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ADSORPTION OF METHYLPHOSPHONIC ACID ON ALUMINA SURFACE STUDIED BY INELASTIC ELECTRON TUNNELING SPECTROSCOPY

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The vibrational spectrum of methylphosphonic acid adsorbed onto alumina surface was obtained by inelastic electron tunneling spectroscopy. An analysis of the spectrum showed that the methylphosphonic acid is adsorbed as the dibasic phosphonate ion onto the alumina surface.

Inelastic electron tunneling spectroscopy (IETS) is a relatively new technique for obtaining the vibrational spectrum of adsorbed species on the oxide of a metal-oxide-metal tunneling junction. The high sensitivity, resolution and wide spectral range of IETS enable the detailed analysis of the adsorbed species.[1)] Tunneling spectra of simple organic acids, e.g., acetic acid[2)] and methanesulfonic acid,[3)] have been measured and their structures have been indicated on the oxide surfaces. In this letter, we report for the first time the tunneling spectrum of methylphosphonic acid on Al_2O_3. Since methylphosphonic acid is one of the simplest organophosphonic acid, it is interesting to analyse this molecule on the surface.

The method of junction preparation and the apparatus for measuring the tunneling spectrum have been described in detail elsewhere.[4)] The surfaces of the evaporated aluminium strips were oxidized in an oxygen dc glow discharge. Methylphosphonic acid (Alfa Products, 98%) was adsorbed onto the surfaces from a methanol or an aqueous solution. The junctions (1 mm^2 area) were completed with a Pb cross strip. The tunneling spectrum was measured at a liquid-helium temperature (4.2 K).

The tunneling spectrum of methylphosphonic acid shows the strong peaks due to the stretching modes of the CH_3 group at 2980 and 2910 cm^{-1}. The peaks at 1400 and 1300 cm^{-1} are due to the deformational modes of CH_3. The peak at 800 cm^{-1} is ascribed to the stretching mode of the C-P bond. The infrared spectrum of methylphosphonic acid has the νP=O (1140 cm^{-1}) and νOH (2900 cm^{-1}) band.[5)] The Raman spectrum has the νP=O (1170 cm^{-1}) band.[5)] The spectra of the monobasic phosphonate ion have the νOH (2200 and 2700 cm^{-1}) and νPO_2^- (1060 and 1150 cm^{-1}) bands.[5)] The tunneling spectrum, however, shows no corresponding peaks. Whereas it shows the medium (900 cm^{-1}) and weak (ca. 1050 cm^{-1}) peak based on the PO_3^{2-} group. It is found that methylphosphonic acid reacts with the alumina by loosing the protons of the PO_3H_2 group and is adsorbed onto the surface as the dibasic phosphonate ion in a tripod configuration with the three phosphonate oxygen atoms. This phosphonate ion is considered to be adsorbed perpendicularly to the surface as in the case of methanesulfonate ion,[3)] which has a similar molecular structure and the same symmetry (C_{3v}) as the phosphonate ion. It is noted that the symmetrical stretching mode of PO_3^{2-} has the lower frequency (900 cm^{-1}) than that of the infrared and Raman spectrum (970 - 980 cm^{-1}) for the phosphonate ion.[5,6] This may suggest the strong interaction between the PO_3^{2-} group and the alumina surface. Further investigations on other organophosphorus compounds are now in progress.

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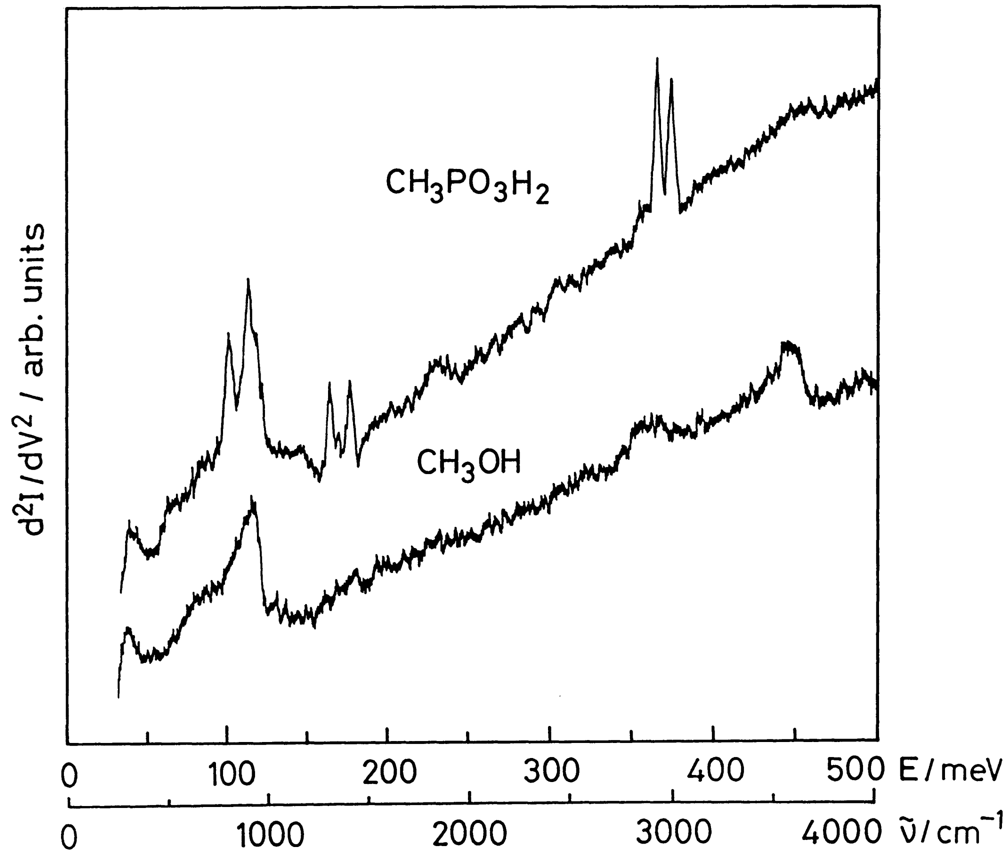

Fig. 1. Tunneling spectrum of methylphosphonic acid adsorbed onto alumina surface from a methanol solution of 0.5 mg/ml. Spectrum of the solvent is shown for comparison; peaks at 3600, 940,and 300 cm^{-1} are due to the vibrational modes of the surface OH group, aluminium oxide and Al phonon, respectively.

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