Dr. J. N. Pitts, Jr., J. K. Foote and J. K. S. Wan (University of California, Riverside) read a paper entitled 'Some correlations between spectroscopic and photochemical processes of simple organic molecules induced by non-ionizing u.v. radiation (300 \approx 150 \text{ nm}) and by electron impact'.

By applying the modifier 'Space' to the terms 'Photochemistry' and 'Spectroscopy', one implies a concern with electromagnetic radiation of wavelengths less than that found at the earth's surface (i.e. $\lambda \leq 300$ nm) and with energetic particles, particularly electrons. To date the effects of (1) non-ionizing u.v. radiation (i.e., $300 \leq 150$ nm), and (2) electron impact on 'simple' organic molecules have been examined.

In the first of these areas, the photochemistry of aromatic systems in the $300 \rightarrow 185$ nm region is being studied. It has been known for some time that in the first aromatic absorption band (at $\sim 250$ nm in benzene and toluene) the energy absorbed is efficiently dissipated by photophysical processes with no appreciable bond scission. A recent spectral study of some of the simple aromatic molecules showed a very low efficiency of the photophysical dissipation of electronic energy absorbed in the second and third absorption bands (at $\sim 210$ nm and $185$ nm respectively in both benzene and toluene).

Current studies of the vapour-phase photochemistry of these compounds at $185$ nm show that, in accord with spectroscopic evidence, the quantum yields of their disappearance are about unity. Small amounts of stable products are formed (e.g. $\Phi C_2H_2 = 0.01$ for benzene) but most of the excited molecules ultimately react or deposit on the walls as carbon and/or polymer. Attempts are being made to trap 'chemically' these excited species before they reach the surface.

Possible relationships between intramolecular decomposition processes observed in the non-ionizing u.v. photochemistry, radiation chemistry and mass spectra of several classes of organic molecules are
explored. The cycloelimination of olefines via a six-membered cyclic transition state is common to the mass spectra of alkyl and alkyl-aromatic compounds with a hydrogen atom in a position gamma to an unsaturated group (e.g. C=O, C=N, C=C). The general nature of the intramolecular cycloelimination process for organic molecules with alkyl chains having H atoms in a position gamma to an unsaturated group would seem to have significant bearing on reactions induced by u.v. light and other forms of radiation (discharges, electrons, X-rays, gamma rays, etc.) under primitive earth conditions. It also has bearing on the photochemistry and photobiology of other planets.

Thus, for example, amides and acids with alkyl groups having hydrogen atoms in the gamma position break down on electron impact in a mass spectrometer to give ions corresponding to acetamide and acetic acid respectively and the olefins corresponding to the rest of the alkyl chain, as shown below:

Since the analogous cyclo-elimination process occurs for aldehydes, ketones and esters (the 'Norrish Type II split') with most forms of irradiation (u.v. light, electrons, X-rays, gamma rays, etc.) it would appear this generality might also be true for alkyl (and aryl-alkyl) acids and amides, alkyl benzenes, olefins, and possibly the aliphatic amino acids, particularly those with the amino group in the beta position.

If this is true one might predict the breakdown under primitive earth conditions (as well as on other planets) of a variety of types of molecules containing unsaturated 'chromophores' and having alkyl side chains with gamma hydrogen atoms into their simplest homologs.
(e.g. acetic acid, acetamide, acetaldehyde, etc.) and olefins. The possible application of correlations of this type and the utilization of mass spectrometric data in problems of 'space photochemistry and photobiology' are currently being investigated in our laboratories. We are particularly interested in beta-amino propionic acid and its derivatives which might undergo the analogous intramolecular cyclo-elimination process which in this case might lead to products containing the C—N group.

Dr S.L. Miller and M. Parris (University of California, La Jolla) read a paper on 'The synthesis of pyrophosphate under primitive earth conditions'. It has been shown that small molecules of biological interest can be synthesized by electric discharges, u.v. light and other sources of energy under primitive earth conditions. The polymerization of these molecules has not been accomplished under conditions that could have occurred to any extent on the primitive earth.

As a first hypothesis it is assumed that these polymerizations were accomplished by 'high-energy' phosphates, as in present living organisms. The most desirable synthesis of high-energy phosphates would be a photochemical synthesis because of the large amounts of such energy available. However, all attempts in this direction have failed so far.

Pyrophosphate has now been synthesized by using cyanate and cyanogen as a source of free energy. Both these molecules are reasonable compounds to have been produced in large amounts on the primitive earth. The phosphate is in the form of hydroxyl apatite. The apatites are the predominant form of phosphorus on the earth today, both in igneous and sedimentary rocks, and this would probably have been the case on the primitive earth. Pyrophosphate is not synthesized to a significant extent with soluble phosphate. The yields (moles pyrophosphate/cyanate or cyanogen) are pH dependent and range from 0 to 30 per cent, the maximum yield being at pH 6.5.

Dr S. Scher (University of California, Berkeley) read a paper entitled 'Planetary photobiology: prospects and problems'. Two aspects of planetary photobiology were discussed: (1) the role of photobiology in problems of extraterrestrial life, and (2) the relation of photo-oxidation reactions to problems of biochemical evolution. The evidence for the presence of vegetation containing chlorophyll in the so-called canals of Mars must now be discounted on the basis of studies of near infra-red reflection spectra. It is possible that alternative photobiological systems have developed on other planets and such systems
could imply the existence of novel pigments and mechanisms for photosynthesis differing from those on earth. If no living forms now exist on the moon or nearby planets evidence of previously existing life may be preserved and palaeobiochemical methods might therefore be used for analysis of fossil pigments.

Photo-oxidation reactions may have taken the place of oxidative reactions in the primitive anaerobic environments. Thus a high potential oxidant generated by the photosynthetic process could serve in reactions which normally occur only in the presence of oxygen, such as certain steps in the biosynthesis of carotenoids and porphyrins. There is evidence for the provision of such an oxidant by photosynthetic bacteria. Strains that utilize aromatic compounds anaerobically in the light have been isolated; the evidence points to a pathway of degradation of the aromatic ring similar to that followed by aerobic organisms in which oxygen is added to the ring prior to cleavage of the aromatic C—C bonds.

Dr M.H. Briggs' (British Interplanetary Society) paper was entitled 'The production of cell-like structures by the action of light on a possible primitive earth hydrosphere'. He described experiments in which simple mixtures of amino acids or of aldehydes and ammonium nitrate were irradiated with light of varying wavelengths under conditions simulating the primitive hydrosphere. Various organic compounds were formed. Also cell-like structures were found in such preparations and these exhibited phosphatase and esterase activity.

Dr Risi and K. Dose read a paper ‘The influence of radiation on the synthesis of amino-acids and peptides’.

Dr C. Ponnampерума and R. S. Young (NASA, Moffet Field, California) read a paper entitled ‘Photochemical synthesis in simulated planetary environments’. U.v. from the sun is known to have been one of the most abundant sources of energy on the primordial earth. The u.v. flux reaching the martian atmosphere today is of a high order of magnitude. The type of organic synthesis which may take place in simulated primitive earth and contemporary martian conditions through the action of u.v. have therefore been examined.

In studies of organic synthesis under simulated primitive earth conditions, it has been found that when a dilute solution of hydrogen cyanide is exposed to u.v., adenine, guanine and urea are formed. Adenine and guanine are the purines in RNA and DNA. Urea is an important biochemical intermediate. When formaldehyde in dilute solution absorbs u.v., several sugars are formed. Among these, ribose
and deoxyribose, the two sugars present in the nucleic acids, were identified. When adenine and deoxyribose in aqueous solution is exposed to u.v. in the presence of cyanide, the nucleoside deoxyadenosine is formed. The formation of these nucleic acid constituents under relatively simple pre-biotic conditions lends support to the hypothesis that life originated on this earth by a gradual process of chemical evolution.

In this study of current martian chemical phenomena the point of departure taken has been Colthup's interpretation of the Sinton reflection spectra with features at 3.45, 3.58 and 3.69 μ as being indicative of aldehydes, especially acetaldehyde. When u.v. acts on acetaldehyde in the presence or absence of water, a number of organic compounds are formed. Among these are molecules similar to naturally occurring carbohydrates. This observation suggests possible abiogenic synthesis in the present martian atmosphere.

A. Krasnovski (Academy of Science, Institute of Biochemistry, Moscow) remarked that Professor Wald had pointed out the discrepancy between the spectral maximum of solar emission and the absorption spectrum of chlorophyll. Plants have compensated for this by forming such high concentrations of chlorophyll that almost complete absorption of green light occurs as well as of red and blue light; thus the aggregation of chlorophyll in chloroplasts is an evolutionary device to absorb and use all the visible part of the spectrum by photosynthetic organisms.

Professor Terenin (Physics Institute, Leningrad University, Leningrad, U.S.S.R.) said that in the course of a study with his collaborators, Lyalin and Kobyshev, on the singlet energy transfer between two different fluorescent molecules in frozen solutions, they obtained a striking confirmation of the point made by Professor Pitts, that the energy of higher excited levels might be utilized in spite of the known fast internal dissipation to the first excited (equilibrium) singlet level.

From the excitation spectra of the fluorescence of a series of binary systems it could be shown that singlet energy transfer occurs in such cases when the strong u.v. absorption bands of the participants are close. Thus a singlet energy transfer has been found from the third excited level of Mg–phthalocyanin to the second singlet level of biacetyl and from the two high singlet levels of azulene to the second excited level of Mg–phthalocyanin. In the second case we also observed the usual energy transfer from the first excited singlet level of azulene to the first one of Mg–phthalocyanin.