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LETTERS TO THE EDITORS

The C–H Stretching Bands of Methanol Adsorbed on Silica

INTRODUCTION

Takezawa and Kobayashi (*1*) have recently reported a correlation between the frequency of the asymmetric CH stretching band of the terminal methyl group of surface alcoholates adsorbed on metal oxides and the electronegativity of the metal atom. They found that the frequency of this vibrational mode increased with increasing electronegativity of the metal atom in the oxide. While not wishing to criticize this correlation, we wish to point out that it is not at all clear in the simpler alcohols which infrared absorption band should be assigned to the so-called asymmetric stretching vibration of the methyl group.

A "symmetric top" methyl group (e.g., in the methyl halides) should give rise to one doubly degenerate asymmetric νCH mode and one symmetric mode. Even in hydrocarbons, the near symmetric top environment is closely preserved and a similar situation exists (*2, 3*). However, when a methyl group is attached to an atom which contains a nonbonded lone pair or pairs of electrons (e.g., nitrogen or oxygen) the symmetric top approximation is a poor one and the degeneracy of the asymmetric νCH mode is removed (*4*). McKean (*4*) has recently shown that in methyl alcohol, the CH bond *trans* to the lone pairs on oxygen is not equivalent to the other CH bonds. In this letter, we present evidence which shows that a similar situation exists for surface methoxyl groups on silica and that it is somewhat meaningless to talk of a single "asymmetric" CH stretching mode.

EXPERIMENTAL

Silica discs weighing 200 mg and of 1-inch diameter were prepared from Cab-O-Sil (H-5) which had been preheated at 700°C for 16 hr prior to pressing (1000 lB/in^2). The discs were placed in a quartz cell and were heated in O_2 (200 Torr) at 500°C for several hours in order to oxidize any hydrocarbon impurities. After removal of the O_2 the sample was then reacted with gaseous methanol (20 Torr) at 400°C for 1–2 hr, replacing the methanol several times. After cooling and evacuation of excess reactant, the samples were transferred to a variable temperature cell (*5*) which was evacuated and then filled with about 5 Torr of helium.

All spectra were run on a Perkin-Elmer 13G spectrometer utilizing a spectral slit width of about 3 cm^{-1}. The spectra did not change with a narrower slit width, this particular value being chosen so as to minimize the noise level for the subsequent measurements for digitization purposes. Computations were carried out on an IBM 360/65 computer and plots were drawn on a Milgo DPS-5 plotter. Methanol-d_2 was obtained from Merck, Sharp and Dohme Ltd. of Montreal and was of 99% isotopic purity.

The spectra shown below are of the νCH region only, 3100–2700 cm^{-1}, and the spectra obtained under similar conditions in other spectral regions are similar to those reported in the literature (*6, 7*).

RESULTS

The spectrum (sample at 25°C) in the CH stretching region of methanol chemi-

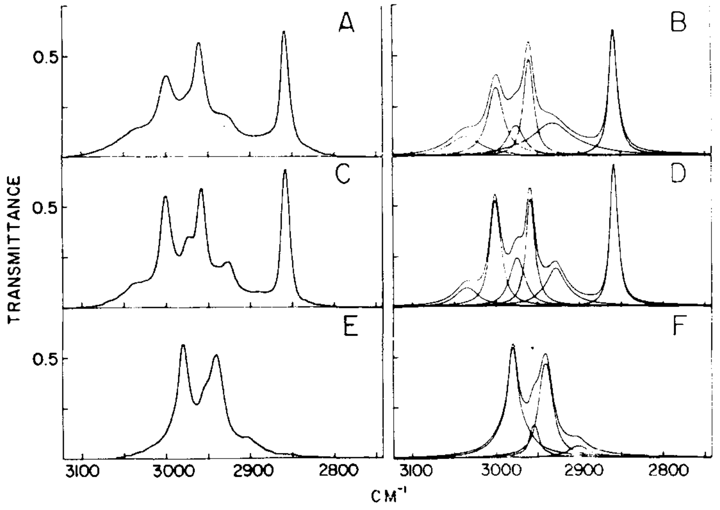

Fig. 1. Experimental and computed spectra of methanol chemisorbed on silica. A: CH_3OH, sample at 25°C; B: Computed spectrum from data in A; C: CH_3OH, sample at −110°C; D: Computed spectrum from data in C; E: CHD_2OH, sample at −110°C; F: Computed spectrum from data in E. See text for computational details.

sorbed on silica is shown in Fig. 1A. This spectrum is essentially the same as that reported previously in the literature (*6*, *7*) but because it was recorded with a relatively large abscissal scale expansion several weaker features in addition to the prominent bands at 3000, 2960 and 2858 cm^{-1} are apparent; these are shoulders near 3035 cm^{-1} and 2930 cm^{-1}, and a suggestion of an additional band at near 2975 cm^{-1}. When the sample temperature is lowered to −110°C, the spectrum shown in Fig. 1C is obtained, and this spectrum differs in overall appearance from that shown in Fig. 1A, in that there is a change in the relative intensity of the six bands. On warming to 25°C the spectrum obtained is identical with that originally obtained at 25°C, and this process of raising and lowering the temperature can be repeated indefinitely and the same spectrum at these temperature limits is obtained. The changes in relative intensity are even more marked on heating the sample up to 200°C (spectrum not shown) and it appears that some sort of temperature-dependent equilibrium exists; however, this will not be discussed here and we will concentrate on the question of assignments. Both spectra can be very well fitted to a 6-band Lorentzian–Gaussian sum function using the computer programs developed for this purpose by Pitha and Jones (*8*) and these fits are shown in Fig. 1B and 1D for the 25°C and −110°C spectra, respectively. These spectra can also slightly less satisfactorily be fitted to a 6-component pure Lorentz function or to a Lorentz–Gauss product function, but, as discussed by Jones (*9*), the sum function gave the best fit. The peak positions derived as a result of this analysis are given in the Table. Since six bands are apparent in the spectrum at 25°C, clearly the question of assignment of two fundamentals for a pure symmetric top-type methyl group is difficult as is that for a three band spectrum corresponding to a nonsymmetric top environment. Either four or three "overtones" or "combinations" have to be postulated to account for the additional features and without further data an unambiguous assignment is not possible. However, one could probably be fairly safe to suggest that the strong 2858 cm^{-1} band is probably attributable to the "symmetric" νCH mode (*3*, *6*).

In an attempt to clarify this assignment problem the spectrum at −110°C of adsorbed CHD_2OH was obtained and is shown in Fig. 1E. In theory, only one νCH

TABLE 1
Computed Wavenumbers and Peak Intensities

Spectrum	Wavenumber (cm^{-1})	Intensity (absorbances)
CH_3OH 25°C	3037	0.045
	3000	0.184
	2976	0.072
	2960	0.287
	2932	0.079
	2858	0.418
CH_3OH −110°C	3036	0.043
	3000	0.325
	2974	0.121
	2958	0.334
	2928	0.092
	2858	0.538
CHD_2OH −110°C	2979	0.347
	2954	0.079
	2940	0.277
	2902	0.027

mode should be observed for a CHD_2 group as long as the properties of the C–H bond do not depend on its orientation with respect to the OH group, and there should be no additional complications due to Fermi resonance interactions with overtones of CH_2 or CH_3 deformation modes.

Two strong and two weak bands are clearly discernible in the spectrum (see Fig. 1F for component analysis) and the wavenumbers are listed in the Table. A similar 4-band spectrum is also observed in the νCD region from chemisorbed CH_2DOH. One tentative interpretation that can be put forward now is that the two strong bands are due to two different types of C–H bonds depending on the orientation of the C–H bond with respect to the oxygen lone pairs; this interpretation would agree with that of McKean for pure methanol (*4*). The other two bands may be due to surface effects, i.e., the orientation of the methyl group relative to the silica surface, or they may arise from an appreciable population of an excited torsional level as a result of a low torsional barrier to rotation, either of the methyl group about the C–O bond [375 cm^{-1} for pure methanol (*10*)] or from a barrier to rotation of the O–CH_3 group on the surface about the SiO bond. This aspect of the problem will not be discussed further here.

The results for CHD_2OH show that the surprising complexity of the spectrum of chemisorbed CH_3OH is not unexpected and does illustrate that extreme caution must be exercised in making arbitrary assignments. As stated above, we are not disputing the trend reported by Takezawa and Kobayashi (*1*), but it would have been desirable for them to have at least presented their spectral data in tabular form, or better still, to have shown some spectra.

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References

1. Takezawa, N., and Kobayashi, H., *J. Catal.* **25**, 179 (1972).
2. Brown, J. K., Sheppard, N., and Simpson, D. M., *Disc. Faraday Soc.* **9**, 261 (1950).
3. Bellamy, L. J., "Infrared Spectra of Complex Molecules." 2nd. Ed., Methuen, London, 1958.
4. McKean, D. F., *Chem. Comm.*, 1373 (1971).
5. Morrow, B. A., *J. Sci. Inst.* **43**, 487 (1966).
6. Low, M. J. D., and Harano, Y., *J. Res. Inst. Catal. Hokkaido Univ.*, **16**, 271 (1968).
7. Borello, E., Zecchina, A., and Morterra, C., *J. Phys. Chem.* **71**, 2938 (1967).
8. Pitha, J., and Jones, N., "Optimization Methods for Fitting Curves to Infrared Band Envelopes." N.R.C. Bulletin No. 12 and 13, National Research Council of Canada, Ottawa, 1968.
9. Jones, R. N., *Appl. Optics* **8**, 597 (1969).
10. Lees, R. M., and Baker, J. G., *J. Chem. Phys.* **48**, 5299 (1968).

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