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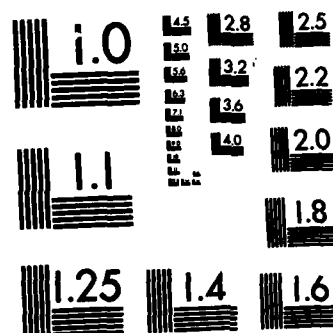
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Esters Dissociatively Adsorb on Alumina
by

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ABSTRACT

Inelastic electron tunneling spectra for esters of the form RCOOR' show that these compounds dissociate on alumina and only the RCOO^- ion bonds to the surface. For phenethyl benzoate, ethyl- d_5 benzoate, benzyl- d_7 benzoate, the benzoate ion is symmetrically adsorbed. For ethyl- d_5 acetate, the spectrum is distinguishable from the spectrum of a symmetrically bonded acetate ion.

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1. Introduction

Vibrational spectroscopy is a powerful technique for studying chemisorbed surface species. The most widely used techniques are infrared and Raman spectroscopies. Two newer techniques are high resolution electron energy loss spectroscopy and inelastic electron tunneling spectroscopy. Tunneling spectroscopy reveals the vibrational modes of organic molecules adsorbed on the oxide of a metal-oxide-metal junction [1,2]. Both infrared and Raman active modes can be observed over the spectral range of 0 - 4000 cm^{-1} .

To date the chemisorption of a variety of compounds have been studied. Among the major groups are carboxylic acids [3-10], sulphonic acids [11], unsaturated hydrocarbons [12], alcohols [13-17], diols [18], amines [17], aromatic ring compounds [19-21], diketones [22], fatty acids [23], biological molecules [24,25] and inorganic ions [26].

In this paper we present a study of the chemisorption of esters on alumina. In particular, we took the tunneling spectra of phenethyl benzoate, phenethyl isobutyrate, ethyl- d_5 benzoate, benzyl- d_7 benzoate and ethyl- d_5 acetate.

2. Experimental methods

Phenethyl benzoate (Aldrich S52804-8) and phenethyl isobutyrate (Aldrich S52852-8) were used directly with no purification. Gas chromatography/mass spectral (GC/MS) analyses showed them to be 99.5+% chemically pure. Ethyl- d_5 acetate (Merck, Sharp and Dohme) was used directly and has a listed isotopic purity of 98 atom%. Ethyl- d_5 benzoate was prepared

from reaction of ethyl-d₅ alcohol (99 atom%, Merck, Sharp and Dohme) with benzoyl chloride. Benzyl-d₇ benzoate was prepared from reaction of benzyl-d₇ alcohol (98 atom%, Merck, Sharpe and Dohme) with benzoyl chloride. Both esters were purified by vacuum distillation; b.p. ethyl-d₅ benzoate, 73° (4 mm) and benzyl-d₇ benzoate, 104 - 106° (0.1 mm). GC/MS analyses showed them to be 99.8+% chemically pure.

To produce the tunnel junctions we: 1) evaporated aluminum strips 700 Å thick onto a clean 1 x 3 inch glass slide, 2) oxidized the strips by venting the chamber to pure O₂, 3) doped the oxidized aluminum strips either with a liquid solution [27] of the molecules of interest or a vapor. For the vapor doped samples the aluminum strips were further oxidized in air at 200°C and cleaned in an argon glow discharge before doping [28]. We chilled the slide to about 200°K with a cold finger during ethyl-d₅ alcohol doping. 4) completed the junction by evaporating 2000 Å thick lead cross-strips.

The completed junctions were mounted on a probe with electrical contacts and immersed into liquid helium. The tunneling spectrum, which is a plot of d^2V/dI^2 versus V , was taken using a modulation technique. The benzoates were run with 0.7 mV, the alcohols and the acetate with 1 mV modulation voltage. The details of the experimental techniques are discussed in review articles [1,2].

3. Results and discussion

Esters have two characteristic absorptions arising from C=O and C-O- groups in their vibrational spectra. The C=O

stretching vibration for benzoates is in the range 1770 cm^{-1} to 1800 cm^{-1} and the C-O stretching vibration is between 1250 cm^{-1} and 1310 cm^{-1} [29,30]. The tunneling spectrum of a junction doped with phenethyl benzoate ($\text{C}_6\text{H}_5\text{CO}_2\text{C}_2\text{H}_4\text{C}_6\text{H}_5$) does not show any strong peaks in these regions (fig. 1). The similarity of this spectrum to the spectrum of benzoate ions on alumina suggests that the compound breaks up on the surface and the benzoate ion bonds to alumina [27]. The close agreement of the peak positions for phenethyl benzoate to the peak positions for aluminum benzoate supports this (Table 1). But, since the modes of the phenethyl group overlap with the modes of the benzoate group, we cannot rule out the presence of the phenethyl group from the spectrum. Further, the presence of weak peaks at 1691 cm^{-1} and 1293 cm^{-1} may possibly indicate the presence of a small quantity of undissociated ester.

The broad peak at $\sim 2900\text{ cm}^{-1}$ is due to C-H stretching vibrations characteristic of alkyl hydrocarbons. This is probably due to contamination generally observed in spectra of samples doped out of a solution.

Fig. 2 is the tunneling spectrum for a junction doped with phenethyl isobutyrate ($\text{C}_3\text{H}_7\text{CO}_2\text{C}_2\text{H}_4\text{C}_6\text{H}_5$). The modes characteristic of the phenyl group, like the aromatic C-H stretch at $3000 - 3100\text{ cm}^{-1}$ or the strong ring mode at $\sim 1600\text{ cm}^{-1}$, are absent from the spectrum. We have taken the tunneling spectrum of isobutyric acid on alumina and observed that the spectrum of phenethyl isobutyrate is similar to that of isobutyric acid. Hence, phenethyl isobutyrate dissociates on the surface and the butanoate ion reacts with alumina.

Can we generalize this result? Does an ester of the form RCOOR' react with the alumina to dissociate and only RCOO^- bond to the surface? If R' is deuterated, we can easily tell if it is bonded to the surface or not since the C-D stretching region is clear of other modes. Figs. 3 and 4 show the tunneling spectra of junctions doped with ethyl- d_5 benzoate ($\text{C}_6\text{H}_5\text{CO}_2\text{C}_2\text{D}_5$) and benzyl- d_7 benzoate ($\text{C}_6\text{H}_5\text{CO}_2\text{CD}_2\text{C}_6\text{D}_5$), respectively. The C=O and C-O- stretching vibrational modes are not observed in either spectra.

The C-D stretching vibrations are missing as well. The C-D stretching vibrations for the ethyl- d_5 group are at 2070, 2110, 2146 and 2215 cm^{-1} as measured from the spectrum for ethyl- d_5 alcohol ($\text{C}_2\text{D}_5\text{OH}$) adsorbed on alumina (fig. 5). The ethyl- d_5 benzoate spectrum has no peaks in that region. For the benzyl- d_7 group, the C-D stretching vibrations occur at 2092, 2171 and 2264 cm^{-1} as measured from the spectrum for benzyl- d_7 alcohol ($\text{C}_5\text{D}_5\text{CD}_2\text{OH}$) adsorbed on alumina (fig. 6). The weak peaks at 347 and 2266 cm^{-1} in the benzyl- d_7 benzoate spectrum can be due to the deuterated benzyl group. Yet, the spectrum is largely free of modes due to benzyl- d_7 . The peak positions for both the ethyl- d_5 benzoate and benzyl- d_7 benzoate spectra are listed in Table 1. Studying the table, we observe that the tunneling peak positions for phenethyl benzoate, ethyl- d_5 benzoate and benzyl- d_7 benzoate are very similar to those of aluminum benzoate. Thus, we conclude that these esters react with alumina to form benzoate ions bonded to the surface.

Fig. 7 shows the tunneling spectra for chemisorbed ethyl- d_5 acetate ($CH_3CO_2C_2D_5$) (trace a) and acetic acid (CH_3CO_2H) (trace b). The ethyl- d_5 acetate spectrum, just like the other deuterated esters, does not contain modes characteristic of the ethyl- d_5 group. The compound dissociates on the surface and only the acetate group bonds. Yet, the spectra for this acetate group adsorbed on alumina is different than the spectrum for the acetate ion resulting from chemisorbed acetic acid (trace b).

In the case of acetic acid, the acetate ion forms a symmetric bidentate bond to alumina. The C-O- and the C=O stretching vibrations are no longer observed. They are replaced by CO_2^- symmetric stretch (1463 cm^{-1}), and the anti-symmetric stretch (1583 cm^{-1}) [5,10]. The comparison in Table 2 shows that the spectrum of the surface species resulting from ethyl- d_5 acetate lacks the symmetric CO_2^- stretch characteristic to the acetate ion. Also, the C-H stretching vibrations are shifted from those of the acetate ion. It is clear that ethyl- d_5 acetate dissociates and only the acetate ion bonds to alumina but the bonding is different than that of acetic acid. The 1259 cm^{-1} peak in trace a of fig. 7 is in the region where C-O- stretch is expected for ethyl acetate ($1245 - 1276\text{ cm}^{-1}$) or for metal acetates with unidentate bonding ($1248 - 1311\text{ cm}^{-1}$). The C=O stretch is at 1740 cm^{-1} for ethyl acetate and between 1623 and 1771 cm^{-1} for metal acetates [31]. The weak band at 1598 cm^{-1} in trace a can be a weakened, downshifted C=O stretch.

These data lead to the following description of the fate of organic esters adsorbed onto an oxidized aluminum surface. Bulk γ -aluminas are known to contain a variety of acidic sites, including both Brønsted and Lewis acid sites [33]. Hansma, et al. have shown that oxidized aluminum has similar physical and chemical properties to bulk γ -aluminas [34]. We suggest that organic esters react with surface bound hydroxyl groups at acidic sites on the alumina surface to form a chemisorbed carboxylate anion species and a free alcohol molecule which is subsequently pumped away during the later stages of sample preparation. This reaction appears to be general, since we have observed it with both esters of aromatic and aliphatic acids.

4. Summary

1. In the case of esters, we cannot study the vibrational spectra of the original molecules, since they react strongly with alumina and dissociate with only part of the compound left on the surface. Treatment of the aluminum oxide to pacify it may prevent the dissociation of these esters.

2. The chemisorbed ion resulting from the reaction of an ester of the form RCOOR' with aluminum oxide includes, at most, only traces of the R' group, where R' is phenyl, alkyl or alkyl benzene.

3. If R is a phenyl or alkyl (isobutyl) group, the predominant surface adsorbed species is the symmetrically bonded RCOO^- ion.

4. If R is a methyl group, the predominant surface species resembles but is clearly distinguishable from the symmetrically bonded acetate ions obtained from the reaction of acetic acid with alumina.

5. Inelastic tunneling spectroscopy can study the chemisorption of organic molecules on alumina. With our present experimental techniques, only compounds that bond to alumina can be studied since weakly adsorbed or physisorbed molecules will be pumped off before the top metal electrode evaporation.

Acknowledgments

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Figure Captions

- Figure 1. Tunneling spectrum of phenethyl benzoate on alumina. The compound was doped from a solution of 3.0 g/l in benzene.
- Figure 2. Tunneling spectrum of phenethyl isobutyrate on alumina. The compound was doped from a solution of 20.0 g/l in benzene. Note the absence of the aromatic CH stretch which would occur at 3000-3100 cm^{-1} .
- Figure 3. Tunneling spectrum of ethyl- d_5 benzoate on alumina. The compound was doped from a solution of 0.8g/l in benzene. Note the absence of the CD stretching vibrations which would occur between 2070 and 2220 cm^{-1} .
- Figure 4. Tunneling spectrum of benzyl- d_7 benzoate on alumina. The compound was doped from a solution of 0.7g/l in methanol. Note the absence of the CD stretching vibrations which would occur at 2090-2270 cm^{-1} .
- Figure 5. Tunneling spectrum of ethyl - d_5 alcohol on alumina. The compound was vapor doped on a chilled substrate with 3×10^3 Langmuirs of exposure.
- Figure 6. Tunneling spectrum of benzyl- d_7 alcohol on alumina. The compound was vapor doped with 1×10^3 Langmuirs of exposure.
- Figure 7. Tunneling spectra of (a) ethyl- d_5 acetate (b) acetic acid on alumina. Ethyl- d_5 acetate was

Figure 7. doped from a solution of 7.0 g/l in benzene. Acetic acid spectrum is by Brown et al (8). It was vapor doped. Note the absence of the CD stretching vibrations from trace (a) which would occur at 2070-2220 cm^{-1} . Trace a is markedly different than trace b, especially the strong mode at 1259 cm^{-1} is absent from trace b.

TABLE 1

Ethyl-d ₅ benzoate (a)	Benzyl-d ₇ benzoate (a)	Phenethyl benzoate (a)	Aluminum Benzoate (b)
cm ⁻¹	cm ⁻¹	cm ⁻¹	ir cm ⁻¹ Raman cm ⁻¹
290 (vw)	290 (vw)		unavailable
403 (m)	347 (vw)	407 (m)	"
436 (m)	403 (m)	436 (m)	"
	436 (m)	501 (vw)	"
613 (w)	536 (vw)		"
686 (s)	613 (mw)	624 (w)	617 (m)
726 (m)	682 (s)	690 (m)	"
823 (m)	722 (m)	727 (vw)	"
847 (m)	823 (m)		"
	847 (m)	854 (m)	858 (m)
936 (mw)		918 (w)	"
992 (m)	936 (mw)	940 (mw)	"
1024 (mw)	988 (m)	994 (vw)	1005 (vs)
1069 (vw)	1024 (mw)	1035 (vw)	1026 (w)
1153 (m)	1069 (vw)	1071 (vw)	1070 (w)
	1153 (m)	1157 (w)	1170 (vw)
1311 (vw)	1307 (w)	1293 (w)	
1375 (mw)	1375 (sh)	1314 (w)	1430 (mv)
1432 (m)	1428 (m)	1379 (w)	1460 (sh)
1492 (w)		1436 (mw)	1498 (m)
1597 (vs)	1492 (mw)	1499 (w)	1602 (s)
	1597 (vs)	1585 (m)	
2847 (s)	1694 (vs)	1601 (m)	
2891 (s)	2266 (vw)	1691 (vw)	
2996 (mw)		2865 (m)	
3028 (m)	2903 (m)	2902 (m)	
3061 (m)	3000 (m)	2996 (mw)	
	3028 (m)	3029 (sh)	
	3053 (m)	3062 (m)	
			3030 (x)
			3070 (w)
			3080 (m)

a. Peak positions are corrected for the superconducting energy gap of Pb [32]; to convert to meV divide by 8.065

b. reference [27].

TABLE 2

<u>Ethyl-d₅ acetate (a)</u>	<u>Acetic acid (b)</u>
<u>cm⁻¹</u>	<u>cm⁻¹</u>
	407
	468 (vw)
614 (vw)	615 (m)
697 (w)	689/
	678 (w)
743 (w)	
816 (m)	
868 (m)	
912 (m)	
	945 (vs)
	1024 (m)
	1046 (s)
1058 (m)	
1259 (s)	
	1341
	1372 (sh)
1400 (m)	
1445 (m)	
	1463 (vs)
1566 (w)	
1598 (w)	1583/
	1597 (m)
2857 (sh)	
	2866 (m)
2900 (vs)	
	2910 (vs)
2957 (vs)	
	2964 (vs)
	3000 (m)

a. Corrected for the superconducting energy gap of Pb; to convert to meV divide by 8.065.

b. from reference 10.

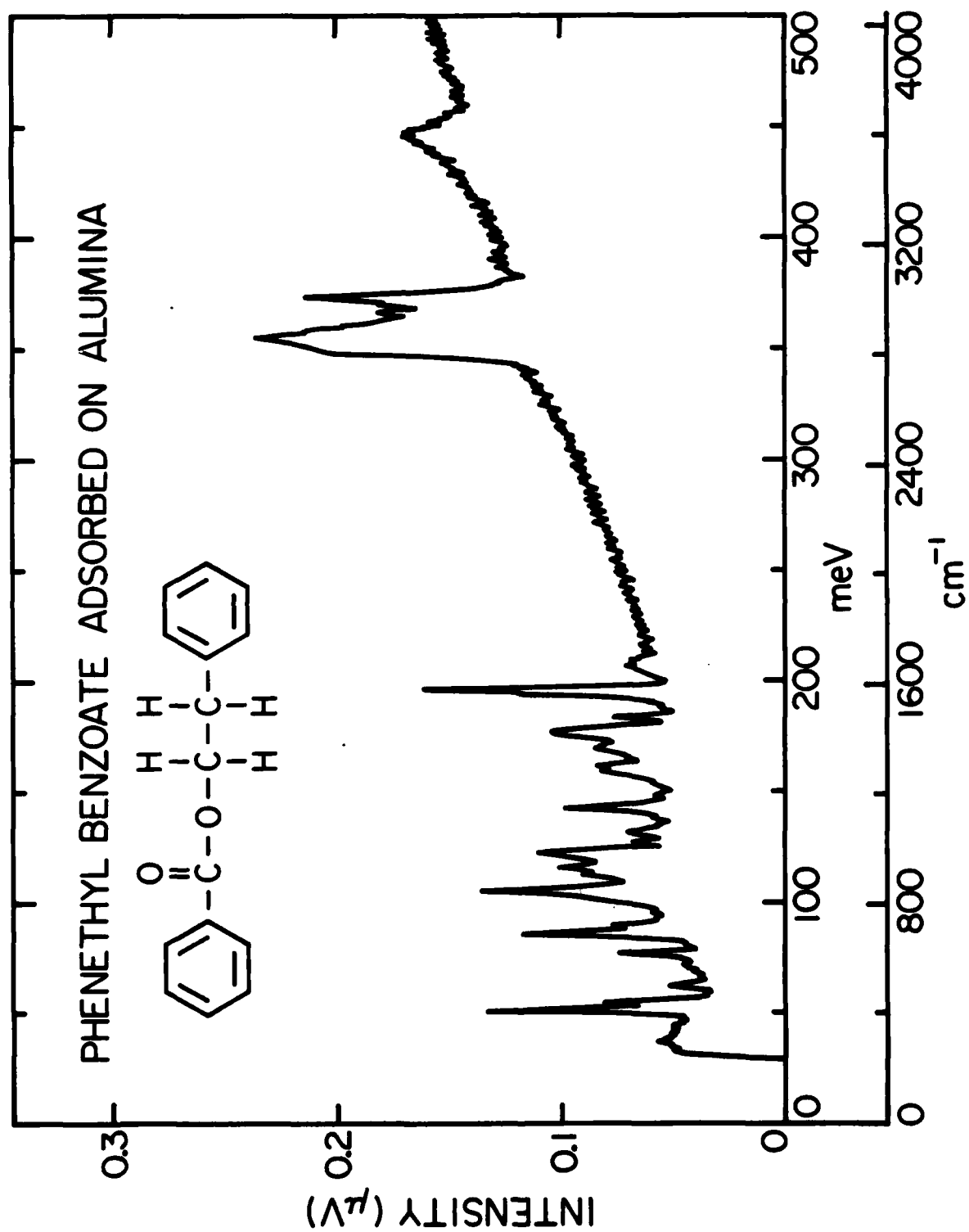


Fig. 1

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and Gale

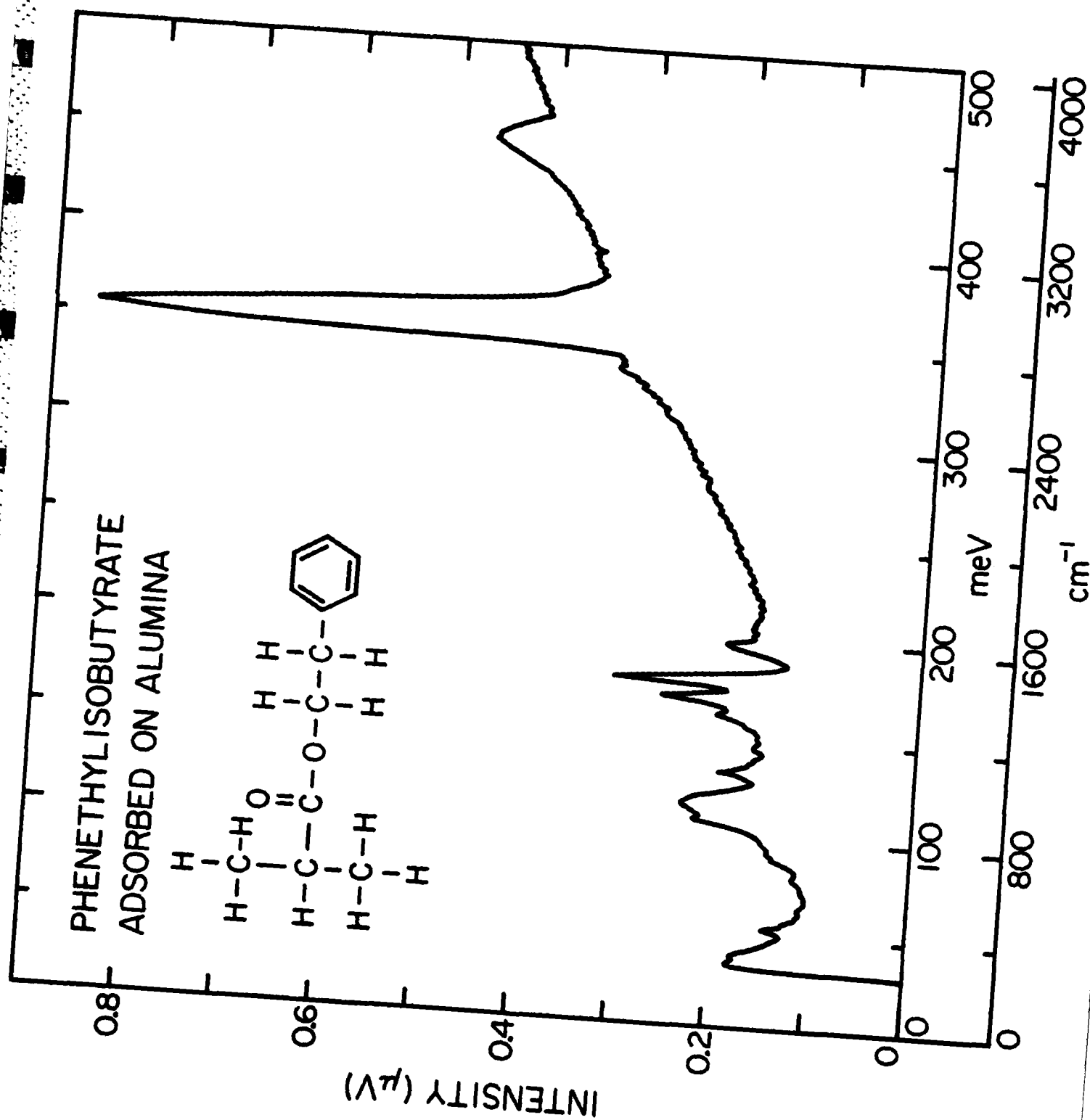


Fig. 2

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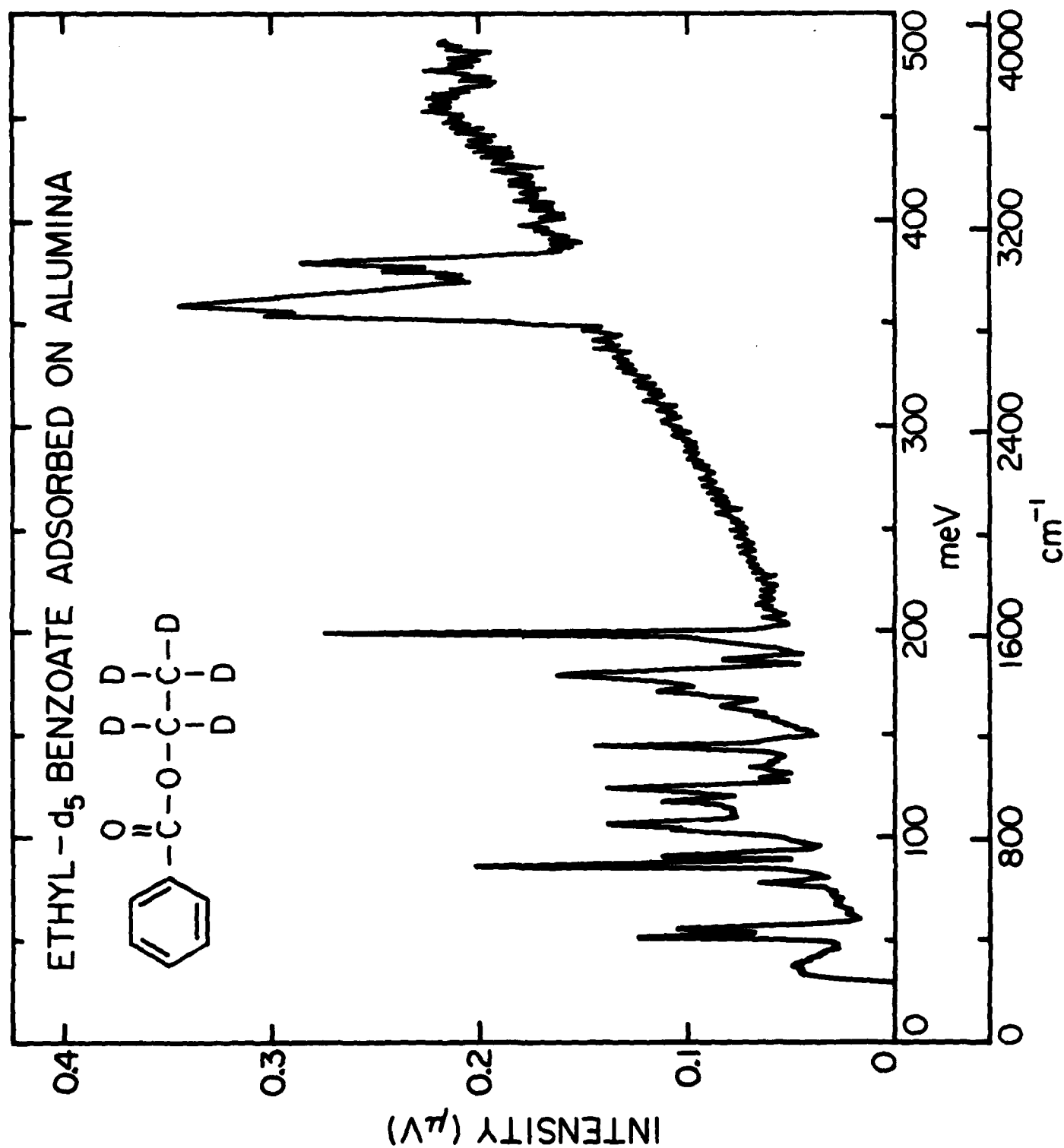


Fig. 3
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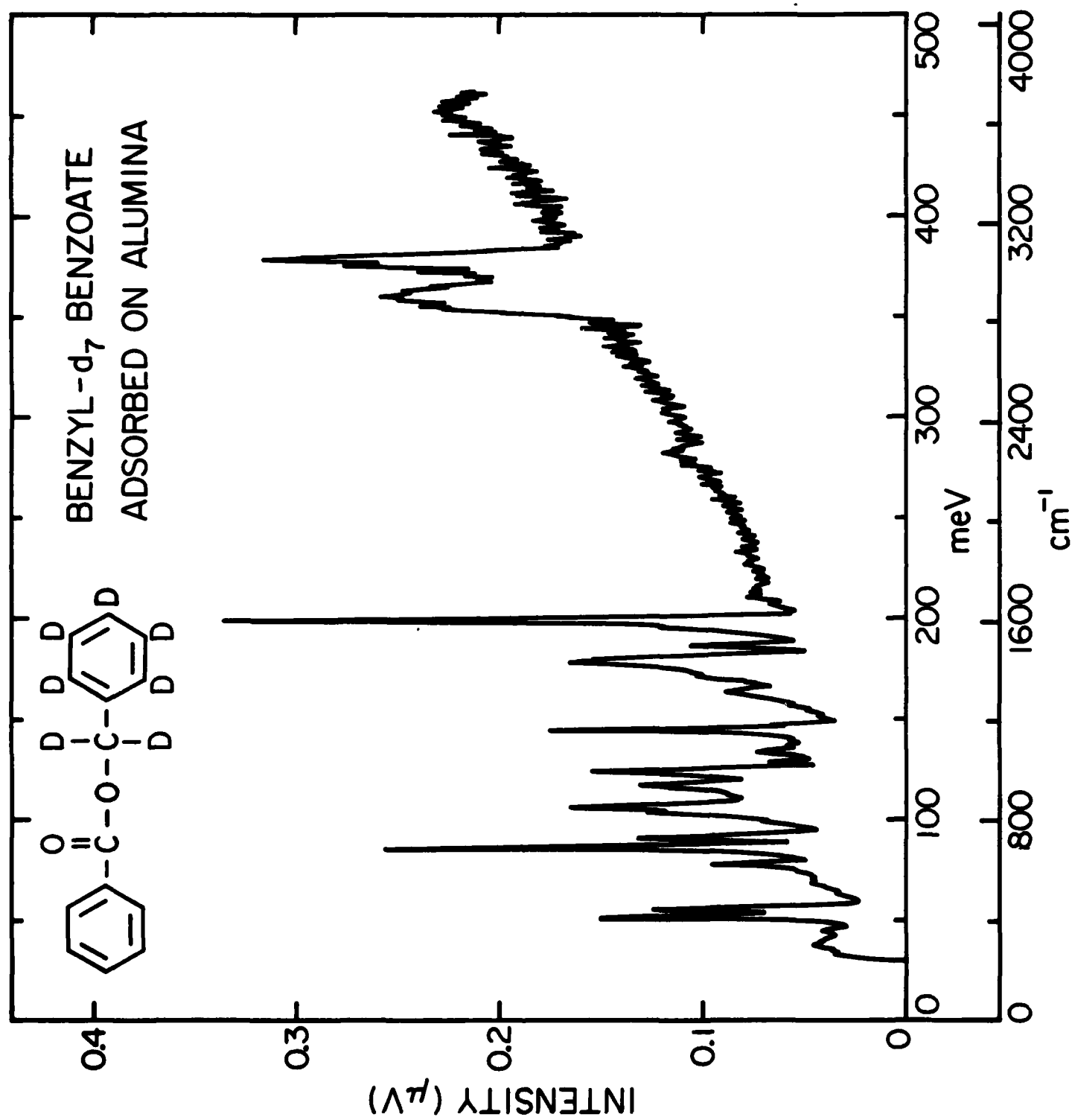


Fig. 4

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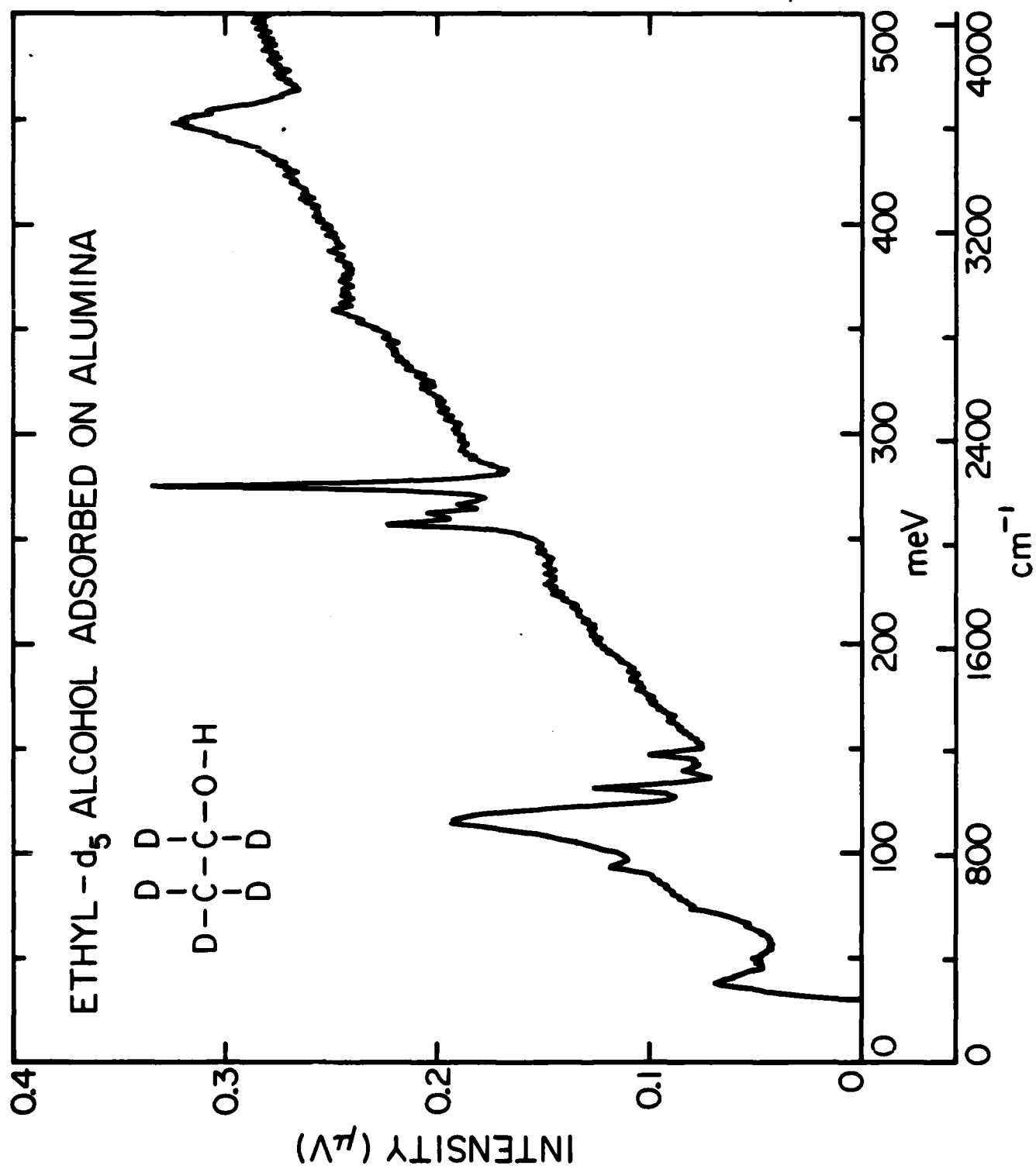


Fig. 5
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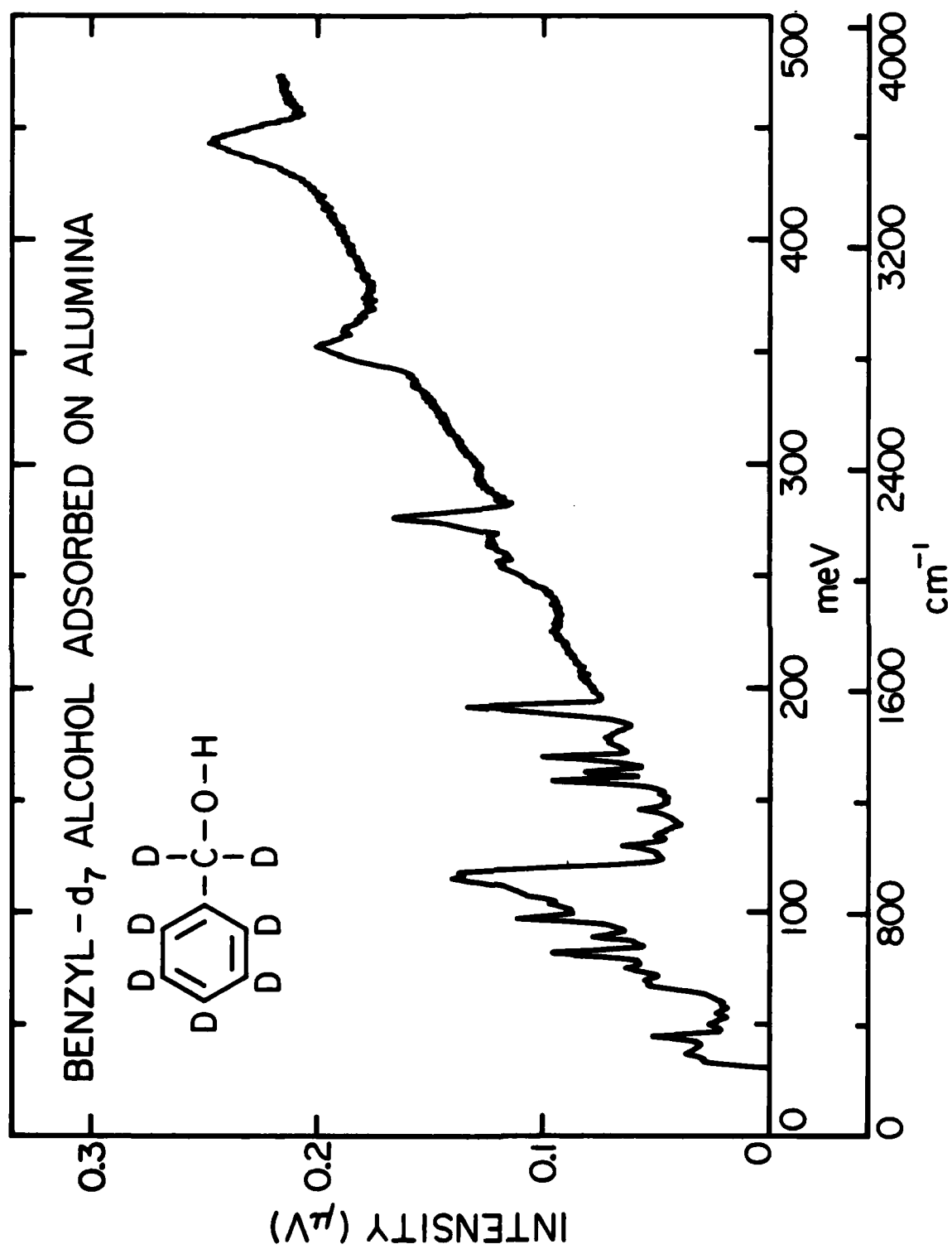


Fig. 6

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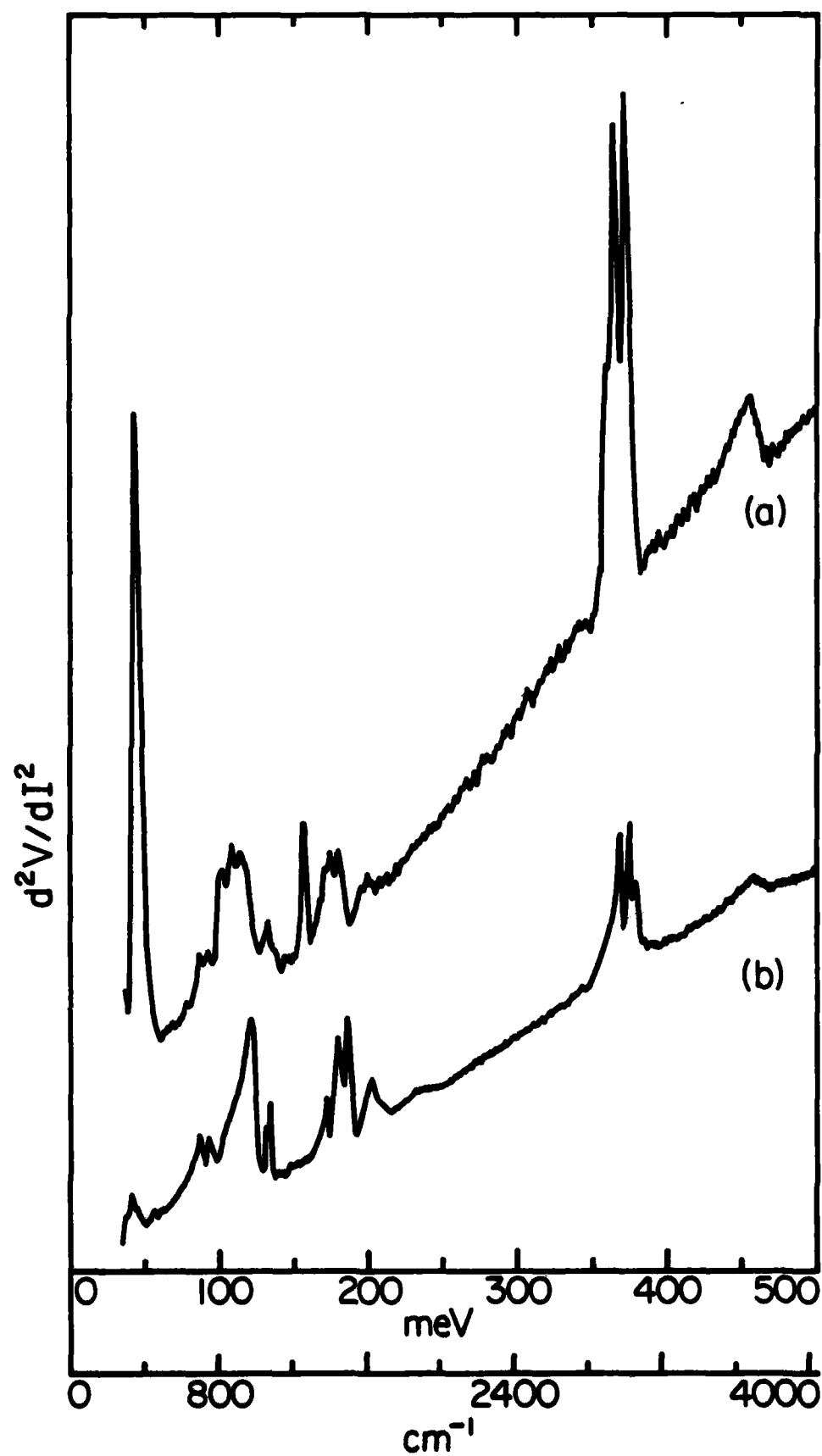


Fig. 7

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