tion of the center in the longitude of Europa;

3) The coefficient of the free oscillation in the longitude of Ganymede, whose argument is $l_3 - \varpi_4$ (the mean longitude of Ganymede referred to the proper apse of Callisto);

4) The daily motion of the proper apse of Callisto; and

5) The daily motion of the proper node of Europa.

The results of such calculations and the values of these quantities derived by Sampson and De Sitter from the observations are shown in Table 2.

The most striking features of Tables 1 and 2 are the very small value found by Sampson for the mass of Callisto and the large difference between the observed and calculated values of item 3. These two facts are correlated in the sense that item 3 is the datum most directly related to the mass of Callisto.

In order to discuss these discrepancies, new values were calculated for items 3 and 4 through a rehandling of Sampson's theory. The modifications lead to a set of equations involving the coefficients of the free oscillations in the longitude of Ganymede, e_4, e_4', e_4'', and e_4''' (Sampson's notation) and the motion of the proper apse of Callisto. The calculation closely follows Sampson's work (including libration), except that the iteration is not made over the values of e_4, e_4', e_4'', and e_4''', but over $\dot{\varpi}_4$ only. Solving the equations with respect to e_4''' (eccentricity of Callisto), the results obtained are in the neighborhood of the actual values given by

$$e_4''' = \frac{0.007373 + 1.2872H}{1 - 1.013 \times 10^6 H}$$

where

$$H = (\dot{\varpi}_4 - 6.5897 \text{ arc sec})/3600$$

For the values of the eccentricity of Callisto derived from the observations by Sampson and De Sitter, namely 0.0073725 and 0.007362, it follows very closely (by reason of the asymptotic behavior of the solution), that $\dot{\varpi}_4 = 6.5897$ arc sec (per day). If this value is adopted, item 3 will be given by

$$2e_4'' = 318 + 4.25 \times 10^4(e_4''' - 0.007373)$$

in arc seconds. If the observed value for the eccentricity is accepted, we have the new value 318 arc sec for item 3. This value is almost the same as that already obtained directly from Sampson's formulas, notwithstanding the slow convergence of the iterative procedure used by Sampson. The dependence of item 3 with respect to the full set of masses has also been computed. In the neighborhood of the actual masses we have

$$\Delta(3) = 4\Delta m_1 + 17\Delta m_2 + 7\Delta m_3 + 49\Delta m_4 \text{ arc sec}$$

where the unity of mass is 10^{-5} of the mass of Jupiter.

From these results it follows that it is not possible to fit the JPL system of masses and the observed values of e_4'' with Sampson's theory. This conclusion may be extended to theories of the same order as Sampson's theory, since the computation of item 3 through Laplace's theory leads to almost the same value (319 arc sec).

Table 2. Computed values, based on Sampson's theory and the JPL system of physical parameters, compared to classical determinations from the observations. The numbers in column 1 refer to the list of quantities in the text.

Item	Value (arc sec)		
	Computed	Sampson (*2*)	De Sitter (*3*)
1	1720	1697.5	1676 ± 7
2	3650	3852.6	3850 ± 10
3	321	265.6	277 ± 26
4	6.59	6.692	6.31 ± 0.1
5	−117.5	−116.9	−117.4 ± 0.2

Future research must decide on three alternatives: (i) the values of e_4'' obtained in different ways by Sampson and De Sitter are too small; (ii) the value of m_4 obtained at JPL from the paths of Pioneer 10 and Pioneer 11 is too high; or (iii) it is not possible to fit e_4'' and m_4 through a theory of the same order as that of Sampson.

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Vibrational Spectroscopy of Chemisorbed Fatty Acids with Inelastic Electron Tunneling

Abstract. *We have measured and assigned the inelastic tunneling spectra of hexanoic acid chemisorbed onto an oxidized aluminum film. We present evidence for gauche-trans as well as all-trans conformers in the monolayer and evidence in support of a recent theory of tunneling intensities.*

Recently there has developed great interest in the relation between the microscopic structure and macroscopic properties of noncrystalline but macroscopically ordered organic systems such as liquid crystals, thin films, and biological membranes. Many techniques have been used to investigate the microscopic positional, orientational, and conformational order of these systems, and numerous theories relate such properties to macroscopic ones (*1*). A major limitation of experimental studies to date is their use of macroscopic samples. A new technique, inelastic electron tunneling spectroscopy (IETS) can measure the vibrational spectrum of monolayer, and even submonolayer, coverage of organic molecules on the oxide of a metal-oxide-metal junction (*2*).

Both infrared- and Raman-active vibrational modes can be observed in IETS with a resolution on the order of 10 cm^{-1} at a temperature of 1°K over the spectral range 300 to 4000 cm^{-1}. A vibrational mode of frequency ν is observed as a peak in the second derivative of the voltage with respect to the current, d^2V/dI^2, at a voltage $V = (h/e)\nu$ (h is Planck's constant and e is the electron charge). The effect of the top metal electrode on the measured vibrational frequencies was less than ½ percent for vibrations below 1600 cm^{-1} in a sensitive experiment (*3*).

Our crossed-film tunnel junctions (Al-oxide-Pb) were fabricated in a clean, high-vacuum evaporator. They were liquid-doped with a solution of the desired acid by general procedures described in detail elsewhere (*2*). In outline, a thermally oxidized Al strip (0.2 mm wide, 1000 Å thick) on a glass slide was doped with a dilute solution of the acid (*4*) in either benzene or methanol (the concentration was not critical, but on the order of 1 : 1000). After any excess solution had been spun off, the slide was returned to a high-vacuum evaporator where five Pb strips (0.2 mm wide, 2000 Å thick) were evaporated across the doped, oxidized Al strip.

The completed junctions were tested

with a low-power ohmmeter. Undoped junctions had resistances in the range 2 to 5 ohms. Acceptable doped junctions had resistances in the range 50 to 1000 ohms. Electrical connections were made to acceptable junctions with small screw clamps. The junctions were then immersed in liquid helium and tested to insure that all the current flow was due to electron tunneling. Finally, tunneling spectra, d^2V/dI^2 as a function of V, were plotted by applying an a-c modulation current at a frequency of 1120 hertz and measuring the voltage at the second harmonic frequency with a lock-in amplifier.

Figure 1 shows two tunneling spectra of two preparations of hexanoic acid (caproic acid) doped onto aluminum oxide from methanol solution from 240 to 1800 cm^{-1}. Above this range lie only the CH stretching modes, which we have not tried to assign. Below this range modes of the Pb top electrode obscure the spectrum of the organic layer. Comparison of the two spectra shows the excellent reproducibility of the major vibrational peaks and the difference between some of the small peaks indicated by the arrows.

There are no systematic changes in the spectra when the sample is applied from benzene rather than methanol solution. Table 1 compares the vibrational frequencies from the infrared (IR) and Raman spectra of potassium hexanoate with the IETS frequencies of hexanoic acid. The tunneling spectra of octanoic (caprylic) and tetradecanoic (myristic) acids were also taken. The analysis of these more complex spectra shows qualitative agreement with the results for hexanoic acid and will be reported elsewhere.

None of the tunneling spectra showed the IR and Raman bands of the solvent used to apply the sample. An approximate assignment of each vibrational mode of potassium hexanoate observed in the IR and Raman between 300 and 1800 cm^{-1} is made by comparison with the salts $\mathrm{CH_3\text{-}(CH_2)_{\mathit{n}}\text{-}COO^{-}K^{+}}$ (n = 6, 12, or 16). Modes appearing at the same frequency in all the salts are assigned to "end group" vibrations, those near frequencies observed in n-alkanes to the methyl end, the others to the carboxylate end. The "chain vibrations" are assigned so as to consistently fit the dispersion curves of the series. The vibrations of the crystalline all-trans chain are labeled by their k-values, indicating that the vibrations of adjacent methylene groups in a chain with free ends and N groups are out of phase by approximately $k\pi/(N + 1)$ (*5*). Table 1 shows that the tunneling spectra of hexanoic acid are similar to the IR and Raman spectra of potassium hexanoate, and thus that hexanoic acid is present as the hexanoate anion, as might be expected from IETS studies of other organic acids (*6*). The tunneling spectra do not show the characteristic carboxylic acid stretching bands near 1200 and 1700 cm^{-1}, but do have a band near 1580 cm^{-1}, which is close to the symmetric stretching frequency of the hexanoate anion. The antisymmetric stretching mode probably contributes to the strong peak in the tunneling spectra at 1430 cm^{-1}. Infrared spectra of the acid salts with different cations show different carboxylate bands (*6*) but the tunneling spectra show bands that do not quite match any of the salt spectra. The lack of peaks characteristic of the free carboxylic acids in the tunneling spectra shows that the spectra obtained are of a monolayer or less of molecules with all the molecules bound to the alumina (*7*).

The bands that appear in the tunneling spectra follow selection rules different from those in either the IR or the Raman spectra. For example, the methylene wags are strong and the methylene twists are weak in the IR spectrum, but the two

Table 1. Vibrational frequencies from the IR and Raman spectra of potassium hexanoate and the tunneling spectra of hexanoic acid. The Raman spectrum is for polycrystalline potassium hexanoate, the IR spectrum for potassium hexanoate in KBr pellets, and the tunneling spectra for hexanoic acid from methanol solution. The assignment notation is from (*5*): IPB, in-plane C-C-C bend; P, rock; ω, wag; R, C-C stretch; T, twist; δ, scissors; ast, asymmetric stretch; and sst, symmetric stretch. The relative intensities (given in parentheses) are denoted: s, strong; vs, very strong; m, medium; w, weak; vw, very weak; vvw, very very weak; and sh, shoulder.

Frequency (cm^{-1})			Assignment
Raman	Infrared	Tunneling	
		300 (s)	
330 (s)		340 (w)	IPB-1
420 (w)		400 (s)	IPB-3
		480 (w)	
	527 (m)*		CO_2-P
590 (vw)	578 (w)*	590 (m)	CO_2-ω
		630 (m)	
	693 (m)*	700 (m)	CO_2-δ
	725 (vs)		P-1
		738 (m)	
754,762 (w, w)	760 (m)	765 (sh)	P-2
	806 (vw)	780,800,810 (w,w,w)	
825 (vw)			
846,860 (w, w)	846,860 (m,w)	846,860 (s,s)	P-3
880,888 (sh,m)	886,895 (w,sh)	880,895 (sh,s)	CH_3-P
905 (w)			
922,928 (sh,s)	911,917,928 (sh,sh,m)	918,926 (s,sh)	
953,965,975,985 (vw,vw, vvw,vvw)	962,975,980 (w,m,sh)	945,963,990 (sh,s,sh)	P-4
1000 (vvw)	997 (sh)		
1013 (vw)	1010 (vw)	1008 (m)	
1034 (w)	1042 (w)	1032,1042 (m,m)	R-4
1052 (w)	1054 (sh)		R-5
1070 (m)	1070 (vvw)	1073 (s)	R-3
1110 (w)	1092,1097,1109 (sh,sh,m)	1113 (vs)	R-2
1125 (s)			R-1
1139 (vw)	1132 (sh)		
1150 (vw)	1145,1155,1167 (sh,m,m)		
		1174 (s)	
1209 (vw)	1185,1205 (w,sh)	1190,1200 (m,sh)	T-4
	1223,1232 (vs,sh)	1218,1230 (s,sh)	ω-1
1255 (w)	1250,1265 (sh,w)	1252,1264 (sh,s)	T-3
1277 (vw)	1275 (w)		
1289 (m)	1290 (s)	1285 (m)	ω-2
1298 (m)	1307 (w)	1307 (m)	T-1,T-2
1325 (vw)		1325 (w)	
1338 (vw)	1335,1343,1350 (w,s,sh)	1340 (m)	ω-3
1364,1379 (vw,w)	1374,1384 (sh,w)	1355,1367,1380 (sh,s,sh)	ω-4
1406 (sh)	1400 (sh)	1405 (sh)	α-$CH_2\delta$
1412 (m)	1411 (s)		CH_3 bend
1430 (m)	1430 (m)	1430 (s)	CO_2-ast
1442 (m)	1438 (w)		CH_2-δ
1454 (m)	1450 (sh)	1455 sh	CH_3-δ
1466 (w)	1460,1472 (m,m)		CH_2-δ
		1545 (sh)	
	1565 (s)	1580,1596 (m,m)	CO_2-sst
		1610 (sh)	

*From (*10*).

sets of modes are of comparable intensity in the tunneling spectra. Furthermore, in the IR and Raman spectra the intensities of the bands characterized by different k-values decrease as k increases, while in the tunneling spectra all the bands due to a particular set of modes are of comparable intensity. This observation is explained by a theory of the tunneling spectra (*8*), which attributes the tunneling intensities to the interaction of the molecules with electrons which have short wavelengths, making the intensities almost independent of k.

The close correspondence between the frequencies of the strong features of the tunneling spectra and the frequencies of the IR and Raman spectra of the solid hexanoates shows that in much of the monolayer, the carbon chains of the hexanoate are in the extended all-trans conformation. Furthermore, some of the chain modes appear split in the tunneling spectra, for example, 945-963-990, 1218-1230, and 1325-1340 cm^{-1}, corresponding to doublets that appear in the IR and Raman spectra. These doublets are due to intermolecular interactions in the solid salts, and their appearance in the tunneling spectra suggests that the all-trans molecules occur in ordered regions with intermolecular interactions like those of the crystal. However, there are some bands in the tunneling spectra which cannot be assigned to the vibrations of the all-trans molecules. The bands at 300, 735, 775, 835, and 1174 cm^{-1}, for example, are not found in the IR or the Raman spectrum of potassium hexanoate and often differ among tunneling spectra for identically prepared samples, as indicated by the arrows in Fig. 1. These frequencies are not near those of the end groups and so are probably not due to the perturbation of the vibrational modes by the electrodes. They are frequencies at which molecules with gauche conformations should have modes (*9*), and therefore we conclude that the monolayers observed contain some molecules with gauche conformations and to this extent at least are disordered. The presence of molecules with different conformations may also account for some of the intensity differences between bands in the tunneling spectra and bands in the IR and Raman spectra of the solid salts.

Finally, one other feature of the tunneling spectra is that the low-frequency chain deformations appear at a lower frequency than those in potassium hexanoate. This shift is expected if the ends of the molecules in the tunneling junction are more constrained than they are in the crystal.

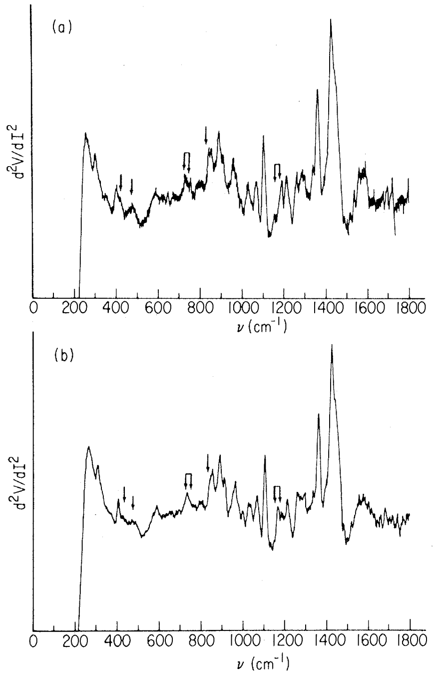

Fig. 1. Inelastic tunneling spectra of two different preparations of hexanoic acid. The spectra show d^2V/dI^2 plotted against voltage, with the voltage scale converted to energy units in wave numbers. Most of the features of the two spectra are identical; the arrows indicate regions where there are differences.

In summary, we have measured and assigned, to the best of our knowledge for the first time, the vibrational spectrum of monolayer chemisorbed fatty acids. The appearance of series of peaks associated with both gauche and trans conformations supports the conclusion that these films are disordered, although they may contain ordered regions of all-trans molecules interacting as in the solid. The different regions may arise as a result of the geometry of the bonding sites on the alumina support. In agreement with recent theoretical work (*8*), the various vibrational modes, such as the twists and wags, are all present with comparable intensity in the tunneling spectrum, regardless of their activity in optical vibrational spectra.

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Methylation of Selenium in the Aquatic Environment

Abstract. *Conversion of inorganic and organic selenium compounds to volatile selenium compounds (dimethyl selenide, dimethyl diselenide, and an unknown compound) by microorganisms in lake sediment has been observed. This conversion could also be effected by pure cultures of bacteria and fungi. Such transformations are significant in the transportation and cycling of elements in the environment.*

Selenium and its compounds have long been recognized as inorganic carcinogens of concern in the spectrum of identified environmental pollutants, based on observations of proved toxic effects and relative accessibility (*1, 2*). Movement of toxic elements through the geocycle and their biological methylation in the environment to volatile products of extreme toxicity further complicates the problem (*3, 4*). It is known that methylation of certain heavy metals, such as Hg (*4*), As (*5, 6*), Sn (*7*), and Pb (*8, 9*), can yield compounds that are more toxic to higher organisms. Apart from the observation that $(CH_3)_2Se$ was produced when sodium selenite was mixed with municipal sewage (*5*), sufficient information on the methylation of selenium in the aquatic environment is not available.

It is known that volatile selenium compounds are produced through methylation by various organisms. For instance, fungi of several genera produce $(CH_3)_2Se$ from inorganic selenium compounds (*10–12*). As well, rats fed with selenite and selenate exhaled a volatile selenium compound identified as $(CH_3)_2Se$ (*13, 14*). Other studies, conducted with higher plants, identify $(CH_3)_2Se$ as the single