

THE SYNTHESIS OF AMINO ACIDS AND SUGARS ON AN INORGANIC TEMPLATE FROM CONSTITUENTS OF THE PREBIOTIC ATMOSPHERE

B. O. FIELD and J. E. D. SPENCER

The Inorganic Chemistry Laboratory, The City University, Northampton Square, London EC1V 0HB, U.K.

(Received July 24, 1989)

Abstract. Inelastic Electron Tunnelling Spectroscopy (IETS) has been used to identify the reaction products present on an alumina surface when it is exposed to likely components of the earth's prebiotic atmosphere. The alumina barrier of Al-AIO_x-Pb tunnelling junctions have been exposed to water; aqueous ammonia; wet carbon monoxide gas and to aqueous formaldehyde vapour under normal atmospheric conditions at room temperature. The water spectrum shows strong coincidence with that of a genuine sample of formic acid. It is proposed that atmospheric CO₂ is involved in this surface catalyzed reaction. The aqueous ammonia spectrum is assigned as an amino acid species produced from ammonia, water and atmospheric carbon dioxide. This spectrum compares very closely with the tunnelling spectrum of a genuine sample of glycine. The wet carbon monoxide spectrum and the aqueous formaldehyde spectrum have been produced by an infusion doping process. These spectra of CO and aqueous formaldehyde are assigned as a sugar like polymer or a sugar formed on the alumina surface. A tunnelling spectrum of D(-) fructose has been produced to aid this assignment. The role of an inorganic template such as alumina in the original prebiotic synthesis of amino acids and sugars is considered.

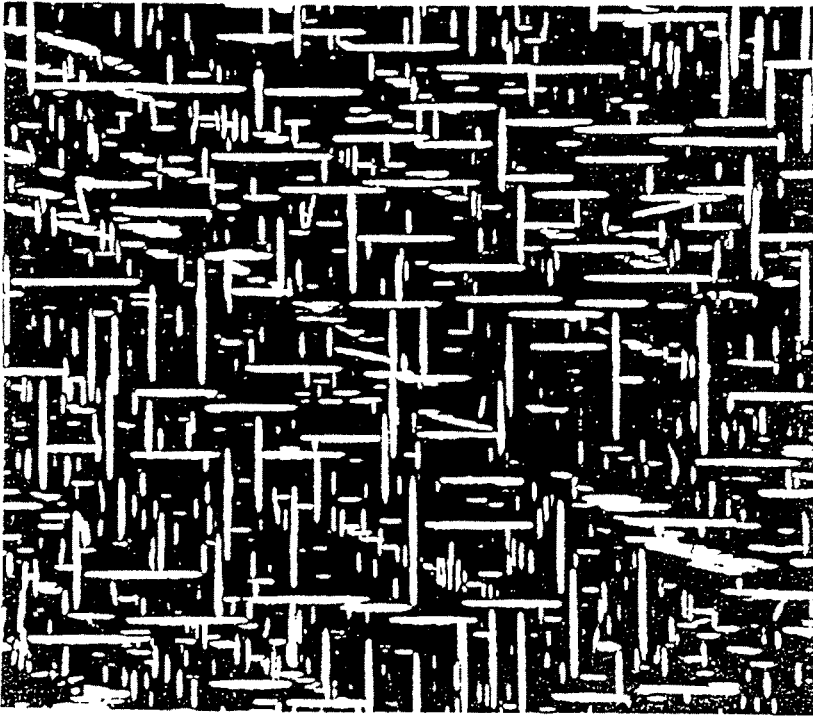
1. Introduction

In 1951, the crystallographer J. D. Bernal (1951) suggested that molecular asymmetry in biologically important molecules may have arisen from the use of an inorganic template such as L- or D-quartz in their original prebiotic synthesis. Graham Cairns-Smith (1975) has more recently taken up and extended this concept by proposing that mineral surface forces were not only the first self-replicating system but that these forces also played a significant role in biogenesis.

Other workers (Gibbs *et al.*, 1980; Lazard *et al.*, 1987, 1988) have considered the template directed synthesis and adsorption onto mineral surfaces of biologically important molecules, already at an advanced state of molecular complexity. The present work provides the first experimental evidence to indicate that both amino acids and sugars could have been produced on mineral surfaces from likely components of the earth's prebiotic environment.

Surface forces may be demonstrated by their orientational effect in epitaxial overgrowths. Figure 1 illustrates the vapour phase deposition of anthraquinone on sodium chloride. The well defined specific growth pattern is clearly visible and the orientational range extends further than 400 Å from the sodium chloride surface (Darling and Field, 1973).

An extensive review of the chemical applications of IETS and the experimental procedures involved has recently been published (Lewis *et al.*, 1988). IETS is a



Photographed under polarised light
 Vacuum sublimation : 10^{-3} torr
 Magnification : $\times 150$
 Temp. conditions : $70/30^{\circ}\text{C}$
 Sublimation time : 5 mins

Fig. 1. Anthraquinone on Sodium Chloride.

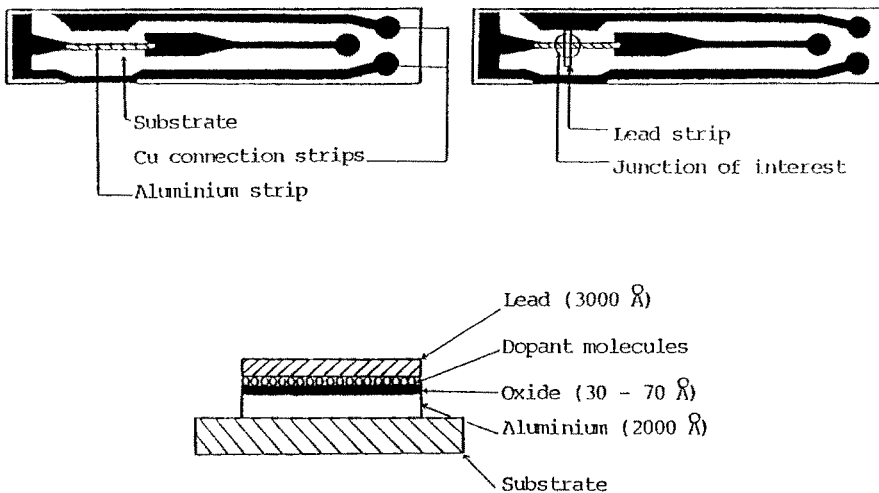


Fig. 2. The Geometry of a Tunnel Junction.

powerful surface analytical technique and the essential features are outlined below.

The catalytic, alumina surface is incorporated into an Al-AlO_x-Pb tunnel junction as shown in Figure 2. The surface is doped in this case at room temperature and pressure with the molecules under study by exposure to the reactants either in gas phase or solution. Surface physisorbed species are subsequently removed by evacuation to 10^{-5} τ before the upper lead electrode is deposited. The current-

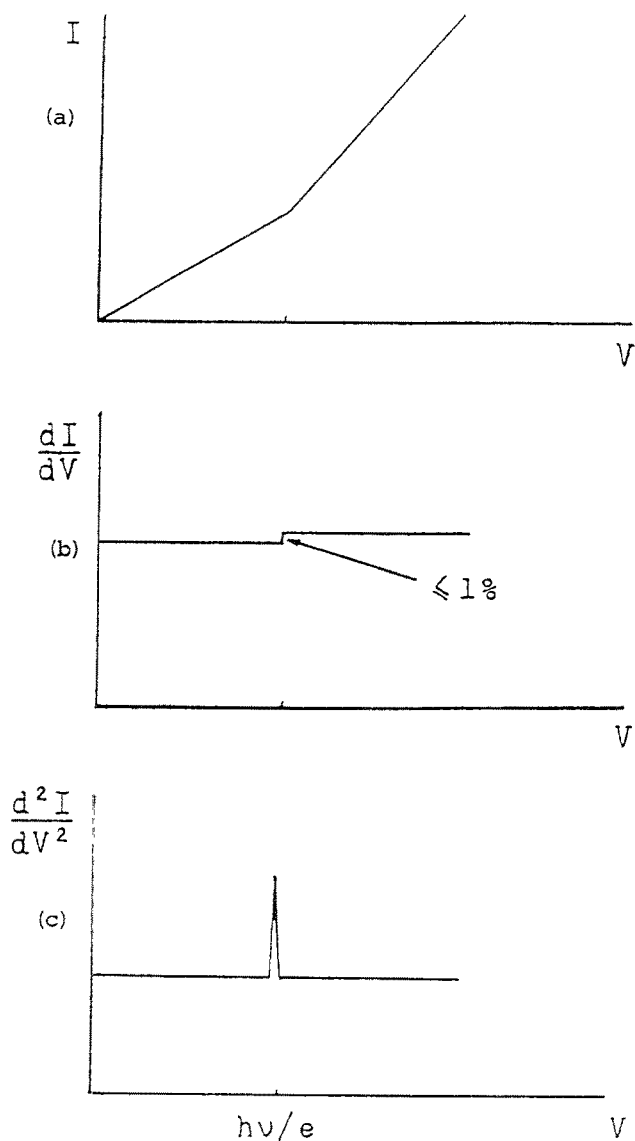


Fig. 3. The Current/Voltage Curve and its Derivatives for the Tunnelling Process.

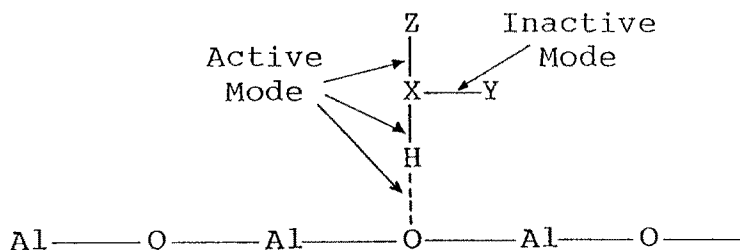


Fig. 4. The Selection Rule.

voltage characteristics of the doped junction are then measured by applying a sweeping D.C. bias across the junction. The change in the slope of the current-voltage plot is due to the onset of inelastic electron tunnelling (see Figure 3a). To optimise the sensitivity and to produce a recognizable spectral response the electronics are arranged to produce the second derivative plot shown in Figure 3c. The tunnelling electron interacts with both Raman and infrared active vibrational modes of the adsorbed molecules and the only selection rule operating is an orientational one. The bonds of the adsorbed molecule that are perpendicular to the oxide surface show a maximum response to the tunnelling electron. Those bonds that are parallel to the surface show a minimal response, as indicated in Figure 4. So by analysis of the IET spectrum both the chemical composition of the adsorbate and its surface orientation can be determined. The spectra are produced with the junction at a temperature of 4.2 K to maximise the electronic response. The technique is highly sensitive, less than a monolayer coverage on the alumina surface will produce a well defined spectrum.

Experimental Results and Discussion

All the reactions involving CO_2 have been carried out both in sealed systems in the absence of air, with the alumina surface only exposed to the reactants concerned and in air utilizing atmospheric carbon dioxide with identical spectroscopic results. We are therefore confident that the surface reactions discussed do not involve atmospheric oxygen or any pollutants.

WATER AND FORMIC ACID DOPED JUNCTIONS

In Figure 5, the top plot represents the IET spectrum of pure water alone, doped in the total absence of air (Jaklevic and Gaertner, 1977). The only peaks present represent the Al-O and O-H stretching interactions. Figure 6 shows the IET spectrum of triply distilled water vapour doped in the presence of atmospheric carbon dioxide gas. Table I indicates the proposed spectral assignment of Figure 6. The predominant peak, at 3041 cm^{-1} , is interpreted as C-H stretching modes. The CO_2^- symmetric stretch and C-H bending interactions are also clearly seen. This spectrum coincides

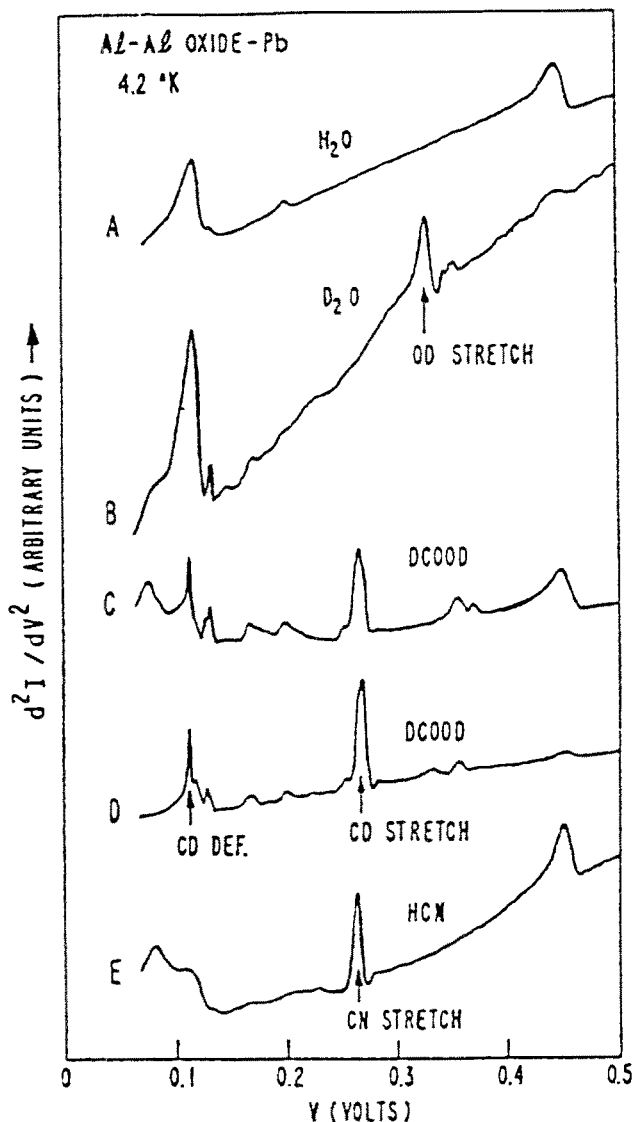


Fig. 5. Top Plot, IET Spectrum of Pure Water in the Absence of Air (Jaklevic and Gaertner, 1977).

closely with that of a genuine formic acid IET spectrum shown in Figure 7. Table II shows the spectral assignment of Figure 7. Spectral differences would be expected since in one case (formic acid) we are considering a pre-formed surface adsorbed species but in the case of water doped in the presence of atmospheric CO_2 , surface catalyzed reactions are proposed resulting in a variety of surface adsorbed species. This would account for the observed reduction in spectral resolution of the water doped junction. But we are unable to explain the presence of strong C-H vibrational modes without invoking surface catalytic reactions involving atmospheric carbon

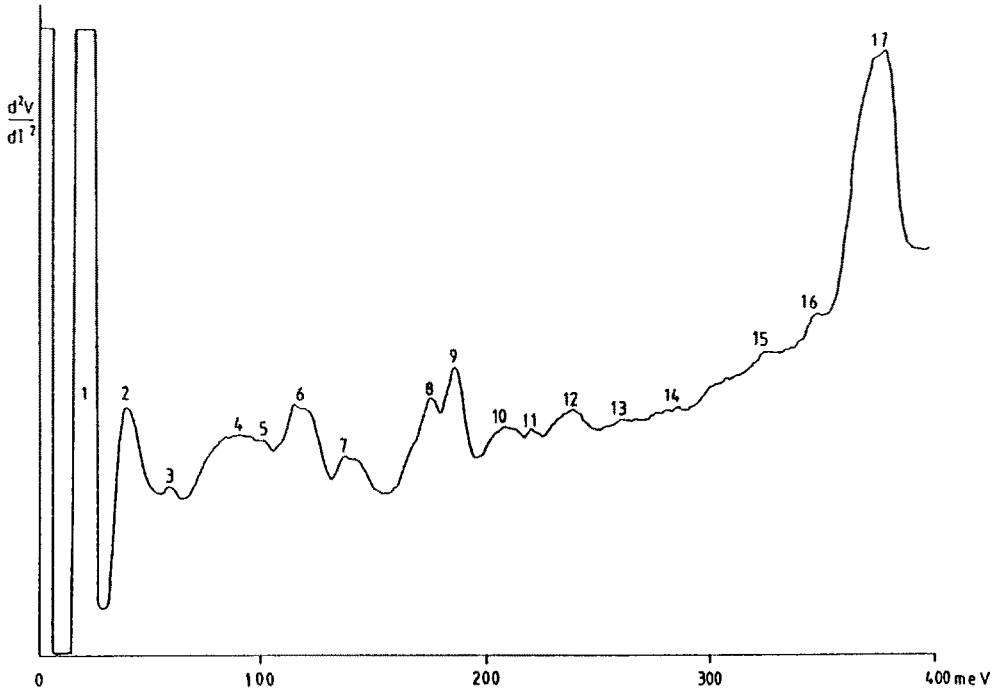
Fig. 6. IET Spectrum of Water (with Atmospheric CO₂).

TABLE I

Peak assignment of the IET spectrum of triply distilled water vapour doped onto an Al-AlO_x-Pb junction

Peak	Peak position		Description	Assignment
	(meV)	(cm ⁻¹)		
1	21	169	S	Transverse Al phonon
2	39	315	S	Longitudinal Al phonon
3	59	476	W	
4	92	742	S	
5	102	823	W	CO ₂ scissoring mode
6	119	960	S	Aluminium oxide stretch
7	133	1073	M	CH out-of-plane bend
8	176	1420	S	
9	187	1509	S	CH in-plane bend
10	210	1694	M	CO ₂ symmetric stretch
11	220	1774	W	CO ₂ asymmetric stretch
12	240	1936	M	
13	262	2114	W	
14	284	2291	W	
15	327	2638	W	
16	349	2815	W	
17	377	3041	S	CH stretch

S = strong, M = medium, W = weak, Sh = shoulder.

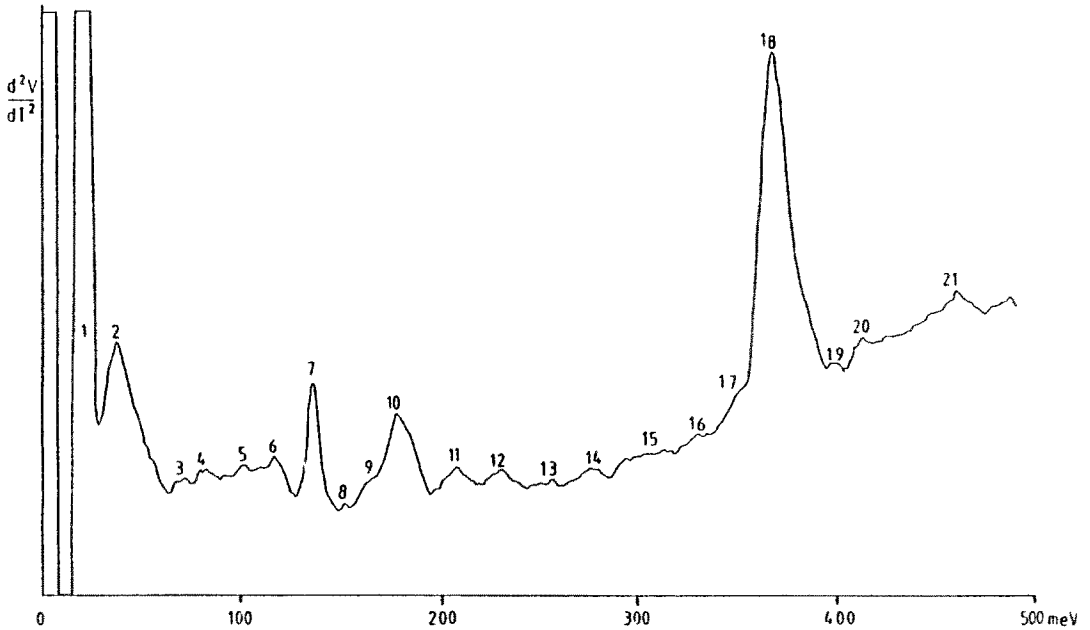


Fig. 7. IET Spectrum of Formic Acid.

TABLE II

Peak assignment of the IET spectrum of an Al-AlO_x-Pb junction vapour doped with formic acid

Peak	Peak position		Description	Assignment
	(meV)	(cm ⁻¹)		
1	22	177	S	Transverse Al phonon
2	38	307	S	Longitudinal Al phonon
3	72	581	W	
4	82	661	W	
5	101	815	W	CO ₂ scissoring mode
6	117	944	M	Aluminium oxide stretch
7	137	1105	S	CH out-of-plane bending mode
8	153	1234	W	OH bend
9	164	1323	Sh	CH in-plane bending mode
10	178	1436	S	CO ₂ symmetric stretch
11	209	1686	M	
12	230	1855	M	
13	257	2073	W	
14	276	2226	W	
15	307	2447	W	
16	332	2678	W	
17	350	2823	Sh	
18	368	2969	S	CH stretch
19	400	3227	W	
20	414	3340	W	
21	461	3719	M	

S = strong, M = medium, W = weak, Sh = shoulder.

dioxide. Organic impurities were not detected by high resolution gas chromatography/mass spectroscopic analysis of the water used in this experiment (Field *et al.*, 1985). This paper also shows that by penetration doping a tunnel junction with a solution of CaO in water, no formic acid or any other organic species could be detected but peaks due to CaCO_3 were assigned. Hence the importance of atmospheric CO_2 and the absence of organic contaminants was demonstrated. Other evidence against atmospheric contamination of the surface, other than by water and carbon dioxide, is also contained in this communication since an alumina tunnel junction surface exposed to laboratory air for 300 times longer than the normal doping period was shown to produce a spectrum of formic acid only.

AMMONIA AND GLYCINE DOPED JUNCTIONS

The tunnelling spectrum of pure ammonia doped in the absence of air is shown in Figure 8 (Shklyarevskii *et al.*, 1978). As expected, all that is observed together with the Al-O interactions are N-H vibrational modes. Figure 9 shows the IET spectrum of wet ammonia gas vapour doped in the presence of atmospheric CO_2 . Table III shows the spectral assignment. Of particular importance for our assignment of this as an amino acid is the C-N stretching mode at 973 cm^{-1} . The spectrum

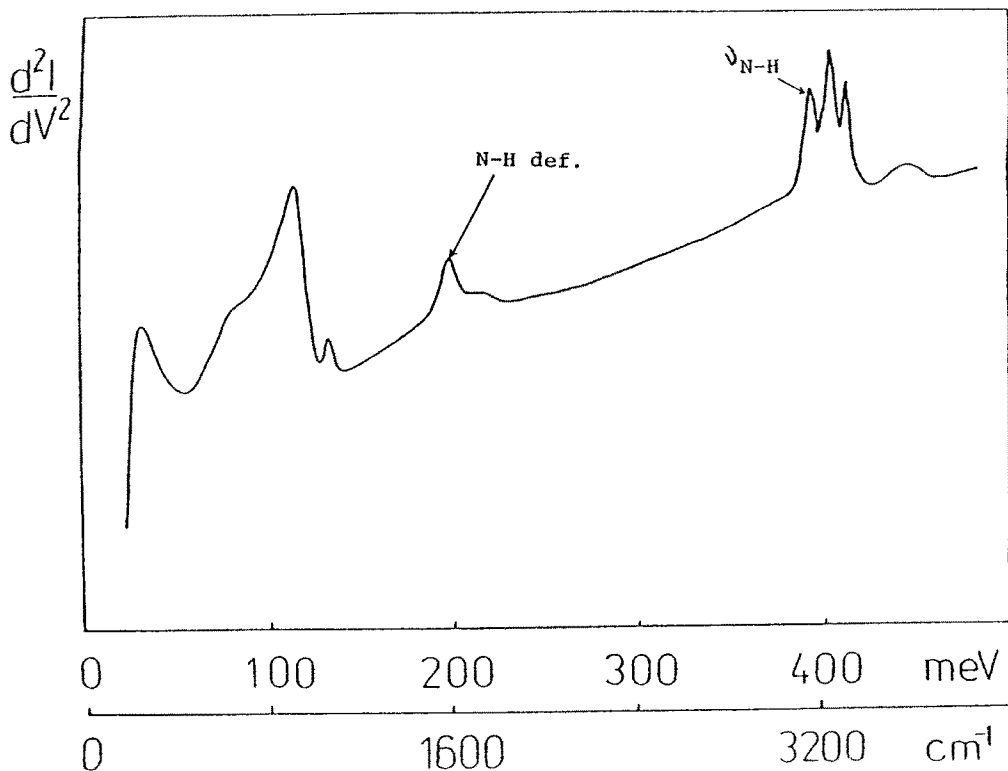


Fig. 8. IET Spectrum of Ammonia Gas Doped *in situ* (Shklyarevskii *et al.*, 1978).

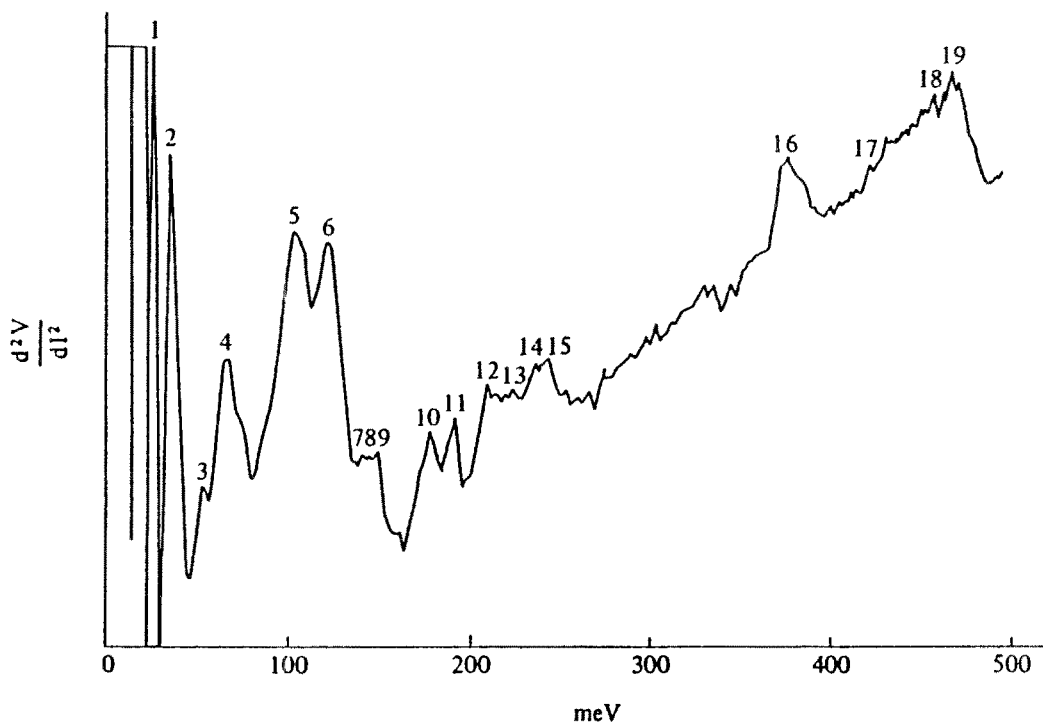
Fig. 9. IET Spectrum of Aqueous Ammonia (with Atmospheric CO₂).

TABLE III

Spectral assignment of a wet ammonia gas doped junction

Peak No.	Energy (meV) ^a	Wavenumber (cm ⁻¹)	Assignment
1	28	224	Trans. AlO _x phonon
2	36	293	Long. AlO _x phonon
3	54	438	CO ₂ ⁻ rock
4	66	536	NH ₃ ⁺ tor.
5	102	823	C-C str.
6	121	973	C-N str.
7	139	1124	NH ₃ ⁺ rock
8	142	1153	NH ₃ ⁺ def.
9	147	1193	C-O str.
10	177	1428	C-H def./CO ₂ ⁻ sym. str.
11	191	1538	CO ₂ ⁻ asym. str./CH ₂ scissor
12	209	1688	N-H def.
13	224	1803	
14	236	1901	
15	243	1959	
16	375	3024	C-H str.
17	421	3399	N-H str.
18	461	3721	O-H str.
19	469	3785	O-H str.

^a 1 meV = 8.065 cm⁻¹.

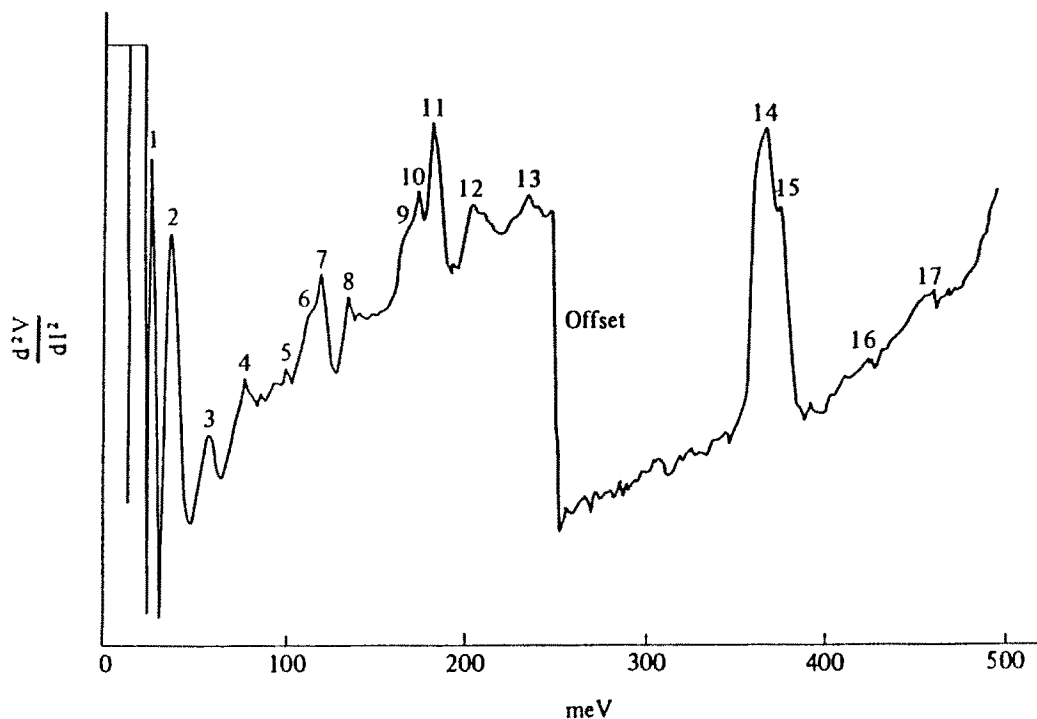


Fig. 10. IET Spectrum of Glycine.

TABLE IV

Spectral assignment of the IET spectrum of a saturated solution of glycine spin doped onto a junction

Peak No.	Energy (meV) ^a	Wavenumber (cm ⁻¹)	Assignment
1	26	212	Trans. AlO _x phonon
2	39	315	Long. AlO _x phonon/-CCN bend
3	59	475	CO ₂ ⁻ rock
4	78	630	CO ₂ ⁻ def.
5	102	825	C-C str. Reduced in energy due to CO ₂ ⁻ on surface.
6	116	934	C-C str.
7	121	974	C-N asym. str.
8	136	1100	NH ₃ ⁺ rock
9	169	1363	CO ₂ ⁻ sym. str./>CH ₂ def.
10	177	1426	>CH ₂ def./CO ₂ ⁻ sym. str.
11	185	1489	>CH ₂ def./CO ₂ ⁻ str.
12	206	1661	NH ₃ ⁺ def.
13	237	1913	Seen also in Figure 9
14	368	2967	C-H str.
15	376	3036	C-H str.
16	425	3431	N-H str.
17	448	3614	O-H str.

^a 1 meV = 8.065 cm⁻¹.

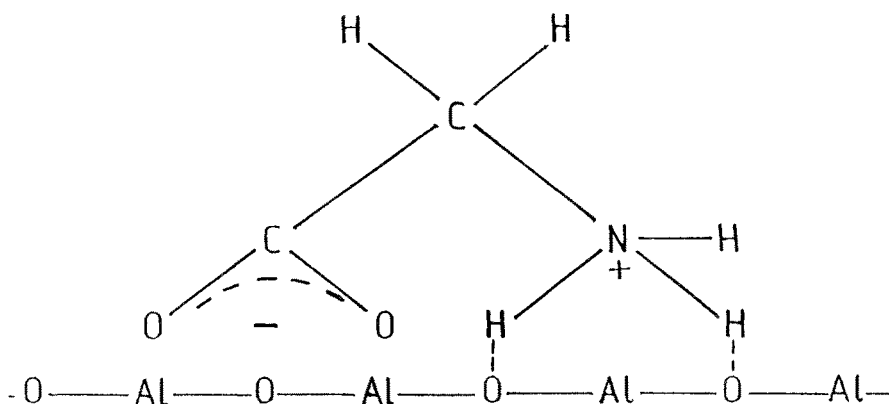


Fig. 11. Orientation of glycine on an Alumina Surface.

TABLE V

A comparison of the IET spectra of glycine (Figure 10) and $\text{NH}_3/\text{CO}_2/\text{H}_2\text{O}$ (Figure 9)

Glycine soln.	Spectral wavenumbers (cm^{-1})	
	NH_3 , CO_2 , H_2O	Possible assignment
212	224	Trans. AlO_x phonon
315	294	Long. AlO_x phonon
	438	CO_2^- rock
475		CO_2^- rock
	536	C-O wag
630		NH_2 torsion
825	823	C-C str.
934		
974	973	C-N str.
1100	1123	C-O str.
	1153	NH_3^+ def.
1362		CO_2^- sym. str.
1426	1428	CO_2^- asym. str./C-H def.
1489		NH_3^+ def.
	1538	$>\text{CH}_2$ def.
1661		
1913	1901	
	1959	
2967		C-H str.
3036	3025	C-H str.
3431	3399	N-H str.
3614	3721	O-H str.

coincides very closely with that of a genuine sample of glycine, shown in Figure 10. Table IV indicates the spectral assignment of Figure 10. From the orientational selection rule it is proposed that the glycine molecule is orientated on the alumina surface as shown in Figure 11. Table V shows the comparison of the peak energies produced in the genuine glycine spectrum (Figure 10) and the aqueous ammonia vapor doped under normal atmospheric conditions (Figure 9). Although Table V indicates a large number of spectral coincidences between these two systems, differences between the two spectra may be observed. As in the previous case of water doped tunnel junctions, a variety of surface species in the NH_3 , H_2O and CO_2 case are produced compared to the structurally much simpler case of the glycine doped tunnel junction. However, we cannot explain the presence of an intense C-N stretching mode in Figure 9 without considering alumina surface catalyzed reactions.

CARBON MONOXIDE AND FORMALDEHYDE DOPED JUNCTIONS

Wet carbon monoxide produces a tunnelling spectrum, Figure 12 and assigned in Table VI, notable for the absence of the expected $\text{C}\equiv\text{O}$ stretching mode at 268 meV and for the presence of C-H modes similar to those exhibited by the IET spectrum of aqueous formaldehyde, shown in Figure 13 and assigned in Table VII. Both the wet CO and the aqueous HCHO spectra and their assignments show

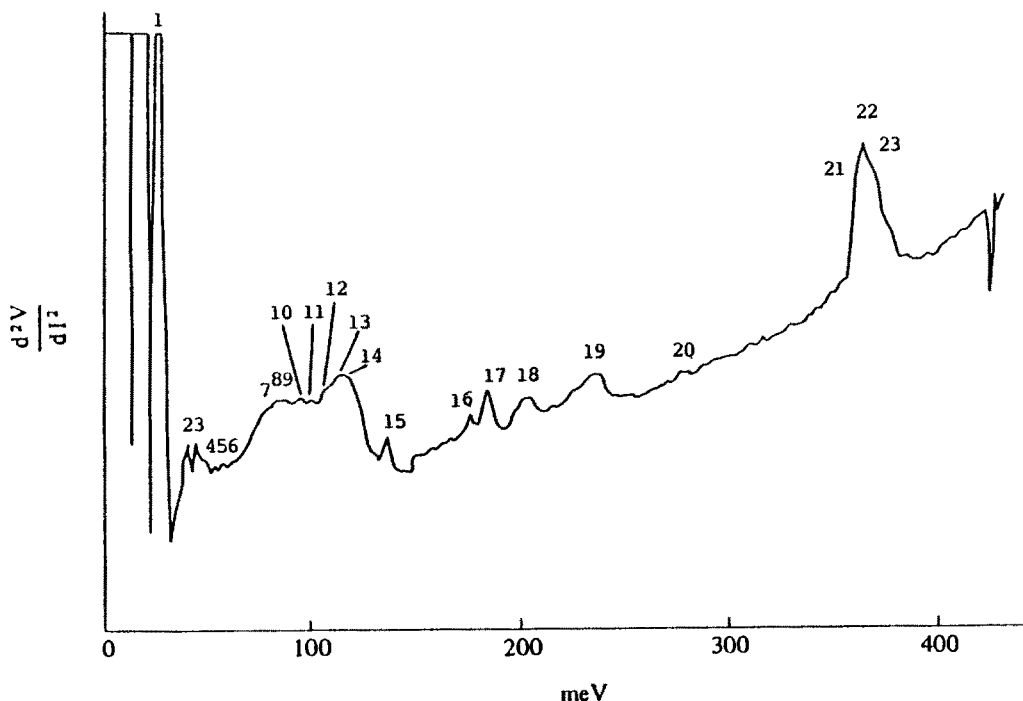


Fig. 12. IET Spectrum of Carbon Monoxide and Water.

TABLE VI
Spectral assignment of infusion doped carbon monoxide gas

Peak No.	Energy (meV)	Wave No. (cm ⁻¹)	Intens.	Assignment
1	26.3	212	VS	Al Phonon
2	41.2	332	S	Al Phonon
3	44.1	356	M	Al-C≡O
4	48.2	389	W	Al-C≡O
5	53.1	428	W	Al-C≡O
6	58.5	472	W	
7	77.7	627	W	C=O tort.
8	81.5	657	W	C=O tort.
9	88.0	710	W	C-H def.
10	94.1	759	W	as in Form.
11	98.7	796	W	C-C str.
12	103.5	835	W	C-C str.
13	111.5	899	W	C-C str.
14	116.7	941	M/Br	Al-OH def.
15	133.8	1079	M	C-O str.
16	173.7	1401	M/W	C-H def.
17	178.3	1458	M	C-H def.
18	201.0	1621	M/Br	C=O (2 Coord.)
19	235.0	1895	M/Br	C=O (4 Coord.)
20	265.8	2174	W	C=O linear
21	357.5	2883	M/Sh	C-H str.
22	361.8	2918	S	C-H str.
23	366.6	2957	M/Sh	C-H str.

S = strong, M = medium, W = weak and Sh = shoulder intensities.
1 meV = 8,065 cm⁻¹.

a close resemblance to the spectrum of a genuine sugar. D(-) Fructose was arbitrarily taken as an example of a typical sugar. The IET spectrum of D(-) Fructose is shown in Figure 14 and assigned in Table VIII (Field and Spencer, 1989). This observation concurs with the findings of Gabel and Ponnampertuma [1967], which indicated that a formose type reaction was catalyzed by alumina to produce sugars.

Conclusions

Table IX summarises our findings in tabular form to date. Having demonstrated the ability of an alumina surface to synthesize sugar and amino acid species from gases thought to be constituents of the earth's prebiotic atmosphere, the credibility of Bernal's and Cairns-Smith's hypotheses is enhanced. Further, the low energy requirements of surface synthesis relative to gas phase reactions may result in the surface catalyzed route being naturally preferred; and since we have demonstrated these syntheses under current atmospheric conditions there is no reason to suggest that, given the requisite reactants, these molecules could not be produced on freshly

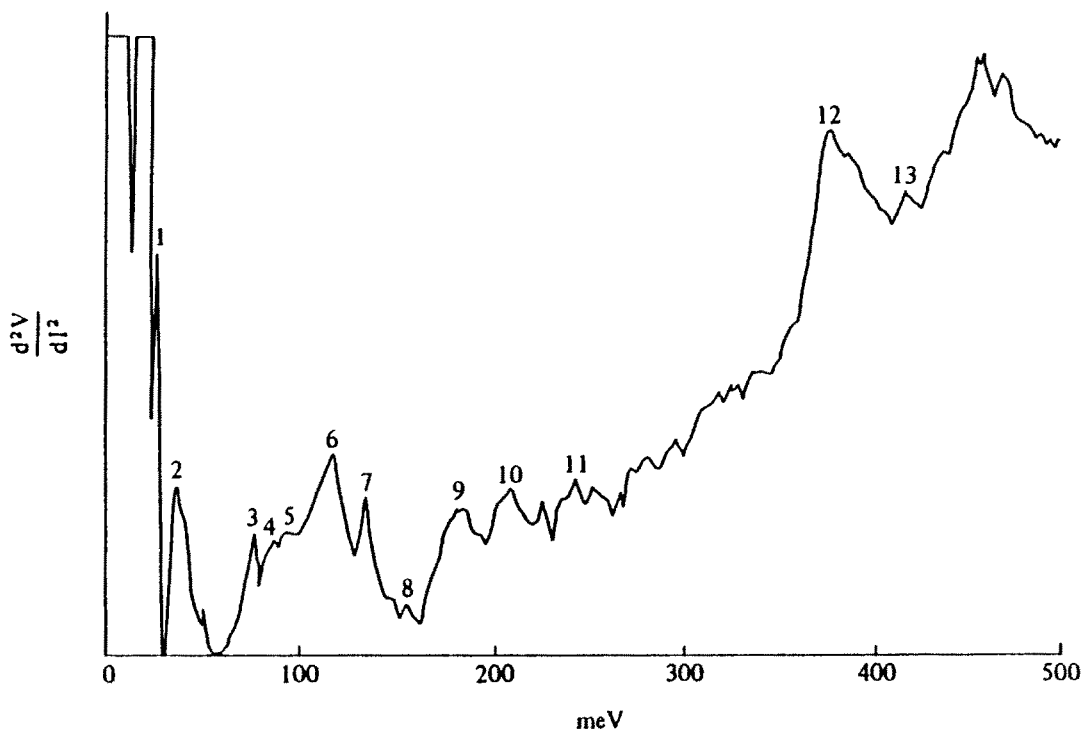


Fig. 13. IET Spectrum of Aqueous Formaldehyde.

TABLE VII
Spectral assignment of Aqueous Formaldehyde

Peak No.	Energy (meV) ^a	Wavenumber (cm ⁻¹)	Assignment
1	27	214	Trans. AlO _x phonon
2	39	316	Long. AlO _x phonon
3	80	643	C-O-H twist
4	89	718	>CH ₂ rock
5	94	756	
6	120	965	Al-OH bend
7	137	1106	C-O str./C-O def.
8	160	1287	
9	187	1507	>CH ₂ def.
10	213	1716	
11	241	1941	
12	378	3045	C-H str.
13	412	3319	

^a 1 meV = 8.065 cm⁻¹.

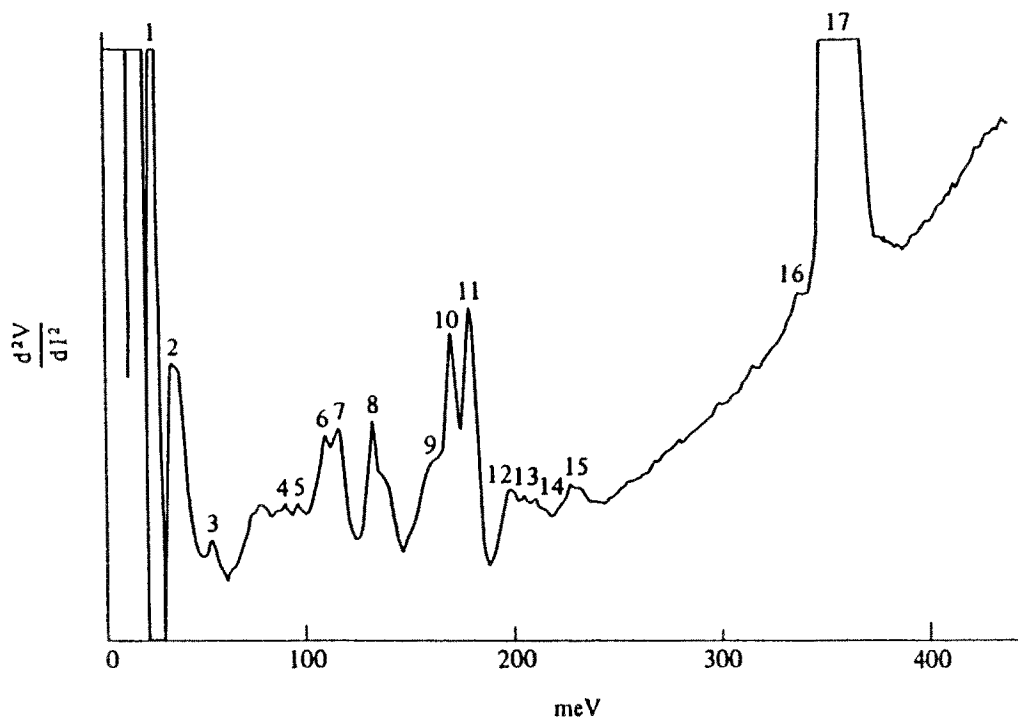


Fig. 14. IET Spectrum of D(-) Fructose.

TABLE VIII

Spectral assignment of a saturated ethanol solution of D(-)Fructose

Peak No.	Energy (meV) ^a	Wavenumber (cm ⁻¹)	Assignment
1	23	189	Trans. AlO _x phonon
2	35	280	Long. AlO _x phonon
3	52	423	ring modes
4	89	714	>CH ₂ rock
5	96	771	
6	108	868	C-H bend (sugar)
7	114	918	C-OH str.
8	131	1057	C-O str.
9	160	1291	C-OH def./O-H bend
10	170	1369	>CH ₂ bend (sugar)
11	178	1439	>CH ₂ def.
12	198	1598	C-O str.
13	204	1649	C=O str.
14	210	1695	C=O str.
15	227	1832	
16	337	2721	C-H str.
17	359	2895	C-H str.

^a 1 meV = 8.065 cm⁻¹.

TABLE IX
Summary of Results

Alumina substrate exposed to	IETS molecular identification of adsorbate
H ₂ O and CO ₂	Formic acid
H ₂ O, CO ₂ and NH ₃	Amino acid
H ₂ O and CO	Sugars
HCHO and H ₂ O	Sugars

cleaved mineral surfaces at the present as well as in prebiotic times.

It is possible to imagine sugars and amino acids being synthesized side by side on the same mineral substrate. This may explain how the various subunits of larger molecules, such as proteins, came together in their preferred manner. In this concept the 'prebiotic soup' is replaced by the structurally more selective and sensitive epitaxially orientated adsorbate. The mineral surface acting not only as a catalyst but also orientating these molecules on the mineral surface to enable them to produce their most biologically useful condensation products. It could well be that in this manner a naturally occurring mineral surface, in a vain attempt to reproduce its own surface forces produced the first self-replicating organic molecule.

This study indicates the potential of the application of IETS to exobiologists studying biomolecular surface interactions. Substrates other than alumina have already been used for IETS studies (Lewis *et al.*, 1988) and no doubt, these could be extended to simulate other mineral surfaces. The isotopic labelling of dopant molecules involved in the reactions sited here would prove informative and help to confirm the specific surface reaction mechanisms proposed.

References

- Bernal, J. D., 1951, *The Physical Basis for Life*, Routledge and Keegan.
 Cairns-Smith, A. G.: 1975, *Proc. Roy. Soc. Lond. B*, 249.
 Darling, D. F. and Field B. O.: 1973, *Surf. Sci.* **34**, 420.
 Field, B. O., Hart, R., and Lewis, D. M.: 1985, *Spectrochim. Acta* **41A**, 1069.
 Field, B. O. and Spencer, J. E. D.: 1989, *Spectrochim. Acta* **45A**, 445.
 Gabel, N. W. and Ponnampertuma, C.: 1967, *Nature* **216**, 453.
 Gibbs, D., Lohrmann, R., and Orgel, L. E.: 1980, *J. Molec. Evol.* **15**, 347.
 Jaklevic, R. C., and Gaertner, M. R.: 1977, *Appl. Phys. Lett.* **30**, 646.
 Lazard, D., Lahav, N., and Orenberg, J. B.: 1987, *Origins of Life* **17**, 135.
 Lazard, D., Lahav, N., and Orenberg, J. B.: 1988, *Origins of Life* **18**, 347.
 Lewis, D. M., Spencer, J. E. D., and Field, B. O.: 1988, *Spectrochim. Acta* **44A**, 247.
 Shklyarevskii, O. I., Lysykh, A. A., and Yanson, I. K.: 1978, *Sov. J. Low Temp. Phys.* **4**, 717.