Observed deepening of the adsorption potential for molecules at a solid surface in a resonant laser beam

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A reversible increase in the adsorption of bromine molecules on the surface of a glass plate by the beam from an argon laser has been observed. This increase in adsorption corresponds to a deepening of the adsorption potential in proportion to the beam intensity.

The adsorption of molecules from the gas phase by a solid surface is determined by the depth of the adsorption potential. If a resonant laser beam acting on the molecule changes the potential of its interaction with the wall, the number of adsorbed molecules will change. A study of the adsorption of molecules by a solid surface in a resonant light beam can thus yield information about the nature of the effect of the light on the interaction of gas molecules with the wall of the vessel holding the gas.

The effects of a resonant laser beam on the diffusion of molecules through fine-pore membranes[1] and fine capillaries[2] have been discussed previously. It has also been found that a laser beam affects the deposition of metal vapor on a transparent insulator.[3] It is difficult to offer a quantitative interpretation of these effects because of the complexity of the systems involved, but an explanation was formulated in Ref. 2 on the basis of a polarizing effect of the resonant beam and an interaction of a field-induced dipole moment of the gas particles with the wall.

In the present letter we report the first direct observation of a deepening of the potential for adsorption of molecules from the gas phase by a solid surface in resonant electromagnetic radiation. Specifically, we have studied the adsorption of Br_2 molecules on the surfaces of glass plates in the beam from an argon laser. The experiment is carried out by a comparison method (Fig. 1). The beam from an argon laser, with a power up to 1 W at the wavelength 514.5 nm, which is at resonance with the $^1\Sigma_{0g}^+ \rightarrow B\,^3\Pi_{0u}^+$ transition of molecular bromine (the cross section for this transition is 1.4×10^{-19} cm^{-2}), enters two cells holding gaseous bromine. In cell 1 there is a stack of 22 parallel-face glass plates. In the absence of the bromine, the transmission of the laser light by this stack is 11.5%. The thickness of the gas layer in cell 2 is equal to the total thickness of the several layers of gas in cell 1. The gas pressures in the cells are held equal and constant by means of a ballast volume. The experiments are carried out at room temperature ($T = 293 \pm 3$ K), and only after a gas equilibrium has been reached in the cells.

We measure the difference in the transmission of the light by the two cells as a function of the light intensity. We attribute the observed difference to the absorption of light by Br_2 molecules adsorbed on the surfaces of the plates. This excess adsorption

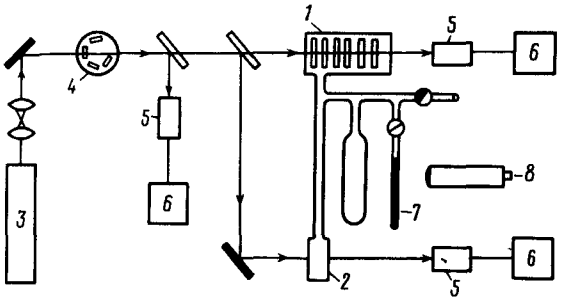

FIG. 1. The experimental arrangement. 1—Measurement cell with plates; 2—compensation cell; 3—argon laser; 4—attenuator; 5—photomultipliers; 6—digital voltmeters; 7—cell holding liquid bromine; 8—microscope used to measure the bromine level.

can be described for our experimental arrangement by $\alpha = -\ln[(I_1/I_2)_p/(I_1/I_2)_a]$ where I_1 and I_2 are the light intensities at the exit from cells 1 and 2, respectively, and the subscripts p and a indicate the presence or absence of bromine in the cells. Figure 2 shows a plot of α versus the intensity of the light incident on the first plate. We see that the absorption of the light by the adsorbed molecules increases sharply with the intensity and remains essentially constant over the range of bromine densities in the gas phase studied in these experiments. The observed change is reversible, by which we mean that when the laser beam is cut off the excess absorption vanishes. Saturation of the absorption at the surfaces and in the gas phase in cell 1 gives rise to an effect of the opposite sign, as does thermal desorption. It was established experimentally that the absorption in the gas phase in cell 2 does not reach saturation.

It is obvious from thermodynamic considerations that, at a gas equilibrium, the density of molecules which are additionally deposited on the surface upon a change ΔU in the adsorption potential is $n^* = n_0 \exp(\Delta U/kT)$, where n_0 is the initial surface density of molecules. If ΔU is proportional to the light intensity I, as it would be, in particular, according to the polarization mechanism for adsorption,[2] we would have $n^* = n_0 \exp(\chi I/T)$. The ratio of the light intensity (I_m) incident on surface m to the intensity (I_{m+1}) of the light transmitted by this surface is then $I_{m+1}/I_m = \exp[-n_0\sigma \exp(\chi I_m/T)]$, where σ is the absorption cross section for the adsorbed molecules. This expression has two unknowns: the coefficient χ and the product $n_0\sigma$. Taking a value of χ from diffusion experiments,[4] and systematically applying this formula from plate to plate, and selecting the values of $n_0\sigma$, we can find that functional dependence $\alpha(I)$ which fits the experimental results best. Using the value[4] $\chi = 2660 \pm 130$ deg·cm^2/W, we find $n_0\sigma = 6.0 \times 10^{-5}$. The calculated results are shown in Fig. 2; the solid line shows the average values, while the dashed lines show the uncertainty due to the errors in the values of χ and T.

Under the assumption that the absorption cross section does not change upon adsorption, we find $n_0 = 0.4n_M$, where n_M is the surface density of a monolayer of Br_2 molecules. The maximum density of molecules deposited by the beam then reaches 230 molecular layers at $I = 0.7$ W/cm^2.

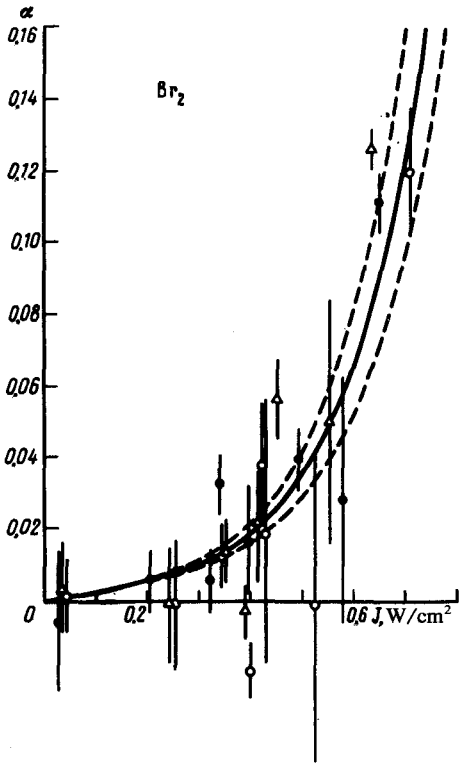

FIG. 2. The absorption coefficient of photoadsorbed bromine, α, versus the intensity of the incident light. Curves—Theoretical; points—experimental. The confidence intervals are shown for a confidence level of 90%. The densities of molecules in the gas phase are: ○—0.75×10^{18} cm^{-3}; △—1.13×10^{18} cm^{-3}; ●—1.32×10^{18} cm^{-3}.

In summary, these experiments offer evidence for a deepening of the adsorption potential of bromine molecules in a resonant laser beam. This result agrees, in particular, with a polarization nature of the interaction of molecules with a solid (or liquid) surface. It would be pertinent to carry out experiments to independently determine the values of the parameters $n_0\sigma$ and χ and also to study the angular dependence of the effect, which would be substantial in the case of a polarization interaction.

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