Laser-induced chemical reaction Na(3*P*) + HCl in the gas phase

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A method of laser-induced luminescence has been used to study the kinetics of the reaction of the Na(3*P*) atom with the HCl molecule in a buffer gas, Ar. The rate constant for this reaction is found to be $k = (0.93 \pm 0.27) \times 10^{-9}\,\text{cm}^3/\text{s}$. This value corresponds to a cross section $\sigma = 100\,\text{Å}^2$ for the most probable velocity of atom-molecule collisions.

Karlov *et al.*[1] have shown that it is possible in principle to use laser light to selectively induce harpoon reactions between metal atoms and molecules containing halogens. The method of intersecting beams which was used in those experiments, however, is not actually capable of providing quantitative measurements of the cross sections or rate constants of such reactions. In the present letter we report measurements of these properties of laser-induced reactions through a study of the kinetics of the reaction Na(3*P*) + HCl→NaCl + H in a flow-through laser-chemical reactor.

The interaction of the laser pulse with the atomic system under conditions of a chemical reaction from an excited state is described in the simplest case of a two-level atom by a system of kinetic equations whose solution, for the population in the second level, is given by

$$n_2(t) = C \exp\left[-\frac{G}{2(G+1)}kt\right], \quad G = \frac{2W}{A+\gamma} \sim \frac{I}{\Delta\nu_{st}},$$

where k is the reaction rate, γ is the quenching rate, A is the rate of the spontaneous decay, and W is the rate of the induced transitions.

By studying the kinetics of the luminescence, $I_{lum}(t) \sim An_2(t)$, and knowing the homogeneous broadening $\Delta\nu_{st}$ of the transition and the intensity of the laser beam, we can thus directly determine the rate constant of the pseudomolecular reaction. A necessary condition here is $[M] \ll [Rx]$, where the quantities on the left and right sides of this inequality are the concentrations of metal and reactant atoms, respectively. The rate constant of the bimolecular reaction is given by

$$k_b \, (\mathrm{cm}^3/\mathrm{s}) = k / [Rx].$$

Since the luminescence kinetics is related to the escape of particles from the interaction region into the product, an interfering factor in these measurements is the subcurrent of particles into the interaction region at velocities comparable to the rate of the reaction. This subcurrent of particles can flow as a result of spatial diffusion and relaxation over the Doppler linewidth if the spectral width of the laser light or the homogeneous width is less than the Doppler width of the transition. Accordingly, we need to know the cross sections for these processes in order to select appropriate experimental conditions.

For the present experiments we chose the system $Na + HCl + Ar$, since information is available on its basic kinetic parameters: the effective cross section for the quenching of $Na(3P)$ by the HCl molecule,[2] $\sigma \approx 10^{-14}$ cm^2; the $Na + Ar$ diffusion coefficient,[3] $D = 0.88$ cm^2/s (655 K); the time scale for intra-Doppler relaxation,[4] $\tau = 3 \times 10^{-7}$ s·torr; the cross section for intermultiplet mixing,[5] $\sigma(3P_{3/2} \rightarrow 3P_{1/2}) \cong 10^{-14}$ cm^2; and the magnitude of the collisional broadening,[6] $\Delta\nu_{st} = 30$ MHz/torr (15 °C).

The transition $3S_{1/2} \rightarrow 3P_{3/2}$ in the presence of Ar, with excitation by linearly polarized light, is actually a multilevel transition, but in view of the large cross sections, $\sigma \cong 10^{-14}$ cm^2 (Ref. 5), for relaxation in the hyperfine components of the state, $3P_{3/2}$ and $3P_{1/2}$, and the intermultiplet mixing, at an Ar pressure of a few tens of torr, it can be assumed a three-level transition. It can be shown that when the laser frequency is tuned to the center of gravity of the hyperfine structure of $3S_{1/2} \rightarrow 3P_{3/2}$ transition, the detuning over the Doppler linewidth allows a single laser to excite both transitions, $3S_{1/2}(F=1) \rightarrow 3P_{3/2}$ and $3S_{1/2}(F=2) \rightarrow 3P_{3/2}$. At an Ar pressure of 80 torr, the homogeneous width of the transition becomes equal to the Doppler width, making it necessary to incorporate intra-Doppler relaxation in the excitation kinetics. On the basis of the discussion above and data on the elementary processes we can select appropriate experimental conditions. The Ar pressure, for example, is chosen to be 80 torr, the Na vapor density is on the order of 10^{11} cm^{-3}, and the HCl density is varied over the interval 10^{13}–10^{14} cm^{-3}.

The design of the laser-chemical reactor is basically similar to that described by West et al.[7] It consists of an externally heated quartz tube with a diameter $d = 40$ mm, with a coaxial quartz capillary for admitting the metal vapor into the reactor (Fig. 1). A weak flow of a buffer gas with an adjustable admixture of the molecular reactant is set up in the reactor. Windows in the quartz tube allow the light to enter and the luminescence to be observed. The pressure is measured with a VDG-1 membrane
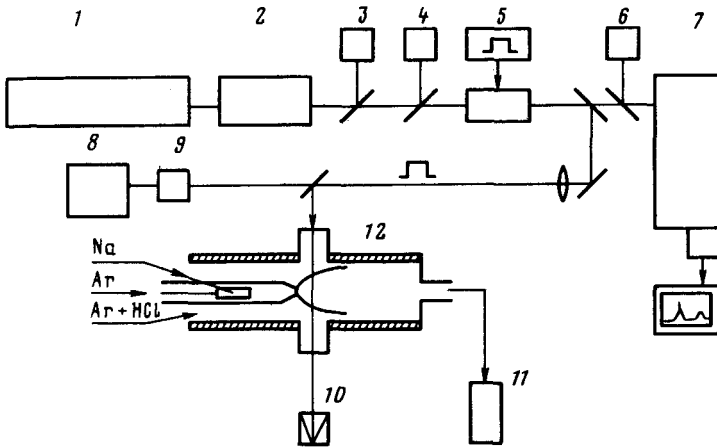
FIG. 1. The experimental apparatus. 1—Argon laser; 2—dye laser; 3, 4—Fabry-Perot etalons; 5—electrooptic modulator; 6—DNA-S18 spectral lamp; 7—monochromator (4 Å/mm) and multichannel analyzer; 8—oscilloscope; 9—array of photodiodes; 10—power meter; 11—roughing pump; 12—reactor.

gauge. The flow is measured on the basis of the flow rate out of a calibrated volume. In the experiments we use "extremely pure" Ar and OÉ grade HCl. The atomic transition is excited by a dye laser with a linewidth of 5 MHz and a power of 150 mW. The laser beam modulated by an ML-102 electrooptic modulator with a pulse length of 500
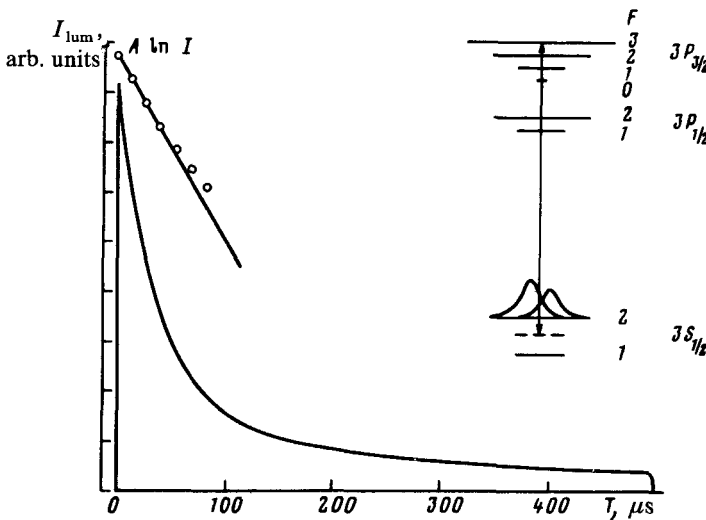

FIG. 2. Kinetics of the luminescence from the $3P$ Na level during excitation of the transition $3S_{1/2} \rightarrow 3P_{3/2}$ by a square 500-μs pulse. The Ar pressure is 80 torr, and the concentration [HCl] is 7.5×10^{13} cm^{-3}. The light power is 65 mW. The temperature is 540 K. The inset at the upper right is the level scheme of Na. The overlap of the hyperfine components caused by Doppler broadening is shown schematically.

μs and a rise time of 0.2 μs. The diameter of the laser beam is continuously monitored by a bank of photodiodes, with output to an oscilloscope. The resolution is 0.2 mm.

Figure 2 shows a typical kinetic curve of the luminescence in linear and semilogarithmic scales. The deviation from an exponential behavior and the steady-state asymptote of the luminescence decay are caused by the Gaussian shape of the laser beam and by spatial diffusion. The analysis was based on the first parts of the luminescence decay curve, which correspond to a small extent of reaction and to a small contribution of the diffusion process.

In analyzing the experimental results we take into account the Voigt shape of the absorption line, the frequency deviations from the centers of the lines of the hyperfine components of the transitions, and the Gaussian profile of the laser beam. The rate constant found for the pseudomonomolecular reaction in this manner is $k = (7 \pm 1) \times 10^4$ s^{-1} at a concentration [HCl] $= 7.5 \times 10^{13}$ cm^{-3}. It is linear in the HCl pressure. The corresponding rate constant of the bimolecular reaction is found to be $k_b = (0.93 \pm 0.27) \times 10^{-9}$ cm^3/s. For the most probable velocity of the atom-molecule collisions ($\bar{v} = 9 \times 10^4$ cm/s) this quantity corresponds to a cross section $\sigma = 100$ Å^2, in good agreement with the cross section measured by Earl and Herm[2] for the quenching of the excited state of Na. The implication is that the quenching in the system is caused primarily by the chemical-reaction path.

We wish to thank N. A. Karpov, F. E. Karulin, and D. N. Kozlov for assistance in the preparation for and in the execution of the experiments.

[1]N. V. Karlov, B. B. Krynetskiĭ, V. A. Mishin *et al.*, Kvantovaya Elektron. (Moscow) 8, No. 3 (1981) [Sov. J. Quantum Electron. 11, No. 3 (1981)].
[2]B. L. Earl and R. R. Herm, J. Chem. Phys. 60, 4568 (1974).
[3]N. B. Vargaftik, Spravochnik po teplofizicheskim svoĭstvam gazov i zhidkosteĭ (Handbook on the Thermophysical Properties of Gases and Liquids), Nauka, Moscow, 1972.
[4]T. W. Hänsh, I. S. Shahin, and A. L. Schawlow, Phys. Rev. Lett. 27, 707 (1971).
[5]B. M. Smirnov, Asimptoticheskie metody v teorii atomnykh stolknoveniĭ (Asymptotic Methods in the Theory of Atomic Collisions), Atomizdat, Moscow, 1973, p. 270.
[6]W. R. Hindmarsh and J. M. Farr, in: Progress in Quantum Electronics, Vol. 2, Part 4 (ed. J. H. Sanders and S. Stenholm), Pergamon, Oxford, 1973.
[7]J. B. West, R. S. Bradford, Jr., J. D. Eversole, and C. R. Jones, Rev. Sci. Instrum. 46, No. 2 (1975).