Adsorption and Orientation of Benzoic Acid on Aluminum Oxide: An Infrared Study

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Fourier transform infrared spectroscopy has been used to show that benzoic acid adsorbs on aluminum oxide as benzoate ions, oriented with their rotational symmetry axes approximately normal to the surface. In addition a benzoic acid surface species, not observed by inelastic tunneling spectroscopy, was found.

INTRODUCTION

Inelastic electron tunneling spectroscopy (IETS) has contributed a large body of information on monolayer adsorption of organic molecules on metal oxide surfaces (1–7) with most of the work being done on thin aluminum oxide layers prepared on evaporated metal films. Previous results indicate that carboxylic acids adsorb on aluminum oxide by proton dissociation (8, 9), and that under suitable conditions monolayer coverages can be obtained (10). However, few examples exist where infrared or Raman spectra have been obtained for substrate/adsorbate systems from which IETS spectra have been obtained (3). We report here the results of transmission infrared spectra obtained from submonolayer quantities of benzoic acid deposited on single crystals of aluminum oxide using solution doping techniques (11, 12) developed by IETS workers.

EXPERIMENTAL

Sample preparation was essentially that of Langan and Hansma (10) except that the aluminum oxide electrode was replaced by commercially available (13) sapphire plates 0.013–0.05 cm thick. The plates were oriented with their (102) axes approximately normal to the surface.

After cleaning using standard procedures for glass, the sapphire plates were heated in a hydrogen flame to drive off remaining surface water, cooled, and placed transversely on a spinner similar to that described in Ref. (10). About 20 μl of dopant solution was dropped onto the cleaned substrate, and the spinner immediately accelerated to 3600 rpm to spin off excess solution. Benzoic acid/aluminum oxide was chosen for initial experimentation because that was the only adsorbate/substrate system for which quantitative surface coverage versus dopant solution concentration was known (14).

Freshly prepared samples were placed in a Nicolet 7001P interferometer equipped with a D1010B cooled mercury–cadmium–telluride detector. The infrared beam was apertured to match the size of the sample drop (usually 2–3 mm diameter). Interferograms obtained from the area of the sapphire containing the overlayer, as well as an area ca. 1 cm away, were processed with a PDP 11/55 computer to give spectra with resolution ranging from 4 to 25 cm^{-1}. In order to prevent channeling (15), for a plate of thickness t the limiting resolution ΔR is given by $\Delta R \sim (2nt)^{-1}$, where n is the index of refraction of the material (ca. 1.7 for sapphire). Since the low-frequency cutoff because of the intense lattice vibrations of the substrate increases with increasing sub-

strate thickness, increased resolution must be traded off (16) with less spectral information at low frequencies. Fortunately, most of the bands of interest here have width greater than 30 cm^{-1} so the extra resolution is not necessary.

RESULTS AND DISCUSSION

Figure 1 shows an infrared spectrum of benzoic acid deposited onto sapphire from a 4 × 10^{-4} M dopant solution, which from Ref. (10) should result in roughly 30% of saturation coverage. The main features are bands at 1720–1695, 1550, 1500, 1450, and 1225 cm^{-1}.

Figure 2 shows reference spectra obtained from (a) benzoic acid and (b) sodium benzoate in KBr for the same spectral region. The main ν(CO) stretches are indicated in Fig. 2, and the various ring vibrations (ϕ) are labeled according to the symmetry of their normal modes with the frequencies taken from Ref. (17).

Figure 3 shows an infrared spectrum of a multilayer film of sodium benzoate on sapphire. The film was formed by placing a 15-μl drop of a 10^{-4} M solution into one of our sapphire substrates and evaporating to dryness at 30°C. Assuming negligible surface diffusion, for a typical 3- to 4-mm-diameter drop, this corresponds to an average film thickness of ten "monolayers." The resem-

blance to the sodium benzoate reference spectrum (Fig. 2b) is obvious, and we assume the same band assignments.

Of particular interest is the intense band at 1550 cm^{-1} in Fig. 1 which is absent in the benzoic acid spectrum (Fig. 2a). Since the 1550-cm^{-1} band is the strongest band in the sodium benzoate spectrum (Fig. 2b), its presence in Fig. 1 is evidence for the carboxyl antisymmetric vibration of ionized benzoic acid, i.e., some of the acid dissociates on adsorption to form a resultant benzoate ion. However, in Fig. 1 the corresponding carboxyl symmetric vibration at 1420 cm^{-1} is either absent or greatly reduced in magnitude. In our experimental setup the infrared light is incident approximately normal to the surface. Hence, the electric vector can couple only to net dipole moment changes parallel to the surface (18). Thus, the resultant benzoate ion must be oriented with its rotational symmetry axis (C$_{2v}$) approximately normal to the surface since the symmetries of the antisymmetric and symmetric carboxyl vibrations are B$_2$ and A$_1$, respectively.

The above result is consistent with that inferred from IETS (1–12) and reflection–absorption (3) data except that the selection rules are reversed, since tunneling electrons couple primarily to vibrations normal to the surface (19). Thus, the infra-
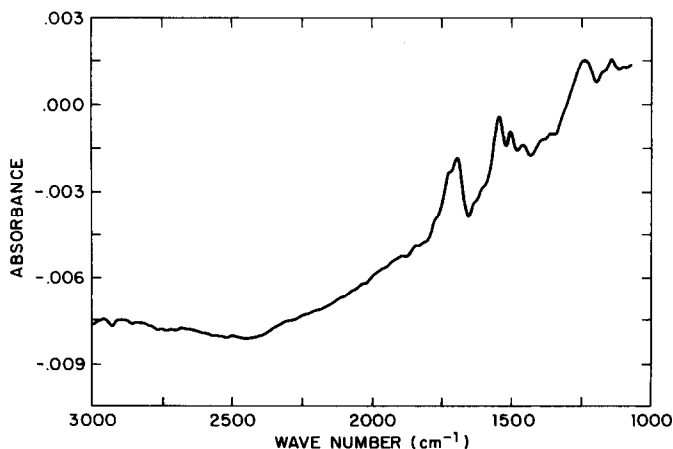

FIG. 1. Infrared spectrum of benzoic acid deposited on sapphire from 4 × 10^{-4} M dopant solution.
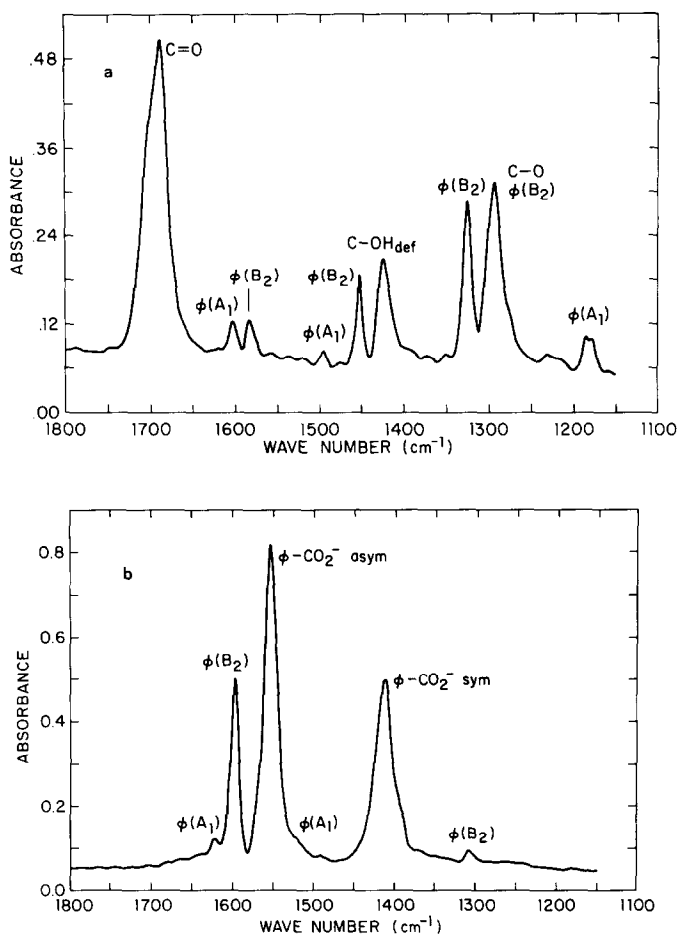
FIG. 2. Infrared spectra of: (a) benzoic acid, (b) sodium benzoate in KBr.

red measurements provide information complimentary to those obtained from IETS and reflection–absorption.

It has been suggested (20) that carboxylic acids bond "canted" to an alumina surface, although no quantitative estimates of the amount of canting have been made (20). The apparent absence of the carboxyl symmetric stretching vibration in this work suggests that the amount of canting should be small although no quantitative estimate can be made with the current signal to noise. Additional experiments utilizing polarized light and variable angles of incidence could help quantify this matter.

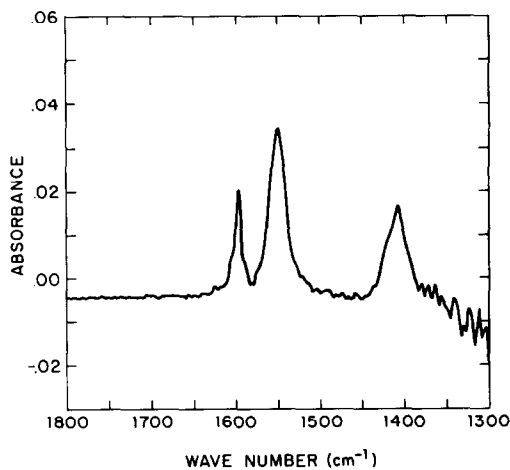The additional bands at 1720–1695 and 1250 cm^{-1} in Fig. 1 are suggestive of the

FIG. 3. Infrared spectrum of ca. ten monolayers of sodium benzoate deposited on sapphire.

TABLE 1

Vibrational Assignments for Benzoic Acid on Al_2O_3

ν (cm^{-1})	Assignment	Intensity		Conclusion
		IETS	ir	
1550	$\nu(CO_2^-)_{as}$	Weak	Strong	Benzoate ion oriented
1420	$\nu(CO_2^-)_{sym}$	Strong	Absent	normal to surface
1720–1695	$\nu(C=O)$	Weak	Strong	Benzoic acid oriented
1250	$\nu(C—O)$	Absent	Strong	parallel to surface

$\nu(C=O)$ and $\nu(C—O)$ stretching vibrations, respectively, thus suggesting the presence of undissociated benzoic acid (21). This form of benzoic acid is probably not present in IETS measurements since it would be removed during the evacuation prior to depositing the Pb counter electrode (22).

The above observations are summarized in Table 1.

Since previous work (23) with copper oxides suggested that carboxylic acids can build up stable multilayer films of the corresponding salts, a second estimate of the amount of benzoate ion present in Fig. 1 was desirable. By comparing the intensity of the 1550-cm^{-1} benzoate band in Fig. 1 with that of the ten-monolayer sample (shown in Fig. 3), we find the amount of benzoate ion in Fig. 1 to be ca. one-half monolayer, a value in good agreement with that estimated by IETS workers (10).

Although we are not explicitly interested in orientation effects in multilayer films (such as shown in Fig. 3), we find that the intensities of the 1410- and 1600-cm^{-1} bands (relative to that of the 1550-cm^{-1} band) varied by two to three times from sample to sample, thus suggesting that these bands are indicative of a disordered benzoate overlayer.

The frequencies and intensities of bands observed together with their assignments

TABLE 2

Observed Bands and Assignments

IETS[a]	"Oriented" C_6H_5COOH	"Oriented" $C_6H_5CO_2^-$	"Unoriented" $C_6H_5CO_2^-$	Assignment[b]	Symmetry class
1741 vw	1720 s				
	1695 s			$\nu(C=O)$	
1599			1600 s	$\nu(C—C)$	B_2
1575 vw		1550 s	1550 vs	$\nu(CO_2^-)_{as}$	B_2
1491 mw	1500 m			$\nu(C—C)^c$	A_1
1450 m	1450 w			$\nu(C—C)$	B_2
1433 m			1410 s	$\nu(CO_2^-)_{sym}$	A_1
1310 w				$\nu(C—C)$	B_2
	1250 w			$\nu(C—O)$	
1153 s	1150 mw			$\beta(C—H)$	A_1

[a] Frequencies taken from Refs. (4, 10, 24).

[b] Symbols used: ν, stretch; β, in-plane deformation; γ, out-of-plane deformation.

[c] Could alternatively be $2\gamma(C—H)$ with B_2 symmetry since the C—H out-of-plane deformation at ca. 750 cm^{-1} gives rise to very strong infrared absorption (25).

and where appropriate, their symmetry class, are given in Table 2.

Also given in Table 2 are frequencies from the analogous tunneling experiments. The assignment of the 1500-, 1450-, and 1150-cm^{-1} bands to oriented benzoic acid and not "oriented" benzoate is arbitrary since a complete analysis of the ring vibrations and their intensities is well beyond the scope of this work.

CONCLUSIONS

We have shown that transmission infrared spectroscopy can provide information complimentary to that obtained from inelastic tunneling and reflection–absorption spectroscopies, primarily because of mutually exclusive selection rules—tunneling and reflection–absorption are sensitive primarily to vibrations normal to a surface while transmission infrared is sensitive to vibrations parallel to the surface.

Transmission infrared spectroscopy has been used to confirm the dissociation of benzoic acid on alumina to produce benzoate ions oriented with their rotational symmetry axes (C_{2v}) approximately normal to the surface. There also appears to be a second surface species, heretofore undetected in inelastic tunneling, consisting of benzoic acid molecules oriented with both their ν(C=O) and ν(C—O) stretching vibrations approximately parallel to the surface.

ACKNOWLEDGMENTS

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21. Since the sapphire substrate has structure at ca. 1250 cm^{-1}, assigning this band to ν(C—O) is tentative. However, this assignment of the 1720- to 1695-cm^{-1} bands should be quite definite.
22. Less likely is the possibility that the undissociated acid is not observable in tunneling measurements because it is oriented with both its ν(C=O) and ν(C—O) vibrations parallel to the surface as might be the case if it were bonded via a hydrogen band through its "acid" hydrogen.
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