Infrared Emission Spectra of Formic Acid Adsorbed on Alumina

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Summary Infrared emission spectra of the formate group absorbed on alumina could be observed (peaks at 1595 and 1380 cm^{-1}) by keeping the temperature of the sample surface facing the detector higher than that of the other side.

The study of chemisorbed species on solid surfaces has advanced markedly since i.r. absorption techniques were successfully applied to surface phenomena.[1] Significant results have also been obtained for opaque materials using i.r. emission instead of absorption methods.[2] However, emission methods require either highly sensitive spectrometers or solid surfaces which are kept at high temperatures.

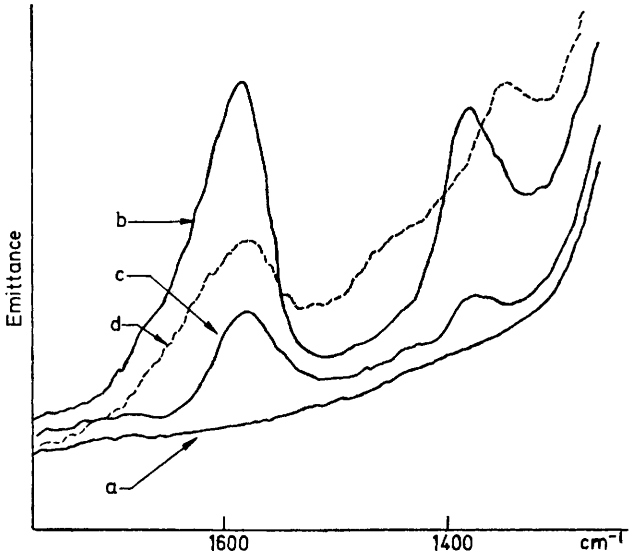

Figure. Emission spectra of formic acid adsorbed on alumina at 130 °C *in vacuo:* (a) alumina background; (b) formic acid adsorbed; (c) same as (b) after evacuation at 300 °C; (d) deuteriated formic acid adsorbed.

Recently Griffiths[3] has pointed out that emission spectra are sometimes distorted because of absorption of emitted radiation by molecules which are less thermally excited in the path to the detector and has suggested the use of thin samples in order to obtain undistorted emission spectra. If the temperature of the surface of the sample facing the detector is kept higher than that of the other side, the thickness of the sample should have no effect. Under these conditions good emission spectra should be obtained even for a thick sample.

In the present work thermal emission spectra of chemisorbed species were successfully observed using a conventional spectrometer equipped with a diffuse reflection apparatus, by maintaining a temperature gradient in the sample as follows.

A JASCO 402G double-beam spectrometer was used with a diffuse reflection attachment DR-2. The exciting radiation was filtered through glass before it was focussed on the sample. This filter absorbs most of the radiation below 2000 cm^{-1}, allowing the sample to be heated by radiation above 2000 cm^{-1}. Emission can therefore be observed in the region below 2000 cm^{-1}. The sample was contained in a glass cell, and the sample holder was cooled with water on the rear of the sample.

Alumina (Degussa) was pressed into the holder to a thickness of *ca.* 1 mm and heated at 400 °C for 1 h *in vacuo.* The background emission spectrum of the alumina at *ca.* 130 °C is in the Figure (a). The alumina was then exposed to formic acid vapour for several minutes and the vapour was then pumped off. Two emission peaks besides the background appeared at 1595 and 1380 cm^{-1} [Figure (b)]. The height of both peaks decreased appreciably after evacuation for 15 min at 300 °C [Figure (c)]. When deuteriated formic acid was used, the peaks shifted to lower frequency: 1585 and 1350 cm^{-1}, respectively. The former peaks are in almost the same positions as absorption peaks for formate adsorbed on alumina and the latter as those for deuteriated formate.[4] The emission peaks at 1595 and 1380 cm^{-1} are, accordingly, assigned to the O–C–O antisymmetric and symmetric stretching vibrations of formate, respectively.

The intensity of the emission at various temperatures was controlled by varying the current supplied to the radiation source. The intensity of the peaks relative to background increased with temperature, as did the intensity of the 1595 cm^{-1} peak relative to that at 1380 cm^{-1}. These phenomena also support the idea that the two peaks are due to emission from the sample. However, owing to large background emission, emission peaks could not be observed when the temperature of the surface was similar to that of the rear of the sample, *i.e.*, when the cell was filled with He (50 Torr) and the rear of the sample was not cooled with water.

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