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ON THE RAMAN SCATTERING SPECTRA OF CERTAIN COMPOUNDS IN THE ADSORBED STATE

(Presented by Academician A. N. Terenin, 14 I 1963)

The application of infrared spectroscopy to the study of adsorption phenomena, begun by A. N. Terenin ([1]) and continued by him and his collaborators ([2], [3]), has in recent years undergone broad development ([4]). In particular, it has been shown that, upon adsorption of a number of molecules containing OH, NH, CO, and CN groups, the frequencies of these groups, as well as of adjacent bonds, change ([2], [3]). However, the study of the entire vibrational spectrum of adsorbed molecules on adsorbents with large specific surface area, such as microporous glass or silica gel, is hindered by their own absorption. For this reason, it was of interest to determine the possibility of applying Raman scattering spectra (r.s.) to adsorption phenomena.

In the present work we set out preliminary results of our investigations on this question. In the first experiments we used, as adsorbent, microporous glass in the form of a cylinder 7 mm in diameter and 50 mm long (with a specific surface area of about 100 m^2/g with respect to CH_3OH), while antimony trichloride ($SbCl_3$) was chosen as the adsorbate, since it has comparatively intense r.s., very sensitive ([5]) to changes in intermolecular interaction.

In this experiment, as well as in all the others, one and the same procedure was used for treating and filling the adsorbent. First the adsorbent was heated for many hours in air at a temperature of 500° in order to burn off possible organic impurities. The sample was then placed in a glass cylindrical cell (10–18 mm in diameter, 120 mm long) with a flat window, in which it was subjected to vacuum conditioning (10^{-4}–10^{-5} mm Hg) for 3 hours at a temperature from 300 to 400°. A glass partition with a magnetic striker* separated the cell with the adsorbent from the capillary side arm in which the $SbCl_3$ was located. Dense filling of the capillary was achieved by repeated melting of $SbCl_3$, previously subjected to repeated fractional sublimation in vacuum. After completion of the conditioning and sealing off from the vacuum apparatus, a measured admission of $SbCl_3$ vapor onto the adsorbent was carried out at room temperature. The amount of adsorbed substance was measured from the level to which the capillary was filled with the substance, with sufficient accuracy, since comparatively large amounts of adsorbent were taken in the experiments: from 2 to 15 g.

Figure 1. Raman spectra of $SbCl_3$ on silica gel

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The spectra were recorded on a DFS-12 instrument—a double monochromator with diffraction gratings and photoelectric recording of the spectrum (dispersion 5 Å/mm). The light source was a spiral low-pressure mercury lamp made by us. The exciting line used was λ 4358; the short-wavelength part of the spectrum was filtered out by a saturated $NaNO_2$ solution.

In addition to microporous glass, silica gel was also used, with a specific surface area with respect to CH_3OH of 250 m^2/g, and with respect to C_6H_6 of 170 m^2/g.

* When working with other adsorbates, instead of the glass partition a vacuum stopcock was used. Special experiments both with pure adsorbates and in the presence of adsorbent showed that use of the stopcock, provided the necessary precautions are observed, introduces no distortions.

Raman spectra of $SbCl_3$ molecules on microporous glass and silica gel could be recorded at relatively small surface coverages (approximately 0.2 monolayer) and followed up to a coverage of 2 layers and further to capillary condensation. These spectra differ in character from the spectrum of the solid phase (see Fig. 1). In the region of stretching vibrations, which in the spectrum of solid $SbCl_3$ are represented by lines at 318 and 343 cm^{-1}, at small adsorbent coverages a band of width approximately 60 cm^{-1} is observed, the center of which (350 cm^{-1}) is shifted relative to the center of the solid-phase lines (330 cm^{-1}) toward higher frequencies. In the region of deformation vibrations, instead of the lines of the solid-phase spectrum at 140, 152, and 167 cm^{-1}, a broad band is observed at about 130 cm^{-1}, closely adjoining the wing of the Rayleigh line, which appears in the spectrum of $SbCl_3$ on the adsorbent instead of the discrete low-frequency spectrum of the crystal. A redistribution of intensities also occurs in comparison with the spectrum of solid $SbCl_3$, namely, an increase in the intensity of the deformation band relative to the stretching-vibration band. At coverages greater than 0.5 layer the structure of the bands becomes increasingly distinct; however, only upon capillary condensation is a line spectrum observed that practically coincides with the spectrum of the solid phase. The Raman spectra of molecules on microporous glass and silica gel showed no substantial differences. It should be noted that only by heating the samples in vacuum at a temperature near the boiling point of $SbCl_3$ (223°) for many hours was it possible to achieve complete disappearance of the Raman spectrum of $SbCl_3$ on the adsorbent (without decomposition of $SbCl_3$), and upon subsequent admission the results were fully reproducible.

Thus, the comparatively strong bond of $SbCl_3$ molecules with the adsorbent surface and the considerable changes in the Raman spectrum indicate a specific interaction when $SbCl_3$ is admitted onto microporous glass and silica gel.

Fig. 2 and Fig. 3

Figure 2: Fig. 2 and Fig. 3

Fig. 1. Raman spectra of $SbCl_3$ on silica gel: *1* –at a coverage of 0.2 monolayer; *2* –0.5 monolayer; *3* –1 monolayer; *4* –2 monolayers; *5* –capillary condensation.

In the Raman spectrum of $SbBr_3$ on microporous glass at small coverage, broadening of the lines was also observed, though not to the same extent as in the case of $SbCl_3$.

For a more reliable interpretation of the Raman spectra obtained as belonging specifically to adsorbed molecules, compounds that had previously been studied in the adsorbed state by infrared spectroscopy were chosen as objects of investigation. Acetonitrile (CH_3CN) was taken; in its infrared spectrum, upon adsorption [3] on microporous glass and silica gel at small coverages, an increase in the frequency of the C N bond by 13 cm^{-1} was observed in comparison with the liquid phase. We studied the Raman spectrum of CH_3CN on silica gel (in the form of beads 1-3 mm in diameter). Because, with excitation by λ 4358, the C N frequency (2253 cm^{-1}) falls in a spectral region where there are many mercury lines, a 10% solution of $NaNO_2$ was used as a filter. This made it possible, when recording the spectrum in the region 4400-4700 Å, to observe the stretching-

frequencies C N and C–H, excited by λ 4047, and the C–C frequency (918 cm^{-1}) and other frequencies under excitation by λ 4358.

In the spectrum of CH_3CN on the surface of silica gel, at a filling up to 0.5 layer, it was found, as is seen from the spectrograms (see Fig. 2), that the C N frequency is shifted toward higher frequencies by 12 cm^{-1} in comparison with its value in the spectrum of the liquid phase. With further filling the C N frequency is broadened, evidently owing to the presence of both shifted and unshifted components, and when approximately 2.5 layers are reached only the unshifted component remains. As regards changes in the other frequencies, only an increase by 5 cm^{-1} of the stretching-vibration frequency of the C–H group of CH_3 is observed.

Fig. 2. Raman spectra of acetonitrile adsorbed on silica gel:
1 –0.5 monolayer of CH_3CN on silica gel;
2 –2.5 layers of CH_3CN on silica gel;
3 –liquid

Fig. 3. Raman spectra of acetophenone (C=O and C=C frequencies).
1 –adsorbed state; 2 –liquid

Analogous changes were also observed in the Raman spectra of acetophenone ($C_6H_5COCH_3$) on microporous glass, which was a parallelepiped of dimensions 16 × 8 × 70 mm^3. Figure 3 gives recordings of spectra in the region of the C=O and C=C frequencies of acetophenone on microporous glass and of liquid

acetophenone. At a filling of not more than 0.5 layer, the C=O frequency is lowered by 10 cm^{-1}, whereas the C=C frequency is not shifted upon adsorption. With further filling (more than one layer), the C=O frequency assumes the value for the liquid.

The preliminary results set out above lead to the conclusion that the observed Raman lines are spectra of adsorbed molecules in those cases where there is a shift of the stretching frequencies of the CN and CO groups, since, first, the shift has the same magnitude as in the infrared spectra obtained at small fillings, and, second, this shift disappears upon further filling. In the case of $SbCl_3$ on the adsorbent there are stronger changes in the spectrum; however, their general course from small fillings to capillary condensation, it seems to us, permits the supposition that here also, at small fillings, spectra of adsorbed molecules were observed. The increase in the intensity of the band of deformation vibrations in comparison with the stretching vibrations upon adsorption apparently indicates a change in the character of the bonds within the molecule.

The spectra of not all substances undergo similar changes upon adsorption; for example, in the Raman spectrum of nitromethane on microporous glass at a filling of 0.5 layer, the maximum frequency changes do not exceed 5 cm^{-1}. Of the many difficulties encountered in carrying out these experiments, we shall mention only that, upon adsorption of certain molecules, for example–

For example, for acetonitrile and acetophenone, even at low coverages a continuous fluorescence spectrum was observed, increasing toward the blue region of the spectrum. We also studied the spectra of other molecules in the adsorbed state, for example CCl_4, naphthalene, toluene, benzophenone, etc.

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