ELEMENTARY CHEMICAL PROCESSES OF ATOMIC IODINE AND BROMINE AS INITIATED

BY EMISSION FROM IODINE (λ = 1.3 μm) AND BROMINE (λ = 2.7 μm) LASERS

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The realization of photodissociation laser operating on the transition from the spin-orbit-excited $^2P_{1/2}$ state to the ground $^2P_{3/2}$ state in halogen atoms does not seem to be a very complicated problem. One has only to choose an appropriate halogen-containing compound which would preferentially produce excited atoms upon photodissociation followed by flash-photolysis with white light, to admit this gas into a long optical cell, and to flash it by using a conventional Xefilled discharge tube. In such a way, widely known iodine (λ = 1.3 μm) and bromine (λ = 2.7 μm) have been developed; a chlorine (λ = 11.35 μm) laser has recently been brought into action in our laboratory [1]; and there is not much doubt in that an atomic fluorine laser will also appear in the near future. In spite of the strongly differing lifetimes relative to spontaneous emission, the cross-sections for stimulated emission are nearly the same for all the halogen atoms, and hence all the above mentioned pulsed lasers could be realized within the same experimental set-up.

Since the lower laser level is the ground state of the atom, these lasers could readily be used for the resonant excitation of respective halogen atoms. In spite of the fact that lasing occurs between determined hyperfine atomic sublevels, the so-called "bottle neck" effect is suppressed by collisions with the molecules of buffer gas: due to the presence of quadrupole moment in the ground $^2P_{3/2}$ state, mixing of hyperfine sublevels is brought about at every collision [2]. That is why all the atoms will be in resonance with laser emission.

However, the main question remains to be answered: what has a photochemist to do with all that? In fact essential acceleration of endothermic reactions at the expense of excitation energy may be expected only for iodine atoms in which spin-orbit splitting is relatively large. For chlorine atom, for example, the excitation energy is only several times greater than thermal energy at room temperature, and the acceleration is no doubt very small.

In the present communication, I would like to demonstrate, with the example of exchange reactions between halogen atoms and diatomic halogen molecules which we have been studying, the occurrence of a number of rather strong and, at first glance, unexpected effects of spin-orbit excitation of the reactant atom on reaction rate, energy state of products and the branching ratio for fast exothermic reactions.

In our kinetic studies, it was convenient to generate the excited atoms by flash-photolysis of halogen-containing compounds, whereas the pulsed laser on the transition in the atom under study was utilized not for excitation, but for monitoring the concentrations of atoms in the $^2P_{1/2}$ and $^2P_{3/2}$ states [3]. The excited atoms are generated upon 5 μs - flash in a long quartz cell with admitted halogen containing compound and reactant molecules. The special optical system provides a possibility of the multiple passage of a probing short "weak" laser beam through the cell, using multiple passes. The absorption thus measured is proportional to the difference of populations at the moment of probing, $n(P_{1/2}) - 1/2\ n(P_{3/2})$; moreover, upon admission of chemically inert gas-relaxant (O_2 for iodine, CO_2 for bromine, freon for chlorine) one may obtain as well a total concentration of the reactant and product atoms at any desirable moment. The kinetic curves were taken both upon the variation of probing delay time and of molecular reactant concentration. The method has a sensitivity of 10^{13} cm^{-3} and time-resolution of 3 μs.

First of all it was of interest to answer the question in what way the excitation of reactant atom influences the state of product atom for the reactions in which the formation of the excited product is possible from energetic considerations. By using iodine and bromine lasers for probing [4] we have confirmed the conclusion [5] that the excited bromine atoms are predominantly generated in the reaction

$$I^* + Br_2 \longrightarrow IBr + Br \tag{I}$$

and have also measured the branching ratios for the three reaction channels: leading to $Br(^2P_{3/2})$, to $Br(^2P_{1/2})$, and to collisional relaxation of I^*. The reaction

$$I^* + IBr \longrightarrow I_2 + Br \tag{II}$$

turned out to behave in a similar way. For both the reactions, the excitation of reactant results also in the acceleration of the process, which is endothermic in the absence of excitation. Therefore of particular interest was the reaction

$$F + Br_2 \longrightarrow FBr + Br \tag{III}$$

which even in the absence of excitation occurs with the rate constant of 2.10^{-10} cm^3s^{-1}, i.e. nearly gas-kinetical value. For this reaction quite by accident the heat release exactly compensates the difference in spin-orbit splittings in fluorine and bromine atoms. And in this case it appears, that negligible (404 cm^{-1}) excitation of fluorine atom drastically changes the yield of the excited Br atoms, i.e. spin-orbit state of F atom dictates the state of Br atom which is formed in the reaction.

These data, obtained by us in 1980, led us to consider whether the rule of spin--orbit state conservation holds true for all the reactions of this kind, and we began a search for other implications. Our attention was first drawn by the reaction

$$Br + BrI \longrightarrow Br_2 + I \tag{IV}$$

which is the reverse of reaction (I). The following reported data were available. As measured by IR luminescence by authors of |6|, the total rate constant for the quenching of the excited bromine atoms by BrI molecules (including both the reaction and collisional relaxation) to be 35 times slower than that of reaction (IV) for the unexcited atoms as measured in |7| by the method of atomic resonant fluorescence. We failed to find any comments in literature on this paradox. So we had a good chance to check these data within the framework of the same experimental approach. This turned out to be true: the excitation results in the strong retardation of chemical reaction.

This effect may be explained from the standpoint of the spin-orbit conservation rule. The rule allows the formation of excited iodine atoms from the excited bromine atoms, while this is suppressed from energetic considerations; but at the same time the reaction pathway leading to the formation of unexcited iodine atoms is prohibited by the rule. In contrast the channel including the lower states of atoms have any restriction. Having understood the reason for the retardation of exchange reactions upon the excitation of atoms, we predicted |4| that it should take place and in other cases, and that the extent of retardation has to be determined not by value of excitation energy but by the extent of the rigidity of the rule.

The recent data for the reaction

$$Cl + ClI \longrightarrow Cl_2 + I \tag{V}$$

obtained in |11| and by us |1| have supported this prediction; reaction (V) is also retarded upon excitation and also about 30 times in spite of the fact that spin-orbital splitling in chlorine atom is 4.2 times lower than that of bromine atom.

The combination of peculiarity of energy diagrams of reactants with the demands of the spin-orbit conservation rule may result in the reaction products being essentially different upon spin-orbit excitation of the atomic reactant.

The reaction

$$Br + ICl \longrightarrow BrI + Cl$$
$$\longrightarrow BrCl + I$$
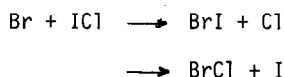
may serve as a good example. For unexcited bromine atoms iodine atoms and BrCl molecules will be the main reaction products. Upon the excitation of Br atoms excited Cl atoms and BrI molecules become the main products. An investigation of this reaction is now in progress.

Attempts to explain the rule of spin-orbit state conservation in exchange reactions have already been undertaken; for the model reaction $I + I_2 \longrightarrow I_2 + I$ it has been confirmed |8| by quantum-chemical calculations. The main problem is seemingly related to the possible interaction of orbital angular electron momentum with molecular rotation.

These effects are of interest not only from a theoretical point of view. For instance, reactions (I) and (IV) provide a possibility to carry out chemical transformation of the active medium of iodine laser (including CW laser) into the active medium of bromine laser, as well as to materialize bromine laser with laser pumping from iodine laser. An important feature of reactions (I), (II) is the fact that they transform noninverse excitation into inverse one, since the reactions of atomic iodine in the ground state are endothermic and hence slow. Reaction (III) makes it possible to transform the small energy splitting of fluorine atoms into the order-of-magnitude larger splitting of bromine atoms. Reactions (IV), (V) may be considered as the processes of depletion of the lower laser level. The occurrence of these processes makes it feasible to base CW bromine and chlorine lasers on IBr and ICl molecules, in particular, solar-pumped lasers |9|. The combination of reactions (II) and (IV) makes it possible to suggest |10| an efficient photodissociation-chemical laser on the mixture C_3F_7I / IBr according to the following scheme:

$$C_3F_7I + h\nu \longrightarrow C_3F_7 + I^*$$

$$IBr + h\nu \longrightarrow I + Br^*$$

$$\longrightarrow I + Br$$

$$I^* + IBr \longrightarrow I_2 + Br^*$$

$$Br + IBr \longrightarrow Br_2 + I$$

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