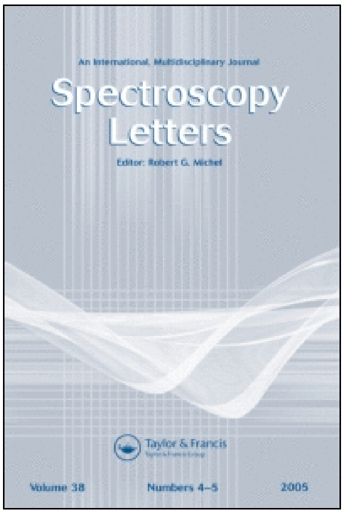

Spectroscopy Letters

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Infrared Observation of Intrinsic Modes on Adsorbent Surfaces by Photothermal Beam Deflection Spectroscopy

M. J. D. Low[a]; A. G. Severdia[a]; T. H. Arnold[a]
[a] Department of Chemistry, New York University, New York, NY

To cite this Article Low, M. J. D. , Severdia, A. G. and Arnold, T. H.(1983) 'Infrared Observation of Intrinsic Modes on Adsorbent Surfaces by Photothermal Beam Deflection Spectroscopy', Spectroscopy Letters, 16: 3, 207 — 214

To link to this Article: DOI: 10.1080/00387018308062336

URL: http://dx.doi.org/10.1080/00387018308062336

SPECTROSCOPY LETTERS, 16(3), 207-214 (1983)

INFRARED OBSERVATION OF INTRINSIC MODES ON ADSORBENT SURFACES BY PHOTOTHERMAL BEAM DEFLECTION SPECTROSCOPY

Key Words: intrinsic surface modes, infrared spectra, surfaces, photothermal deflection-photoacoustic spectroscopy, adsorbents.

M.J.D. Low, A.G. Severdia and T.H. Arnold
Department of Chemistry
New York University
4 Washington Place
New York, NY 10003

INTRODUCTION

Boccuzzi *et al.*[1] pointed out that the infrared (IR) spectra of fine powders, i.e., materials typical of the texture of adsorbents and catalysts, are the sum of (a) nearly bulk modes; (b) · surface modes due both to first-order (surface truncation) and second order (change of the surface bond force constant) effects; and (c) impurities and/or adsorbed species. Studies of the latter have led to the valuable and voluminous literature of "IR of adsorbed species." The second order effects are also of interest to surface studies, but little information has been available. In an elegant and detailed study of silica, Boccuzzi *et al.* observed various impurity modes associated with surface hydroxyl groups, and also intrinsic

0038-7010/83/1603-0207$3.50/0

modes associated with the clean silica surface and related to the different strength and geometry of the surface bonds with respect to the bulk. Their observation demonstrated that new surface and subsurface siloxane groups were spectroscopically distinguishable from those characteristic of the bulk and "...this implies that surface vibrational states not associated with adsorbed impurities can be observed by IR spectroscopy. This fact, if further checked on other solids, could open a new field in IR studies."[1]

The statements are based on observation of absorptions on the low and high wavenumber sides of the intense silica bands centered near 1100 and 800 cm^{-1}, i.e., on the edges of the minute "window" in the silica transmission spectrum in which Morrow and Cody[2] observed new bands with degassed silica. However, finely divided silicas scatter radiation extensively and absorb so very strongly that silicas are usually considered to be opaque below about 1300 cm^{-1}. In order to carry out IR work in the window region, very thin and fragile samples requiring fastidious and arduous preparation must be used and exacting measurements at very low IR intensities are required; suffice it to say that such work is extremely difficult with IR transmission methods. We propose and demonstrate an easier alternative approach.

EXPERIMENTAL

The technique employed is IR Fourier transform photothermal beam deflection spectroscopy (PBDS). It is an off-shoot of photoacoustic spectroscopy[3] and is based on the method invented by Boccara et al. and used to record spectra in the visible region of the spectrum.[4] The instrumentation and techniques are described elsewhere.[5,6] Relatively thick sample pellets of ~50 mg/cm^2 were prepared from Cab-O-Sil M-5 silica and Alon-C alumina and examined within a cell under the conditions normal to surface studies.[6] The spectra shown are at 8 cm^{-1} resolution. Spectra are usually recorded with 800 scans, i.e., a measurement time of ~20 min.

RESULTS AND DISCUSSION

Spectrum A of Fig. 1 is a typical IR transmission spectrum obtained with a thin silica pellet; the small transparency "window" is marked with an arrow: it is in this region of very low energy that measurements must be made. Spectrum B is the PBD spectrum of silica; the entire range can be observed. The transparency window obviously falls between the intense absorptions near 1100 and 800 cm^{-1}. When the silica is degassed, then (a) the transparency in the window region increases slightly, as described previously,[1,2] so that the photothermal signal decreases, and (b) the absorption on the high and low wavenumber sides of the window increases slightly, as reported,[1] so that the photothermal signal increases. These minor changes occurring on the edges of intense bands as

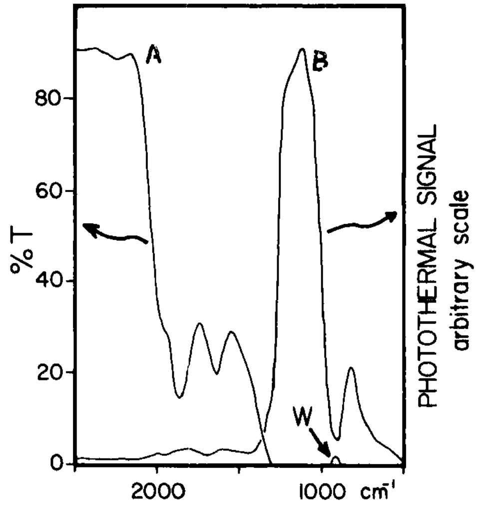

Fig. 1: Spectra of silica.
A: transmission spectrum. B: PBD spectrum.

in the scale-expanded spectrum A of Fig. 2 are difficult to define (and also to demonstrate on a greatly reduced, printed figure) but become clear when spectra of silicas at various stages of degassing are ratioed, as in the example spectrum A/B. The latter is the result of ratioing the spectrum A of a silica pellet degassed at 350^{o}C for 2 hrs. against the spectrum B of the pellet after degassing at room temperature (spectrum B is not shown), thus using the silica as its own reference so that intensity differences are brought out. In the differential spectrum A/B, the large "negative" excursion toward the abscissa is caused by the decrease in the photothermal response accompanying the decreased absorption brought about by the mild degassing, i.e., the sample became more transparent in

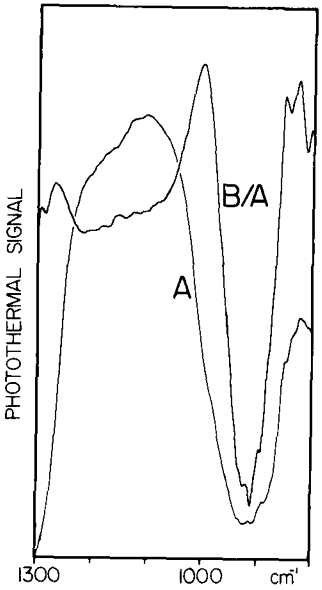

Fig. 2: PBD spectra of silica.
A: silica degassed at 350°C.
A/B: the ratio of spectrum A and the spectrum of silica degassed at 22°C.

the middle of the window region, as described.[1,2] There is also a poorly defined "positive" band in the 850 cm^{-1} region and a clearly defined band peaking near 1000 cm^{-1}, indicating increases in photothermal response and absorption, corresponding to the 1020-975 and 860-810 cm^{-1} absorptions observed by Boccuzzi _et_ _al_. and thought to be basically associated with coupled asymmetric and symmetric vibrations mainly localized on the outer and hence more distorted siloxane bridges. In addition, a minor absorption on the high wavenumber side of the intense 1100 cm^{-1} absorption was observed, shown as the small positive band centered near 1270 cm^{-1}. This absorption, which was not observed before and the cause of which is unknown, was found in all spectra of samples degassed to 700°C.

Some exploratory results obtained with alumina are shown in Fig. 3. Spectrum A is the transmission spectrum of an alumina sample and, as is well known, shows a region of intense absorption below 1100 cm^{-1} which prohibits that region to be observed. PBD spectra of alumina were recorded at 22°C and after degassing at 500 and 800°C, and the ratioed traces marked 500/22, 800/22 and 800/500 were computed, i.e., the ratio

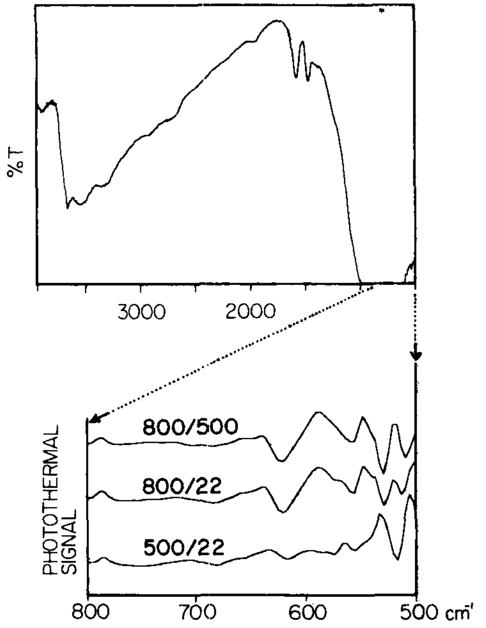

Fig. 3: Spectra of alumina.
A is the transmission spectrum. The other traces are differential PBD spectra; see text.

of the spectrum of the alumina sample degassed at 800°C versus the spectrum of the sample at 22°C, and so on. It is apparent from these differential traces that degassing brought about changes in absorption. The precise causes of these is not known at present. What is pertinent is that it was possible to observe, with relative ease, spectral changes in a region usually inaccessible to transmission techniques.

CONCLUSIONS

With silicates, mixed oxides and similar materials, it seems likely that the structure of groupings at or near the surface, and of special adsorption or reaction sites analogous to the "strained siloxane bridges" on silica, will be very similar to the structure of the bulk material; this seems to have been shown for silica. The absorptions of such surface groupings would thus fall very close to the very intense bulk modes. Detecting surface groupings via transmission techniques then requires the measurement of small differences of small signals and involves the preparation of extremely thin samples; indeed, in some cases it may not be possible to make the samples thin enough. In constrast, what is involved with PBDS is the somewhat easier task of discerning small differences of large signals; it may be possible that saturation effects[3] be encountered, but the sample preparation steps become trivial. IR-PBDS thus seems a preferable method. Such measurements might also be profitably made with photoacoustic spectroscopy, assuming that the problem arising from that technique concerning the contamination of the sample can be overcome.[6]

ACKNOWLEDGMENT

Support by NSF grant CHE-811778 is gratefully acknowledged.

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Received: November 22, 1982
Accepted: January 4, 1983