Reports of the Academy of Sciences of the USSR

L. M. ROEV

1960

SovietRxiv

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Abstract

Full Text

Reports of the Academy of Sciences of the USSR
1960. Volume 133, No. 3

PHYSICS

L. M. ROEV

BROAD ABSORPTION BANDS IN THE INFRARED SPECTRA OF ADSORBED MOLECULES

(Presented by Academician A. N. Terenin, March 18, 1960)

In the course of work on the investigation of the infrared spectra of adsorbed molecules (1), it was observed that the transparency of a number of adsorbents over a broad region of the infrared spectrum decreases when vapors of the adsorbed substance are admitted into the cell. Figure 1 shows the change in the transparency of alumogel with time at 2000 cm^{-1} when water vapor is admitted into the cell containing alumogel. Admissions 1 and 4 correspond to the admission of saturated water vapor at 18°, and admissions 2 and 3 to definite doses with an initial pressure of 1 mm Hg. Pumping out the vapors of the adsorbed substance from the cell leads to restoration of the transparency of the sample to its initial value.

Fig. 1. Change in the transparency of alumogel at 2000 cm^{-1} when water vapor is admitted into the cell

The magnitude of the decrease in the transparency of the adsorbent depends on the pressure of the vapors of the adsorbed substance admitted into the cell. Figure 2 gives the dependence of the transparency of alumogel near 2000 cm^{-1} on the pressure in the cell of carbon tetrachloride vapor. As the pressure increases, the transparency of the sample decreases, reaching a certain constant value when the pressure approaches the pressure of vapors saturating at room temperature. The described decrease in the transparency of adsorbents occurs over a broad region of the infrared spectrum, considerably exceeding the half-width of the absorption bands of the adsorbed molecules, creating the impression of an

Fig. 2

Figure 2: Fig. 2

absorption background arising upon adsorption. Figure 3A gives the spectral dependence of the background intensity for the alumogel—chloroform system, where I_0 and I are, respectively, the intensities of light transmitted through pure alumogel and through alumogel in the presence of chloroform vapor. I_0 is taken as 100% and corresponds to the upper horizontal line. At the top and bottom, small marks indicate the positions of the absorption bands of the adsorbed substance and of the adsorbent, respectively. Curves 1 and 2 refer to different pressures of chloroform vapor admitted into the cell. As is seen from the figure, the width of the resulting background is more than 2000 cm^{-1}.

The appearance of the background has been checked for a number of adsorbents: MgO, SiO_2, Al_2O_3, Cr_2O_3, Fe_2O_3, CaF_2, upon adsorption of H_2O, CCl_4, $CHCl_3$, CH_3CN, pyridine, nitrobenzene, cyclohexane, NH_3, CO, NO, CH_3OH, C_2H_5OH, and others. In all the indicated adsorbent—adsorbate systems, a decrease in the transparency of the adsorbents takes place upon adsorption. Detailed consideration of the spectra obtained makes it possible to conclude that the intensity of the arising

the background depends on the boiling point of the adsorbed substance. In this case, the higher the boiling point, the more intense the background.

In order to interpret this phenomenon, experiments were carried out on the adsorption of gases at different sample temperatures, from -160 to $+100°$. Comparison of the spectra obtained shows that the character of the background that arises does not change as a function of the adsorption temperature, but the intensity of the background increases when the temperature is lowered.

Fig. 2. Dependence of the transparency of alumogel at 2000 cm^{-1} on the vapor pressure of carbon tetrachloride in the cuvette

The nonselectivity of the appearance of the background with respect to the nature of the adsorbent and the adsorbed substance, the dependence of the background intensity on the pressure and boiling point of the adsorbed substance, and also the temperature dependence make it possible to suppose that the appearance of the background is connected with the physical adsorption of molecules.

Very important for interpreting the background is a comparison of the maxima of the background with the absorption spectra of the adsorbents and the adsorbed molecules. In Fig. 3 B the spectra of the alumogel-acetonitrile system are shown at different vapor pressures of acetonitrile. On curve 3, along with the background, there are observed absorption bands of acetonitrile in a state of capillary condensation on the surface of alumogel. In Fig. 3 B it is seen that the maxima of the background intensity at 1400 and 2200 cm^{-1} co-

Fig. 3

Figure 3: Fig. 3

incide in absorption with the absorption bands of acetonitrile; the maximum at 3200-3300 cm^{-1} lies between the absorption bands of acetonitrile and the OH groups of the alumogel surface. The same coincidence of the background maxima with the positions of the absorption bands of the adsorbent and the adsorbed substance is also observed in other spectra (Figs. 4 and 3 A). Therefore the background arising upon adsorption may be regarded as a very strong broadening of the absorption bands of the adsorbent and of the adsorbed molecules during adsorption. However, as can already be seen in Figs. 3 A and 4, not all absorption bands of the adsorbed molecules undergo such broadening, but only the high-frequency ones. Nor are the absorption bands of the adsorbents lying below 1000 cm^{-1} broadened (all the adsorbents used by us have absorption bands below 1000 cm^{-1} corresponding to vibrations of their crystal lattices).

Fig. 3. Infrared spectra of alumogel. **A** –in the presence of chloroform vapors: 1 –at a pressure of 15 mm Hg, 2 –170 mm. **B** –in the presence of acetonitrile vapors: 1 –at $P/P_s \approx 0.1$, 2 –at $P/P_s \approx 0.5$, 3 –at $P/P_s \approx 1$

On the basis of the data given above, several different interpretations can be offered for the phenomenon of the absorption background during adsorption, of which, apparently, the most probable is the supposition of photodesorption of molecules under the action of infrared light.

Molecules adsorbed on the surface of the adsorbent absorb

an infrared quantum and transfer this energy to the molecule-adsorbent bond. If this energy proves sufficient to break the bond of the molecule with the adsorbent, the molecule desorbs into the bulk. A necessary condition for photodesorption of the molecule is $h\nu > Q$, where $h\nu$ is the energy of the absorbed quantum, i.e., the energy corresponding to the vibrational transition in the molecule, and Q is the heat of adsorption per molecule.

The transfer of the vibrational energy of the molecule to the bond with the adsorbent is accompanied by a radiationless transition of the molecule to a lower vibrational level. The possibility of such a radiationless transition leads to a decrease in the lifetime in the excited state and, consequently, to a broadening of the given energy level. In the infrared spectrum this should manifest itself as broadening of the absorption bands corresponding to transitions to the given vibrational level. Only those absorption bands should broaden which correspond to transitions with an energy exceeding the heat of adsorption per molecule, i.e., $h\nu > Q$. It follows from this that low-frequency absorption bands, for which this condition is not satisfied, should not broaden and create an absorption background. Energy can be absorbed and transferred to the bond between the adsorbed molecule and the adsorbent not only by adsorbed molecules, but also by the adsorbent itself. However, for most adsorbents, of all the vibration

Fig. 4. Infrared spectrum of fluorite (CaF_2) in the presence of ethanol vapor

Figure 4: Fig. 4. Infrared spectrum of fluorite (CaF_2) in the presence of ethanol vapor

frequencies, only vibrations of structural OH groups have energy sufficient for desorption of molecules, and therefore only the absorption bands of the adsorbent hydroxyls broaden.

Fig. 4. Infrared spectrum of fluorite (CaF_2) in the presence of ethanol vapor

It should be noted that the interpretation given here for the origin of the background is not definitive. The assumption that the appearance of the background may be connected with a change in the scattering properties of the adsorbent upon adsorption is refuted on the basis of experiments carried out for this purpose.

I take this opportunity to express my deep gratitude to Acad. A. N. Terenin for his help and unfailing interest in the performance of this work.

Physical Institute
of Leningrad State University
named after A. A. Zhdanov

Received
5 II 1960

CITED LITERATURE

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Note: Figure translations are in progress. See original paper for figures.