ATP by Endogenous UV Radiation

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Abstract

Chemiosmosis in mitochondria is thought to synthesize ATP by oxidative phosphorylation in an inward flow of H+ protons across the inner membrane. However, ATP synthesis has a history of controversy. Although a high-energy chemical intermediate provided a more rational explanation, chemiosmosis survived as the ATP mechanism because the high-energy intermediate was never found. Chemiosmosis in chloroplasts differed as ATP was produced by photosynthesis from an outward flow of H+ protons across the thylakoid membrane. Oxidative phosphorylation in both mitochondria and chloroplasts occur by a chain of complex redox reactions with electron transfer from donors to acceptors assisted by enzymes. In this paper, chemiosmosis comprising electron chain reactions is superseded by simple QED conserving heat in nanoscopic features within the mitochondria and chloroplasts by creating endogenous UV radiation instead of increasing in temperature. ATP synthesis therefore proceeds from ADP and a phosphate group in a dehydration reaction mediated by UV instead of hydrolysis.

Background

Chemiosmosis (1) in mitochondria assumes a proton H+ gradient across the inner membrane to explain ATP synthesis by oxidative phosphorylation and in chloroplasts by photosynthetic phosphorylation across the thylakoid membrane. The main differences are the mitochondrion produces an inward proton flow by fuel-consuming redox reactions while the chloroplast produces an outward proton flow by photochemical charge separation. Both mitochondria and chloroplast phosphorylate ADP + Pi to ATP by a chain of complex chemistry. In chloroplasts, sunlight absorbed by chlorophyll produces heat that creates a charge separation across the thylakoid membrane, the outward H+ flow through the membrane-bound ATPase producing ATP from ADP and Pi. The mitochondrion differs as the proton flow across the inner membrane is inward, opposite to that of the chloroplast. Unlike charge separation in chloroplasts which is uniform, the inward H+ flow in mitochondria need not be uniform to pass through the ATP synthase to produce ATP. In 1961, chemiosmosis in mitochondria by a proton gradient was not accepted. A later review (2) claimed a high-energy chemical intermediate provided a more rational explanation with chemiosmosis surviving as the chosen ATP mechanism because the high-energy intermediate was never found.

Later on, chemiosmosis by oxidative phosphorylation in mitochondria using a H+ gradient was supported (3) by photosynthetic phosphorylation in chloroplasts using the reconstituted purple membrane *Bacteriorhodopsin* (bR) in a lipid membrane shown in Figure 1.

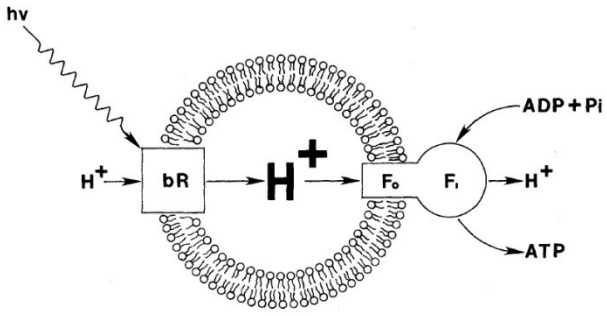

Figure 1. Chemiosmotic photophosphorylation in artificial lipid vesicles.

Figure 1 illustrates combining bR with the F0-FI ATPase from mitochondria into lipid vesicles formed an inside-out model. Upon illumination with VIS light, the protons then flow outward through the ATPase, causing it to phosphorylate ADP + Pi to ATP. In contrast, oxidative phosphorylation in mitochondria differs in that oxidation first produces H+ protons that flow outward. ATP is produced as the H^+ protons flow back into the cell, the subsequent inward proton flow producing ATP from ADP + Pi consistent with oxidative phosphorylation.

Similar to mitochondrial oxidative phosphorylation, chloroplasts use the photosynthetic thylakoid membranes to phosphorylate ADP + Pi to ATP. Pi stands for phosphate group. In 1967, the oxidative chemiosmosis was first supported by photosynthetic phosphorylation (4) in acidified spinach chloroplasts suddenly subjected to a basic medium. The pH gradient was created by holding the chloroplasts in a pH 4 solution for several hours and then rapidly mixed them with a neutral pH 8 buffer containing ADP and Pi. ATP synthesis was observed as the pH gradient across the membrane disappeared. The so-called acid-bath experiment was thought to unequivocally support the chemiosmosis theory that ATP synthesis is driven by pH gradients.

Problem

Chemiosmosis in mitochondria supported by the acid-bath chloroplast experiment showing ATP produced in a pH gradient across the thylakoid membrane is depicted in Figure 2(a).

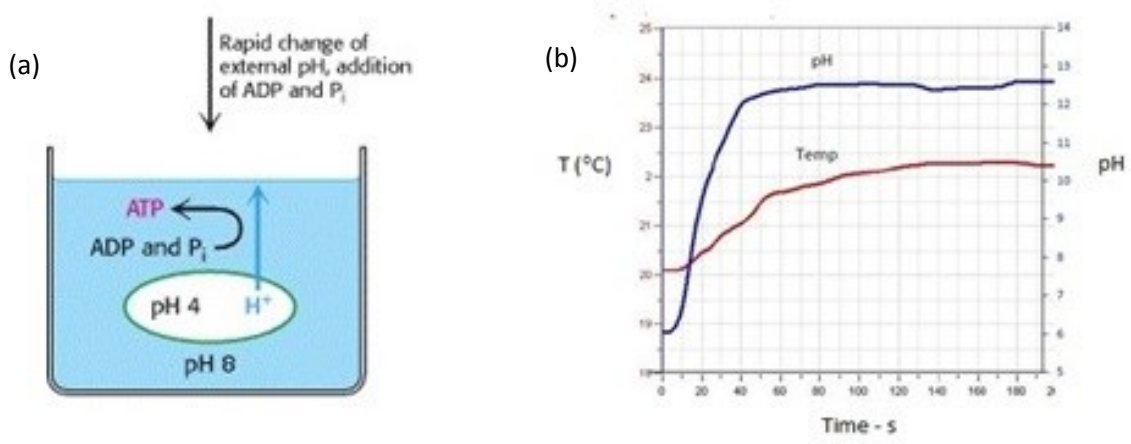

Figure 2. Chloroplast Acid-bath Experiment

However, ATP may not be produced by the pH gradient, but rather by a release (5) of anaerobic heat that increases bath temperature. In the titration of a weak acid with a base, Figure 2(b) shows rapidly changing an acidic pH 4 solution to a basic pH 8 produces a pH gradient of 4 also increases bath temperature. But the nanoscopic grana cannot increase in temperature as the heat capacity vanishes by the Planck law. Instead, thylakoid grana conserve the anaerobic heat by simple QED creating EM radiation beyond the UV that produce the ATP by the dehydration reaction,

$$ADP + Pi + UV \rightarrow ATP + H_2O$$

Simple QED was developed (6) for nanoscale heat transfer. Unlike classical physics that conserves heat by an increase in temperature, simple QED based on quantum mechanics denies atoms under the high EM confinement in nanostructures denies constituent atoms the heat capacity to conserve heat by an increase in temperature.
Instead, simple QED conserves heat by creating EM radiation at UV levels.

Photo Oxidation

Chemiosmosis explains ATP synthesis in mitochondria by oxidative phosphorylation through complex chemistry with enzymes in a sequential electron transport chain. The flow of electrons pumps H+ protons out of the matrix across the inner membrane into the intermembrane space, whereupon the H+ protons flow back through the F1-Fo ATPase to provide the energy for ATP synthesis.

Setting aside the difficulty in chemiosmosis of H+ protons flowing back through the F1-Fo ATPase and not elsewhere in the membrane, the electron transport chain is otherwise consistent with modern chemistry. However, Nature may not have chosen chemiosmosis as the mechanism for ATP synthesis as a more direct path is UV photo oxidation of food glucose similar to the photosynthetic phosphorylation in chloroplasts. If so, chemiosmosis with complex sequential electron chain reactions would not be required, specific enzymes in the inner membrane would not need to be instantly available, electrons from the reduced coenzymes would need not be passed from one electron carrier to another. Alternatively, the final oxidative electron transfer forming O_2 oxygen is more directly reached by UV assisted dehydration reactions (7) to produce ATP from ADP + Pi, where Pi is a phosphate group.

Although dehydration reaction by UV radiation is simpler than chemiosmosis, the difficulty is UV creates reactive oxygen species (ROS) that damage DNA in mitochondria and chloroplasts. But ROS is not a problem as mitochondria release ATP to protect against UV damage. The ability of ATP to protect mitochondria (8) allows the dehydration reaction to proceed during UV radiation. Perhaps, Nature took advantage of the simplicity of UV oxidation of food to glucose by allowing ATP synthesis to sustain life at the expense of expending some ATP in protecting the mitochondria.

Purpose

In this paper, ATP synthesis is proposed to occur by simple QED induced endogenous UV radiation assisted dehydration reactions of ADP + Pi preceded by UV conversion of glucose to ADP. The ATP expended in protecting the mitochondria against UV damage is only a fraction of the ATP produced. Moreover, the fraction of ATP protecting the mitochondria is not lost, but rather is a source of heat to produce the endogenous UV that allows ATP synthesis to proceed by dehydration.

Analysis

EM Radiation

Simple QED induced UV requires mitochondrial and chloroplast having nanoscopic features with at least one dimension < 100 nm. Otherwise, the EM confinement produces VIS and IR radiation that lacks the energy to activate ATP synthesis by UV mediated dehydration and food oxidation. The Planck energy E of the EM radiation,

$$E = \frac{hc}{2nd}$$

where, h is Planck's constant, c the speed of light, n and d are the refractive index and minimum dimension of the nanoscopic feature. For protein structures, n ~ 1.5 having d ~ 10 nm, E ~ 40 eV which is in the EUV. Although EUV fluorescence produces UV, the efficiency is reduced. With EUV fluorescence, structures having $10 < d < 80$ nm more efficiently produce UV > 5 eV. Regardless, simple QED requires the heat supplied to the nanostructure to produce EM radiation. The source of heat is the UV oxidation of food molecules and the binding of ALP to the nanostructure. Absent heat, simple QED does not produce EM radiation.

Experimentally, the efficiency of UV emission from EUV fluorescence data of ATP binding to nanoscopic mitochondrial and chloroplast structures is not available. But controlled oxidation of glucose to gluconic acid and other monosaccharides (9) by UVA fluorescence from d < 8 nm Ag/TiO2 nanoparticles shows < 10% efficiency.

Applications

In the application of simple QED induced UV activation of ATP synthesis by dehydration, the EUV produced in mitochondria and chloroplasts are presented in the following.

Mitochondria

ATP synthesis in mitochondria is proposed to occur by simple QED induced UV radiation standing between adjacent cristae surfaces. The human lung showing the mitochondria with the EM wave standing in the fold formed between adjacent cristae is noted in Figure 3.

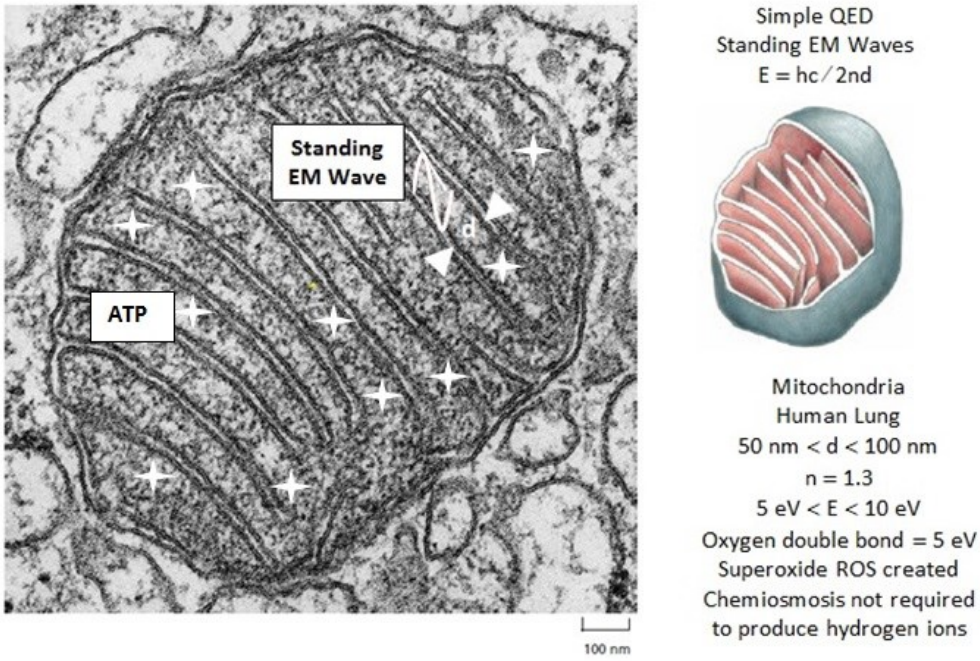

Figure 3. Human Lung Mitochondria
Showing ATP protecting DNA while providing heat source to EM standing wave

The EM wave standing in the mitochondria matrix with a spacing d between adjacent cristae is defined by (50 < d < 100 nm). ATP molecules – white stars – are shown dispersed throughout the matrix in Figure 3. ATP binding is the likely heat source for simple QED to produce EM radiation. For simplicity, glucose food molecules oxidized by UV radiation to produce ADP are not shown. The Planck energy E of the standing EM waves based on a refractive index n ~ 1.3 is beyond the UV at 5 to 10 eV.

In the oxidation of food molecules, the UV produces the oxygen anion superoxide by breaking the double bond of dissolved oxygen and the H+ protons from the OH radical. The UV radiation creates ADP from breaking down glucose from foods, the ATP produced from UV enhanced dehydration in the presence of ADP and Pi, but also forms ROS. In the mitochondria, simple QED is both the source of ATP synthesis and ROS.

Unlike chemiosmosis, simple QED does not depend on the H+ gradient across the inner membrane to produce ATP by hydrolysis. For over 50 years, chemiosmosis claimed the unlikely sequence of electron chain reactions powered by the H+ proton gradient across the inner membrane produced ATP by hydrolysis , when in fact simple QED in the UV and beyond actually mediated ATP synthesis by dehydrogenization of ADP + Pi.

Submicron Particles

In 1964, after chemiosmosis was proposed, mitochondria were mechanically treated with ultrasound. Electron microscopy (10) revealed numerous submicron spherical vesicles of inner mitochondrial membrane. A typical micrograph is shown in Fig. 4.

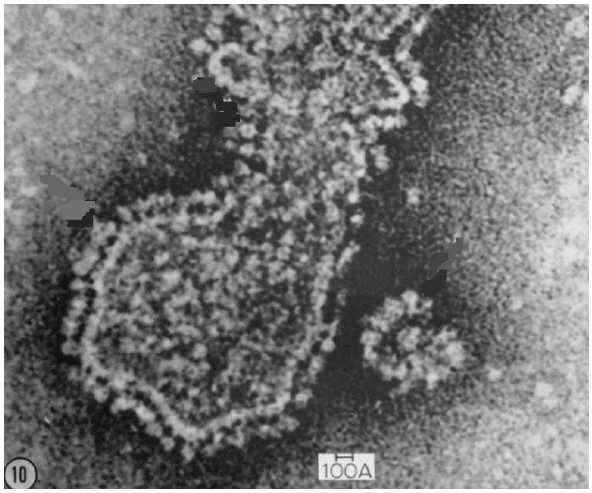

Figure 4. Submicron Spherical Vesicles from Ultrasonic treated Mitochondria

The submitochondrial particles (SMP), were spherical having diameters of 8-10 nm located on the surface of the cristae, but are also dispersed throughout the matrix. Comparison with intact mitochondria for bovine heart muscle shows the SMP display an inside-out orientation of ATPase compared with intact mitochondria, i.e., the globular SMP structures seen facing the matrix on the surface of cristae are found on the outer face of SMP outside the matrix as shown in Figure 5.

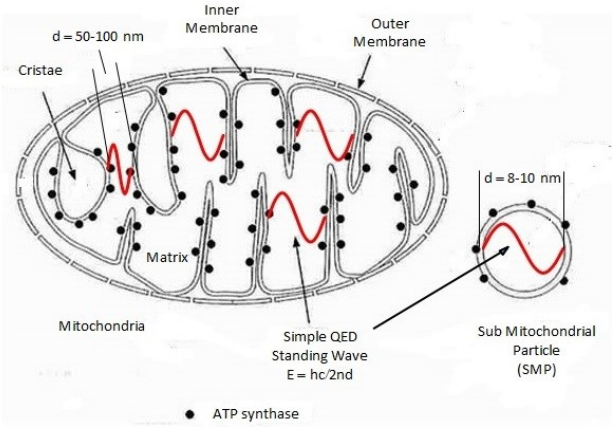

Figure 5. Simple QED standing EM waves in Mitochondria and SMP

Simple QED produces standing EM radiation in the UV and beyond as shown everywhere in the mitochondria and SMP depending on the ATP energy release regardless of which surface the ATP synthase is bound, i.e., the EM waves are conserved from ATP regardless of the binding surface. In the mitochondria, the spacing d between crista is, d = 50-100 nm producing EM radiation in the UV and beyond. However, the EM radiation in the spherical SMP having d = 8-10 nm is far higher in the EUV at about 40 eV, the lower quantum states in the UV excited by EUV fluorescence at the expense if low efficiency.

Chloroplasts

In chemiosmosis for chloroplasts, photophosphorylation of ADP to ATP occurs by light absorption in the thylakoid membrane producing H+ protons moving outward through membrane-bound ATPase to make ATP from ADP and Pi. The ATPase comprise a stalk segment (F0) embedded in the membrane with a head (F1) which extends into the aqueous stroma as shown in Fig. 4. When the intact F0--F1 ATPase is inserted into a phospholipid membrane and a pH difference is imposed across the membrane, the ATPase is thought (1) to consume protons while phosphorylating ADP with Pi to ATP. However, a pH gradient may not be necessary as cleaving the F1 head from the F0 stalk, the F1 head alone (3) in aqueous solution, produces ATP from ADP + Pi. Regardless, whether the pH difference or anaerobic heating produced the ATP in the acid-bath experiment is an open question.

Heat Q is the commonality in ATP production in chloroplasts. The outer membrane of the chloroplasts absorbs VIS radiation to provide heat Q to the lumen thylakoids. Hence, VIS cannot reach the thylakoids. Depending on dark or light adapted conditions, the lumen space (11) is about 17 nm containing water including plastocyanin (PC) and photosensitive PSII complexes. The ATP synthase located on the convoluted ends of the thylakoid membranes along the side of the stack exposed to the stroma is shown in Figure 7.

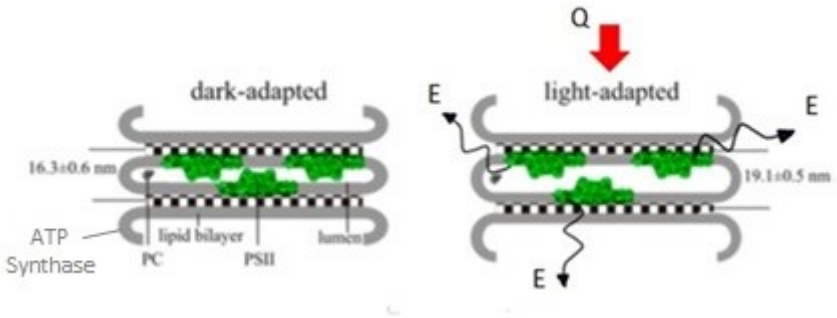

Figure 7. Lumen structure containing OEC and PC

VIS radiation wavelengths $\lambda > 400$ nm is excluded in the 17 nm EM confinement space of the lumen having EUV wavelengths $\lambda < 50$ nm. Hence, PC can only be absorbent below 300 nm. What this means is VIS photosensitivity of PC and PSII complexes has no meaning in chloroplasts. The EM absorption spectra (12) of oxidized and reduced PC peaks at UV wavelengths < 200 nm are shown in Figure 8(a). Only UV radiation is important in ATP synthesis. Similarly, the UV spectra of adenine in forming ADP shows peaks at about 205 and 265 nm is given in Figure 8(b).

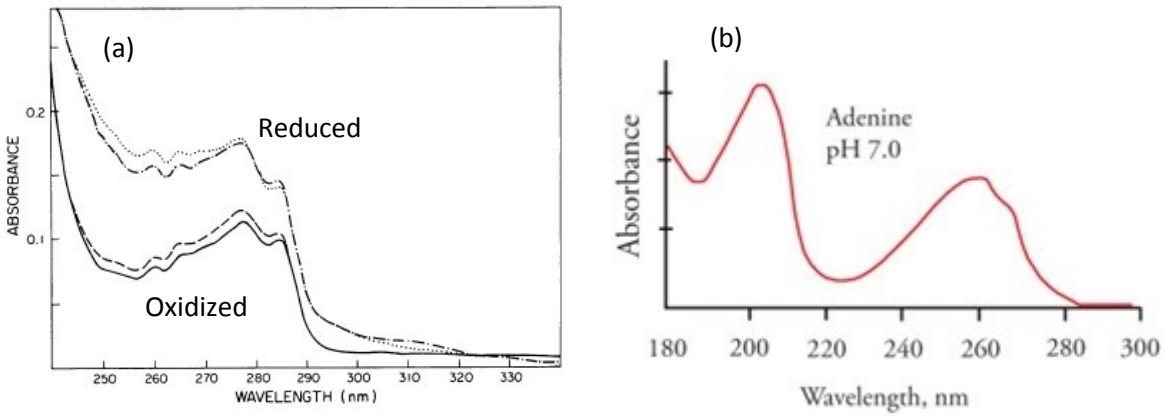

Figure 8. PC and Adenine absorption spectra

Of interest is the UV absorption spectra of glucose, ATP, and ADP spectra shown in Figure 9. Figure 9(a) shows ATP and ADP spectra (13) are almost identical at 300 nm, but differ in the VIS. The inset shows the ATP spectra below 300 nm to peak at about 260 nm. Figure 9(b) gives the UV absorption spectra (14) of glucose solution before and after irradiation for alkaline pH 11.5 and acidic pH 2 conditions. The spectral peak of the alkaline glucose solution at 267 nm is proximate the ATP peak at 260 nm consistent with the 260 nm peak of adenine shown Figure 8(b). Contrarily, chloroplast photosynthesis today is based on VIS and not UV light.

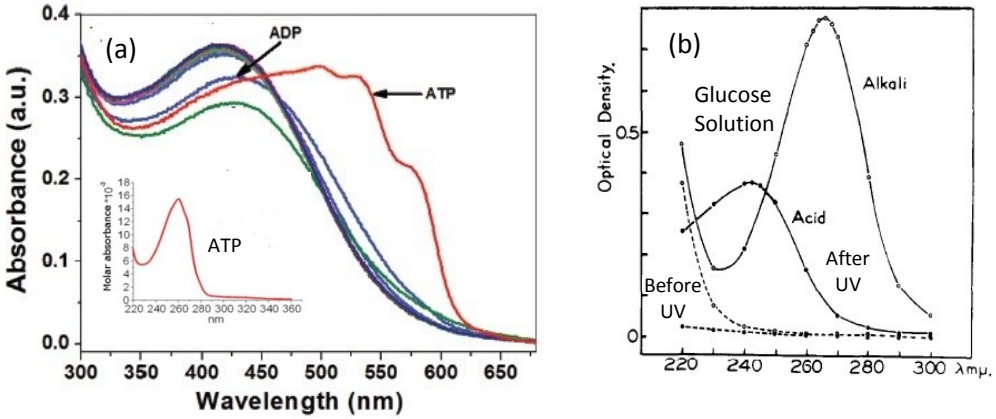

Figure 9. ATP and Glucose absorption spectra

Since ADP is converted to ATP in the stroma adjacent to the convoluted ends of thylakoid membrane in the grana stack which cannot be reached by solar light, ATP synthesis may only proceed by EUV radiation from the heat Q absorbed in the outer chloroplast membrane. Upon reaching the lumen, the heat Q is precluded by QM from increasing in temperature., and instead is conserved by simple QED creating EUV radiation within the lumen space. For water having refractive index $n = 1.33$, the Planck energy E in the EUV radiation produced in the lumen space of $d \sim 17$ nm is, $E \sim 27$ eV and $\lambda \sim 45$ nm. At the convoluted ends of the thylakoid membranes exposed to the stroma, the EUV fluorescence excites adenine, glucose and ADP near their spectral peak at 267 nm to overcome the barrier to dehydration of ADP + Pi to ATP without the complex electron chain reactions of chemiosmosis. In chloroplasts, simple QED is summarized in Figure 10.

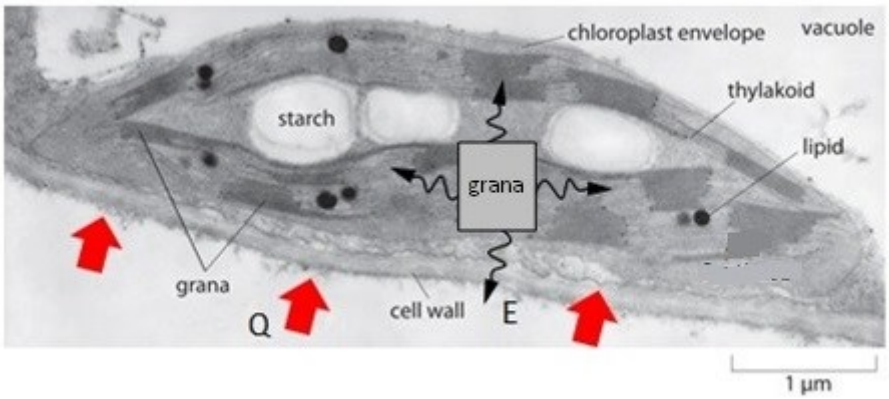

Figure 10. Simple QED in Chloroplasts

In summary, EUV is common to other sources of ATP created from EM confinement in nanoscopic structures. In 1976, ATP synthesis was reported (15) from aqueous suspensions of inorganic nanoparticles of ZnO and CdS heated by UV light, again without a pH gradient across a membrane. Indeed, the direct utilization of the hydrogen and oxygen in water for organic reactions (16) in glucose was realized by splitting water upon heating Pd/TiO2 nanoparticles with UVB irradiation at 350 nm. But for ATP synthesis and water splitting to occur, simple QED requires heating the nanoparticles and nano structural features of mitochondria and chloroplasts to produce the EUV energy to split water or assist the dehydration reaction ADP + Pi to ATP.

Discussion

Unlike hydrolysis in chemiosmosis, ATP synthesis by dehydration is a condensation reaction common in amino acids to proteins, sugars to carbohydrates, sugars to sugar phosphates, purines to nucleosides, and nucleosides to nucleotides. Although dehydration is direct chemistry compared to hydrolysis, an endergonic source of energy is required to activate the non-enzymatic production of ATP. On the primitive Earth, the energy source was suggested (7) to be UV radiation from outer space, i.e., pH gradients across membranes not required. UV irradiation of dilute solutions of purine or pyrimidine bases, specifically adenine, and phosphorus compound produced the nucleoside adenosine. Since adenosine has strong UV absorption peaks near 260 nm, the transparency of the early terrestrial atmosphere may have allowed ATP synthesis by dehydration reactions to proceed from dilute solutions of adenine. In ethyl metaphosphate, adenine yielded ADP and ATP.

Although exogenous UV radiation provides an understanding of the mechanism of ATP production in the evolution of life on the primitive Earth, only endogenous UV produced within the mitochondria and chloroplasts is relevant to the question of how molecular evolution proceeded. Perhaps, the lack of an endogenous UV source was implicit in the acceptance of hydrolysis in chemiosmosis theory driven by H+ proton gradients instead of dehydration reactions. The simple QED induced endogenous UV energy source proposed here to activate dehydration reactions in producing ATP from ADP + Pi groups is proposed to supersede chemiosmosis.

Endogenous UV within the mitochondria and chloroplasts not only allows ATP production, but also is the source of ROS. The literature is silent on the source of ROS, simply stating ROS are just present in biological systems. However, UV beyond UVC having energy $E > 5$ eV is required to create hydroxyl and super oxides. ROS damage to DNA is proposed (17) as the cause of neurodegenerative diseases by disrupting ATP synthase in chemiosmotic electron chain reactions, but the mechanism of ROS

production is not identified. In contrast, endogenous UV as the source of ROS may at first appear a detriment to the ATP synthase by dehydration reactions, but may not be a problem as mitochondria release ATP to protect (8) against UV damage. Perhaps, Nature took advantage of the simplicity of UV oxidation of food to glucose by allowing ATP synthesis to sustain life at the expense of some ATP in protecting the mitochondria.

In the origin of life, the concept of primordial soup remains central to mainstream thinking. But soup is homogeneous in pH and so has no capacity (18) for energy coupling by chemiosmosis. Instead, chemiosmosis is claimed central to the origin of life as proton gradients form naturally at alkaline hydrothermal vents allowing ATP synthesis powered by the ion gradient by means of vectorial electron transfer from a donor to acceptor. As described above, however, the notion of pH gradients across the thylakoid membrane of the chloroplasts as the source of ATP production in the acid-bath experiment is questionable (1,3,4) because of the anaerobic heat released in mixing acids and bases. Instead of chemiosmosis, the simple QED induced UV produced by the anaerobic heat of mixing provides the activation energy (7) for the ATP synthesis by dehydration reactions. Extended to mitochondria, the heat required to produce UV assisted ATP synthesis is the binding of a fraction of the total ATP produced to the cristae surfaces.

In support of chemiosmosis as the basis for the origin of life, heat flow across the inner membrane of mitochondria as the mechanism for sustaining pH gradients was simulated (19) by thermophoresis for specified temperature gradients across sub-millimeter sized water-filled channels. For heat flow based on a temperature difference $\Delta T = 30$ K across channel widths > 153 μm, pH differences of ~ 2 were found after 4 hours. The pH differences are caused by the heat from temperatures specified across the channel. Perhaps applicable to rock fissures, the relevance of temperature changes across > 153 μm wide channels in producing pH gradients is hardly support for ATP chemiosmosis across the < 5 nm inner membrane of mitochondria. Moreover, the simulation of pH gradient based on temperature differences is not relevant. Perhaps, simulating the heat flow in nanoscale channels based on specifying a pH gradient would be meaningful. Regardless, thermophoresis based on temperature differences across channel widths < 100 nm are meaningless as temperature changes are denied by QM. Consistent with QM precluding temperature changes, simple QED conserves heat from ATP binding to the membrane wall producing the UV radiation that activates ATP synthesis from ADP + Pi by dehydration.

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