The influence of non-equilibrium vibrational excitation of CH$_3$F molecules on the rate of their reaction with bromine atoms has been investigated. A three-fold increase in the reaction rate has been registered at CH$_3$F and Br$_2$ pressures of 0.07 Torr and at 100°C. The increase is shown not to be associated with equilibrium thermal heating.

To study the relative role played by vibrational and translational molecular energies in removing the potential barrier in bimolecular reactions is of great interest for chemical kinetics. Previously /1/ it was shown that vibrational excitation of methane did not play any essential role in its reaction with chlorine atoms. This is qualitatively consistent with Polanyi’s concepts /2/, according to which, vibrational energy should play an important role only in endothermic reactions (the reaction of chlorine atoms with methane is thermoneutral). The present paper gives results on the effect of the vibrational excitation of CH$_3$F molecules on the rate of their reaction with bromine atoms. This reaction is by 12 kcal/mol endothermic, its activation energy being 15.7 kcal/mol /3/.
Vibrationally excited CH$_3$F molecules were obtained upon absorption of radiation of a continuous-wave CO$_2$ laser operating on the rotational line P(20) of $^0O^1 - ^0O^2$ transition, at 1046.85 cm$^{-1}$ frequency (10 W). During absorption excitation of the stretching vibration $v_3$ of the C-F bond occurs. Equilibrium of all vibrational molecular states, however, results from fast V-V relaxation, whereas the rates of V-T and V-R relaxations are much lower. Thus, for example, according to the data of Ref. /4/, to transfer a vibrational quantum from $^{12}$CH$_3$F to $^{13}$CH$_3$F and to excite CH$_3$F to a higher vibrational state ($2v_3$) upon collision of two molecules in the $v_3$ state, fewer than 10 collisions are needed, whereas the deactivation of CH$_3$F($v_3$) molecules colliding with those non-excited requires $1.5 \times 10^4$ collisions, and with argon atoms this number is equal to $2 \times 10^5$. As a result, at low pressures superequilibrium population of the vibrational levels of the CH$_3$F molecules is achieved.

The reaction of CH$_3$F with bromine atoms was studied in a 50 cm long cylindrical quartz reaction vessel with an inner diameter of 2 cm. Windows made of NaCl served as end-faces of the vessel. Through a $\sim 10 \mu$m diameter pinhole in a glass diaphragm the vessel was connected with the ion source of a MX-1808 mass-spectrometer. This enabled us to perform a continuous analysis of the gas mixture during the reaction. To measure very slow reaction rates, the ion current of the mass-spectrometer was recorded by an electron multiplier. Atomic bromine was produced via dissociation of molecular bromine absorbing radiation of the DRSh-500 mercury lamp. To reduce relaxation of the excited molecules by walls, the reaction mixture was diluted with argon. Methyl fluoride, bromine and argon were purified by repeated vacuum distillation. The reaction rate was determined from the dependence of CH$_2$FBr concentration on time. These molecules were formed in the reaction CH$_2$F + Br$_2$ $\rightarrow$ CH$_2$FBr + Br, rapidly following the initial reaction Br + CH$_3$F $\rightarrow$ HBr + CH$_2$F, which is the rate-limiting step of the process.