion.

The appearance of essentially non-equilibrium luminescence in the course of various gas reactions (chemoluminescence) has been known for a long time [3]. The purpose of this paper is to point out the possibility of obtaining electron-vibrational inversion in the reaction of oxidation of carbon disulfide in the gas phase ($CS_2 + O_2 \rightarrow CO, SO_2$).

Let us examine the oxidation of carbon disulfide, which goes through the following stages [3]:

$$CS_2 + O \rightarrow CS + SO, \qquad \text{(I)}$$

$$CS + O_2 \begin{cases} \rightarrow CO + SO \\ \rightarrow COS + O, \end{cases} \qquad \text{(II)}$$

$$SO + O + M \begin{cases} \rightarrow SO_2 + M & \text{(III)} \\ \rightarrow SO_2^* + M. & \text{(III*)} \end{cases}$$

The third reaction produces, with appreciable probability, the electron-excited molecules SO_2 (excitation energy $\hbar\omega \approx 3.5$ eV), and this produces strong luminescence of the reacting gases. This luminescence is interpreted as triple-single transitions in the SO_2 molecule, which are allowed when it collides with paramagnetic particles (O_2, O, SO). The ratio of the recombination constant of the radicals SO and O in the triplet (III*) and singlet (III) states of SO_2 is approximately equal to the ratio of the statistical weights of these states [4], i.e., 3. Although the rate of formation of the SO_2^* molecule is three times the rate of formation of SO_2, this is not enough to obtain inversion of the pure electronic populations. At a rapid relaxation of the vibrational energy, however, there can exist electron-vibrational inversion, and this can indeed be used to obtain the effect.

The excited triplet molecules emit spontaneously with extremely low probability ($1 - 10^2$ sec^{-1}). Emission is more probable when the SO_2^* molecule collides with some intermediate paramagnetic particle. The cross section of such a process is of the order of

$$\sigma_{TS} \cong \sigma_0 W_0 \tau_c , \tag{1}$$

where σ_0 is the gas-kinetic collision cross section (10^{-15} cm^2), $W_0 \sim 10^8$ sec^{-1} is the probability of the spontaneous allowed transition in the complex made up when the molecules collide, and τ_c is the collision time. At a temperature $\sim$2000°K and at atmospheric pressure we have $\sigma_{TS} \simeq 10^{-19}$ cm^{-2}, and the emission probability is equal to $A = \sigma_{TS} N_p v = 10^5$ sec^{-1}, where N_p is the density of the paramagnetic particles. Let us examine the dynamics of this system. We shall trace, for simplicity, only the density n^* of the SO_2 molecule in the electron-excited state at the zeroth vibrational sublevel1) and the density n_v of the molecules in the ground state on the vibrational sublevel numbered v,2) to which the radiative transition takes place, and also the spectral density of the emission at the generation frequency $u_\omega(t)$. The equations take the form

$$\frac{dn^*}{dt} = -(n^* - n_v) B u_\omega(t) - (A + k_d) n^* + q^* , \tag{3}$$

$$\frac{du_\omega(t)}{dt} = u_\omega(t) [\sigma_{iv} c (n^* - n_v) - p]. \tag{4}$$

Here A and B are the Einstein coefficients in the case when the transitions are allowed in the collisions, k_d is the probability of nonradiative deactivation of SO_2^* upon collision. From the experimental data [3] on the glow of the carbon disulfide flame we have $k_d/A \sim 10$. The cross section σ_{iv} of the induced emission of light is equal to [5]

$$\sigma_{iv} = \frac{A}{\Delta\omega} \frac{\pi^2 c^2}{\omega^2} s_v , \quad s_v = e^{-(a_1 + a_2)} \frac{a_1^{v_1} a_2^{v_2}}{v_1! \, v_2!} , \tag{5}$$

and amounts to $\sigma_{iv} \simeq 10^{-19}$ cm^2 under the conditions (2), if the spectral width of the emitted line is3) $\Delta\omega \sim 0.01$ and the Franck-Condon factor is $s_v \sim 0.1$ (for $v_1 = 1$ and $v_2 = 1$).

The cross section of the triplet-singlet pure radiative transition is smaller by one or two orders of magnitude at these pressures. q^* and q_0 are the

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1) n^* is the molecule density in the excited state, divided by the statistical weight of this state.

2) v determines the quantum numbers of two normal vibrations of the SO_2 molecules, viz., the valent-symmetrical v_1 ($\omega_1 = 11.50$ cm^{-1}) and the deformational v_2 ($\omega_2 = 525$ cm^{-1}).

3) Such a width is due to the fact that the transition takes place in a collision.

rates of production of the molecuels SO_2^* and SO_2 in the processes (III*) and (III). p is the coefficient of radiation loss in the resonator (10^7 sec^{-1}). n_v satisfies the usual relaxation-vibrational equations [7], and in their solution it is important to assume that the vibrational relaxation is the fastest process (the vibrational relaxation time is $\sim 10^{-9}$ sec4)).

Without stopping to solve these equations (similar ones were investigated, e.g., in [9]), let us formulate some conclusions. After a time t_0, which is expressed in terms of the system parameters in the following manner

$$t_o = k_d^{-1}\left(\frac{2}{R}\ln\frac{kd}{2u_\omega(0)B}\right)^{1/2}, \qquad R = \frac{\tilde{q}c\sigma_{iv}}{k_d^2} \tag{6}$$

($u_\omega(0)$ is the initial radiation density at the frequency ω), the radiation density in the volume grows to the level $u_\omega \sim R(k_d/B)$. In the derivation, we have assumed that the following conditions

$$Q = \frac{q^* c\sigma_{iv}}{k_d p} > 1, \qquad R \gg 1 \tag{7}$$

(as a result of which the loss coefficient drops out from the expression for t_0) are satisfied, as is also the natural condition5)

$$\tilde{q} = q^* - q_o \exp\left[-\frac{\hbar}{kT}(\omega_1 v_1 + \omega_2 v_2)\right] > 0. \tag{8}$$

At $t > t_0$, the stimulated emission processes will prevail over the nonradiative deactivation of the SO_2^* molecules, and the system will be in a regime in which the entire excitation energy of the molecules goes over into coherent radiation.

Since SO_2 molecules in the ground state accumulate in the reaction volume, the generation time will be shorter than $\sim 1/k_d$. Naturally, $t_0 < 1/k_d$ and we consequently have from (6)

$$R > \ln\frac{k_d}{A} + \frac{\hbar\omega}{kT} \cong 20. \tag{9}$$

If the mixture explodes, the rate of release of chemical energy is limited by the denonation speed [10], u_{det} = 2 - 5 km/sec; $\tilde{q}$ is proportional to u_{det} and equals $\sim 10^{23} - 10^{24}$ $(cm^3 sec)^{-1}$ at an initial pressure 1 atm. Under these conditions, R can reach 100 - 300.

In the case of a stationary regime6), the necessary rate $\tilde{q}$ of particle production is determined from the condition Q > 1 (7). This yields $\tilde{q} > 10^{22}$ $(sec\text{-}cm^3)^{-1}$, which is attainable in principle for a stationary regime.

It is difficult to obtain a mixture of carbon disulfide with oxygen at high pressures (above 1 atm), for at 80 - 100° (and at the stoichiometric composition) such a mixture ignites spontaneously at low pressures (10 mm Hg). It

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4)From [6] we have $\alpha_1 \sim \alpha_2 \sim 1.5$.

5)Without which population inversion is generally impossible.

6)The advantages of a stationary regime, as well as the estimate that follows, was pointed out to us by V.L. Tal'roze, to whom we are deeply grateful.

is known, however, that at the same temperatures and higher pressures such mixtures have second and third spontaneous-ignition pressure limits, between which such a gas mixture can exist quite well [3]. The conditions for the transition to these pressures are quite difficult to indicate, since there are no published quantitative experimental data on the ignition peninsular (with variation of the CS_2 and O_2 content). Another interesting possibility is that of obtaining the necessary combustion conditions in a compression shock wave.

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[1] N.G. Basov, V.I.Igoshin, E.P. Markin, and A.N. Oraevskii, Kvantovaya elektronika 1, 3 (1971) [Sov. J. Quant. Electr. 1, 1 (1971)].
[2] V.L. Tal'roze, Kinetika i kataliz 5, 11 (1964). T.L. Andreeva, V.I. Malyshev, A.I. Malov, I.I. Sobel'man, and V.N. Sorokin, ZhETF Pis. Red. 10, 423 (1969) [JETP Lett. 10, 271 (1969)].
[3] V.N. Kondrat'ev, Kinetika khimicheskikh gazovykh reaktsii (Kinetics of Chemical Gas Reactions) AN SSSR, 1958.
[4] S.W. Benson and T.O. Fueno, J. Chem. Phys. 36, 1957 (1962).
[5] I.I. Sobel'man, Vvedenie v teoriyu atomnykh spektrov (Introduction to the Theory of Atomic Spectra) GIFML, 1963.
[6] N. Metropolis and H. Beutler, Phys. Rev. 57, 1078 (1940).
[7] E.V. Stupochenko, S.A. Losev, and A.I. Osipov, Relaksatsionnye protsessy v udarnykh volnakh (Relaxation Processes in Shock Waves), Nauka, 1965.
[8] J.D. Lambert and R. Salter, Proc. Roy. Soc. A243, 78 (1957).
[9] V.A. Kochelan and S.I. Pekar, Zh. Eksp. Teor. Fiz. 58, 854 (1970) [Sov. Phys.-JETP 31, 459 (1970)].
[10] Ya.B. Zel'dovich, Zh. Tekh. Fiz. 11, 492 (1941).

POSSIBLE EXISTENCE OF AUTOLOCALIZED STATES OF CARRIERS IN MAGNETIC SEMICONDUCTORS WITH NARROW BANDS

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It is shown in the present paper that autolocalized states can be thermodynamically favored in ferro- and paramagnetic semiconductors with $A \gg \Delta E \gg zIS^2$ (ΔE is the width of the band, $-2AS^{-1}\vec{s}\cdot\vec{S}_n$ and $2I\vec{S}_n\cdot\vec{S}_{n'}$, are the exchange energies of the electron interaction with the n-th and the neighboring atoms, z is the coordination number, and S is the spin of the atom).

It will be shown here that autolocalized fluctuon states, i.e., bound states of a carrier and magnetization fluctuation, can be thermodynamically favored in ferromagnetic and paramagnetic semiconductors with $A \gg \Delta E \gg zJS^2$ (ΔE is the width of the conduction band, $-2AS^{-1}\vec{s}\cdot\vec{S}_n$ and $-2J\vec{S}_n\cdot\vec{S}_{n'}$, are the exchange energies of the interaction of the electron with the n-th atoms and of the neighboring atoms with one another, z is the coordination number, and S is the spin of the atom).

Such large-radius states were investigated earlier for the opposite case $\Delta E \gg A \gg zJS^2$ [1 - 4]. On the other hand, in the case $A \gg \Delta E$, according to [5 - 7], the strong interaction leads to the formation of bound states of the electron and the atom spin. The resultant spin-electron complexes move in the