degrees of freedom and 0.05 probability level is 2.034, and, since this value is larger than the calculated value of t, the hypothesis that $\beta_2 = 0$ is not rejected.

The above analysis indicates that the model proposed by Frilette, Mower and Rubin must be rejected because in the light of the available experimental data the coefficient of *tert*-butanol activity is negative and the coefficient of water activity has a probable value of zero.

It should be pointed out that statistical analysis of the data for each separate run leads to exactly the same conclusions, i.e., rejection of the model.

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Raman Scattering from Water Adsorbed on Oxide Surfaces

Raman spectra recorded using laser excitation have been used to study adsorbed species on oxides (*1*) including, recently, an investigation on silica surfaces (*2*). The use of this technique is reported to be limited by the strong scattering background (SB), which is found to extend over a wide range of wavelengths and to decay when the sample is irradiated with the laser beam for long periods of time. Procedures to eliminate this SB, usually termed "fluorescence," have been given for porous Vycor glass by heating in oxygen at 500°C, because the fluorescence was suggested to arise from a small amount of surface species derived from hydrocarbons (*3*). However, quite similar SB was found in this laboratory in liquid (*4*) and solid proteins (*5*), and was attributed to Raman scattering from the water tightly bound to the protein. The purpose of this letter is to show that the SB observed in oxide surfaces correlates with the presence of water molecules tightly hydrogen-bonded close to Lewis sites, and that it cannot be accounted for in terms of pure fluorescence.

The Raman laser apparatus used in this investigation has already been described (*5*). The photon flux density was kept below 10 mW/cm^2 to eliminate as far as possible the time decay. The samples have been prepared in the conventional way as pressed discs from powdered solids. A metal-Pyrex cell has been constructed in order to heat the pellet to 800°C under vacuum (better than 10^{-4} Torr) without being removed from the Raman laser system. γ-Al_2O_3 samples have been kindly provided by Dr. B. Notari (Laboratori Snam Progetti, Milano), and were prepared according to U.S. Pat. 3,416,888. The other samples were commercial products.

The first group of results concerns the behavior of a sample of γ-Al_2O_3 in different conditions of hydration under vacuum. The spectrum recorded at room temperature is shown in Fig. 1 and displays the typical very intense SB which is found also in air in ordinary conditions of hydration. Upon heating to high temperatures in vacuum, the intensity is reduced as shown in Fig. 2 while the overall shape is preserved. The original intensity can be recovered after admission of moist air and exposure at room temperature for several weeks.

A second group of experiments was devoted to the investigation of particular features. The results included:

a. The lowering of the SB intensity by a factor of 100 by adding Na to γ-Al_2O_3 according to the procedure of Parry (*6*).

b. The occurrence of the phenomenon with different peak intensity in different samples as follows: γ-Al_2O_3 (445000), silica–alumina activated under vacuum at 500°C (540000), silica–alumina untreated (19000), silica (370), MgO (1600) and ZnO (20).

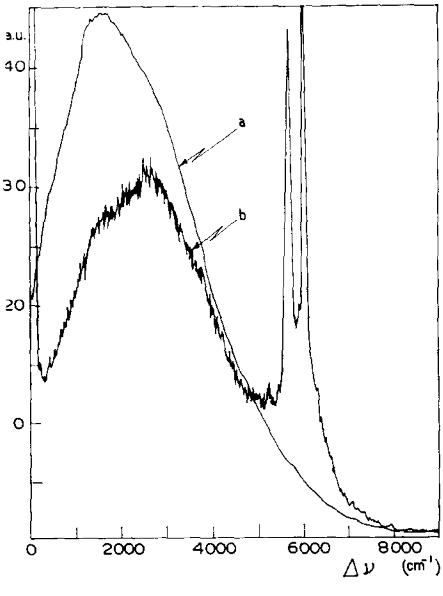

FIG. 1. Light scattering intensity (arbitrary units) from pressed discs of alumina plotted versus wavelength; (a) γ-Al_2O_3; (b) α-Al_2O_3 (scale expanded by a factor 100). The doublet near 6000 cm^{-1} is attributed to ordinary fluorescence. Excitation at 4880 Å.

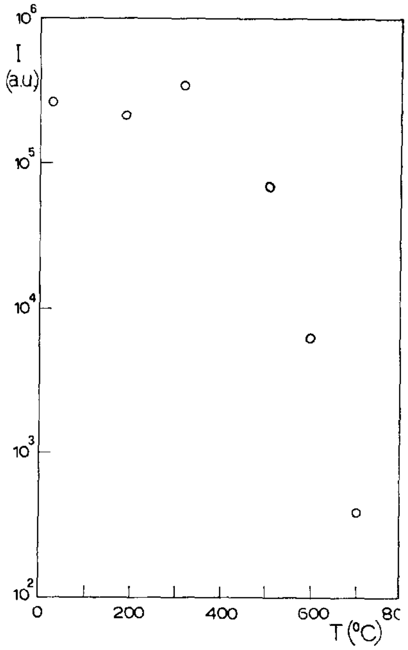

FIG. 2. Light scattering intensity *I* (at 2000 cm^{-1} from the exciting wavelength) in γ-Al_2O_3 heated in high vacuum, plotted versus temperature. To avoid black body radiation the spectra have been recorded at temperatures not higher than 500°C.

c. A 50 times increase of the SB intensity in a decationated X Zeolite, after it was heated in vacuum at 500°C and then cooled to room temperature and exposed to air in ordinary conditions of hydration.

The above results can be rationalized by attributing the scattering to the water molecules on the surface, tightly hydrogen-bonded close to Lewis sites, the contamination by hydrocarbons remaining as a remote possibility.

Evidence for this statement can be gathered as follows:

i. Our data reported in Fig. 2 on the one hand and the ir spectra of partially hydrated γ-Al_2O_3 reported by Peri and Hannan (*7*) on the other hand (see Figs. 3 and 4 of their paper), suggest a close parallel trend between the intensity of the SB and that of the low frequency tail of the ν_{OH} bands (already recognized (*7*) to arise from the OH stretching mode of tightly hydrogen-bonded water).

ii. The SB decrease in the γ-Al_2O_3 samples poisoned by sodium lead one to conclude that some acidic sites of the surface must become involved, because of a previous study by Parry (*6*).

iii. According to Peri (*8*), chemisorption of H_2O on γ-Al_2O_3 occurs particularly on sites where Al^+O^{2-} are available [to produce Al $(OH)^-$ groups on the surface when heated above 300°C]. It is easy to conceive that this H_2O can be tightly hydrogen-bonded to O^{2-} (*9*) and also coordinated to the Al^+ Lewis acidic site. Moreover it is well known that quite a similar mechanism of water chemisorption holds for silica–alumina (*10*) and also for the decationated zeolites (*11*, *12*), while in silica the water is chemisorbed in a different way (*13*); then the SB intensity in the different samples reported above in (c) could also be explained.

Although the chemical species responsible for the SB seems to have been identified, there are some features of this phenomenon which need further study. For instance, at the present time it is difficult to say how many water molecules are involved in one scattering process. The decay of the SB intensity upon laser light irradiation and the subsequent recovery in the dark are essentially accounted for by the desorption–adsorption kinetics of this chemisorbed water, but the process seems to be described by several time constants and further analysis is needed. Finally, the shape of the Stokes band changes somewhat with the exciting wavelength, a feature which is under study at the present time.

Work is in progress in this laboratory to assess the physical aspects of this phenomenon and it will be published elsewhere. But in view of the difficulties (*14*, *15*), of characterizing the acidity of these surfaces in chemical terms by adsorption of NH_3 or other bases, we believe this physical approach to be worth consideration even as an empirical tool at this time.

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