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Emission in the deep vacuum ultraviolet from a plasma formed by incandescently heating hydrogen gas with trace amounts of potassium carbonate

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Abstract
A hydrogen plasma with intense extreme ultraviolet and visible emission was generated from low pressure hydrogen gas (0.1–1 mbar) in contact with a hot tungsten filament only when the filament heated a titanium dissociator coated with K_2CO_3 above 750°C. The electric field strength from the filament was about 1 V cm^{-1}, two orders of magnitude lower than the starting voltages measured for gas glow discharges. The emission of the H_α and H_β transitions as well as the L_α and L_β transitions were recorded and analysed. The plasma seemed to be far from thermal equilibrium, and no conventional mechanism was found to explain the formation of a hydrogen plasma by incandescently heating hydrogen gas in the presence of trace amounts of K_2CO_3. The temporal behaviour of the plasma was recorded via hydrogen Balmer alpha line emission when all power into the cell was terminated and an excessive afterglow duration (2 s) was observed. The plasma was found to be dependent on the chemistry of atomic hydrogen with potassium since no plasma formed with Na_2CO_3 replacing K_2CO_3 and the time constant of the emission following the removal of all of the power to the cell matched that of the cooling of the filament and the resulting shift from atomic to molecular hydrogen. Our results indicate that a novel chemical power source is present and that it forms the energetic hydrogen plasma that is a potential new light source.

1. Introduction

Table-top sources emitting radiation in the deep ultraviolet spectral range are gaining more and more interest in photochemistry due to the increased importance of functionalization of surfaces, particularly in combination with lithographic processes [1]. The range and complexity of applications are wide and range from simple sterilization of large surfaces to sophisticated nano-patterning in production processes of microelectronics and biotechnology [2]. Well known sources such as electric sparks [3], capillary discharges [4], pseudosparks, hollow cathode discharges [5], laser sparks, and barrier discharges [6], to name a few, are suited for such photochemical work and are selected and developed further according to the specifications of the particular application.

Previously reported VUV emission of incandescently driven potassium carbonate cells in hydrogen [7–9] seemed to depend more on the chemistry of the potassium with hydrogen and on the temperature of components in the cell than on a particular voltage or current applied to the cell. No VUV emission was observed with Na_2CO_3 replacing K_2CO_3, and emission was observed even when the electric field was set to zero as shown in figure 1. The temporal behaviour of the plasma was recorded via H_α emission, which is indicative of

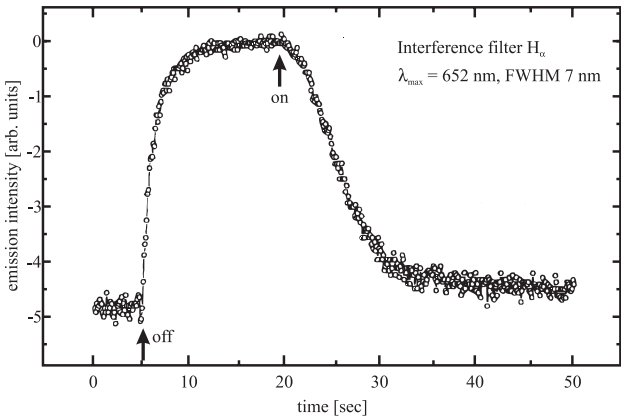

Figure 1. Emission of the cell as a function of time while the filament current was turned off and on. The plasma decay with no electric field present followed the decay of atomic hydrogen from the filament dissociator. Upon restoration of the filament temperature, dissociation and the plasmas resumed.

an associated VUV emission, when all power into the cell was terminated. A two second decay of the plasma was observed after a fast decay (several milliseconds) of the electric field to zero. With restoration of the original heater power, 10 s elapsed before the H_α emission reached its maximum again. These time constants are typical of cooling and heating of the tungsten filament; thus, the temporal emission behaviour matched the corresponding shift between atomic and molecular hydrogen due to degree of dissociation by the filament.

This paper addresses the properties of the plasma and the VUV radiation generated in such a cell. The emission of H_α and H_β as well as L_α and L_β transitions were recorded with higher spectral resolution than before [9], and in contrast to earlier investigations, the tungsten wire was heated by external radiation as well as by Ohmic heating.

2. Experimental set-up

2.1. The cell

Three different types of cells were used to investigate the formation of a low-voltage hydrogen plasma and the emitted radiation. One design, type I, was described previously [9]. In the second design, type II, the helical tungsten wire heater was replaced by two commercial 120 V halide bulbs connected in parallel. A tungsten wire was wrapped around the outside of the bulbs to serve as a hydrogen dissociator [10]. The tungsten wire in the type II cell as well as the titanium mesh were at a floating potential. All other components were the same as those of the type I cell. In the third design, type III, the thermal insulation of the quartz tube vacuum vessel of the type I cell was removed to allow for unobstructed observation of the interior of the cell. To maintain the high operating temperature of the cell, the removed section of insulation was replaced by an oven surrounding the cell. A wide slot in the oven permitted 'side-on' observation of the cell radiation. A brass tube adjacent to the slot extended to a cap which provided the different supplies. The voltage supplied to the tungsten wire heater was increased step-wise from 20 to 70 V. At 70 V, the colour of the tungsten wire was similar to the one in the centre of the oven.

For the Lyman series measurements, all of the cells were windowless and connected to a VUV spectrometer directly for 'end-on' observation. The visible radiation was coupled to the spectrometer by glass fibres for 'side-on' observation.

2.2. The spectrometers

The light in the visible spectral range was analysed by a grating spectrometer in Czerny–Turner mounting and recorded by a photomultiplier and oscilloscope as well as by an optical multichannel analyzer (OMA) system. A 1200 lines mm^{-1} grating blazed at 1000 nm was used. The spectral sensitivity in the range between H_α and H_β was essentially constant. The error in the relative intensities of the two lines was less than 20% when the background near each line was subtracted. For the determination of the electron temperature of a hydrogen plasma, the line ratio could only be used for cold plasmas ($T_e \ll 1$ eV) due to the uncertainty in the spectral sensitivity of the spectrometer.

The light in the vacuum ultraviolet was analysed by a scanning 1 m grating spectrometer in Eagle mounting (McPherson, model 225) equipped with a grating of 1200 lines mm^{-1} blazed at 120 nm. The spectra were detected by a photomultiplier coated by a p-Terphenyl scintillator and recorded by an oscilloscope. The entrance and exit slits had a width of 50 μm. The absolute spectral sensitivity of the spectrometer in the range between L_α and L_β was not known. However, relative intensities of spectral lines of successively recorded spectra could be compared. A pressure gradient was maintained between the cell and the pumped spectrometer.

3. Experimental results

3.1. The cell

The work was started with a type I cell. As soon as the temperature between the quartz wall and the thermal insulation of the cell exceeded 700°C, light was observed from the annulus between the helical tungsten heater and the titanium mesh coated with a thin film of potassium carbonate. The temperature outside of the quartz tube was increased to and held constant at 750°C. The bluish-white-coloured emission that lasted for about one hour increased with temperature and was brighter than the reddish glow of the tungsten heater.

A series of experiments was performed next using the type II cell. With an electrically floating tungsten wire wrapped around the outside of the bulbs, the light in the annulus became bright after 10 min of heating and was observed to be different in colour compared to the bright light emitted from the interior of the bulbs. The bluish-white light was easily observed by eye. The cell wall temperature was again 750°C. The light emission lasted about half an hour. Without the tungsten wire wrapped around the halide bulbs, no bluish-white light emission was observed and the temperature in the annulus and the adjacent parts was lower as demonstrated by the absence of signs of plasticity of the bulbs that was observed in the case with the tungsten spiral present. Since the operative temperature at the quartz wall of the type II cell was 750°C as well, it was concluded that an exothermic reaction was responsible for the generation of light in the annulus that also required the tungsten to be at a sufficiently high temperature and the presence of

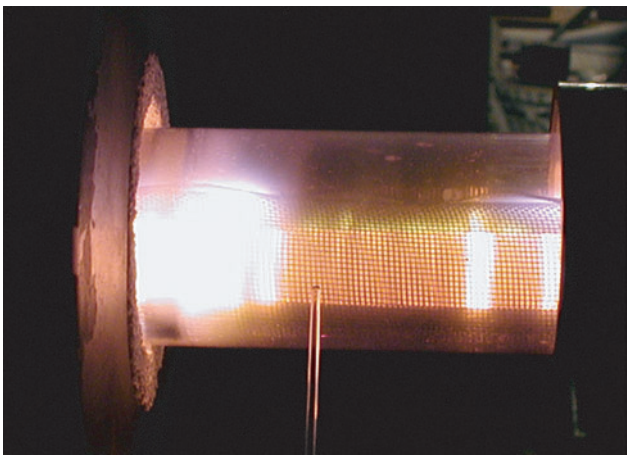

Figure 2. Photograph of the type III cell. Bluish-white light can be seen at positions up to a few centimetres outside of the oven (left) and the brass insulator (right).

potassium carbonate on the titanium mesh. No significant difference in the spectral emission or general performance could be determined between the type I and type II cells.

Next, a type III cell was studied. As shown in figure 2, bluish light was emitted from the region between the titanium mesh and the quartz wall as well as from the annulus between the tungsten coil and the titanium mesh. A similar pattern was observed for the emission of white light. It was observed that a necessary condition for this kind of emission was the existence of sufficient potassium carbonate on the titanium mesh, and the intensity of the bluish and white emission was related to the potassium carbonate concentration on the titanium mesh. In addition, it became evident that the temperature of the titanium mesh had to be sufficiently high to enable the emission. This was demonstrated by removing the oven and setting the tungsten coil at the rated voltage of 70 V for a time longer than that required to achieve strong emission. Only the red emission of the tungsten wire was observed. As soon as the oven was slipped over the quartz tube, the bluish and white emission started instantly.

Since the oven heating was sufficient to maintain the temperature of the titanium mesh sufficiently high for emission, the tungsten-coil heater power was reduced by decreasing its voltage. It was possible to sustain VUV light emission down to 20 V corresponding to about 0.2 V per winding and a field of about 0.1 V cm^{-1}. The light emission stopped with a voltage just below 20 V and returned at once when the voltage was restored to 20 V. When the voltage was set to zero for a while, the return of the light emission was delayed even when the voltage was quickly increased to 70 V. From these observations, it was concluded that the condition of a minimum tungsten-wire temperature was required in order to trigger the bluish and white light emission, when all of the other conditions were fulfilled. Anomalous after glow duration and the requirement of a minimum filament temperature for this and similar plasmas has been reported previously [11]. From the experiments with the light bulbs as heaters together with these findings and the observation of the temporal behaviour when the field was turned off and on such as that shown in figure 1, it was concluded that axial electric fields are not required for the unusual formation of a hydrogen plasma and the VUV light emission. Rather, an appropriately elevated temperature of the cell and a higher temperature of the tungsten wire were necessary. These results indicate that a high vapour pressure of K_2CO_3 and the dissociation of hydrogen at the hot filament may be required. The dependence of the emission on potassium carbonate and atomic hydrogen indicates that chemical reaction is the source of emission. The novelty of the chemistry and the elimination of conventional plasma based explanations of the observations are addressed in section 4.

At times, the plasma was uniform, and at other times slow spatial fluctuations of the plasma were observed with time. The possibility of plasma induced electric fields such as those of plasma striations in glow discharges is unlikely due to absence of a strong external electric field, the low electron density of $n_e = 2 \times 10^9$ cm^{-3} [12] compared to that modelled for glow discharges of 10^{11} cm^{-3} [13, 14], and the absence of a significant spatial variation of the electron density determined with a Langmuir probe [12]. The fluctuations could be due to a multitude of mechanisms ranging from temperature and pressure gradients, K_2CO_3 vapour pressure variations, decomposition of K_2CO_3 to potassium metal, and variations in the conductivity of the filament versus the plasma due to any of these causes. The latter was supported by observation of bright and darker zones on the filament that were correlated with those in the plasma. The K_2CO_3 dependence of the plasma emission intensity was evident since the emission ceased when the K_2CO_3 was consumed by decomposition to the metal and thermal migration.

3.2. The spectra

For the investigation in the visible spectral range, the wavelength was calibrated using a cold standard lamp that also served for the determination of the apparatus function which was fit by a Voigt profile of 0.96 pixels Gaussian and 3.89 pixels Lorentzian widths. In the first order, the width of the H_α transition ($\lambda = 656.28$ nm) corresponded to that of the apparatus profile; whereas, in the second order, a broader and slightly asymmetric H_α profile was observed. Figure 3 shows the emission of the H_α transition measured in the second order with a reciprocal dispersion of 7.0 pm/channel together with a least-squares fit. The calculated profile consisted of three wavelength shifted Gaussian profiles according to the three fine structure transitions of H_α taking into account the intensity ratios given by [15]. The calculated profile was still asymmetric when it was convoluted with the measured apparatus function. Therefore, the asymmetry on the measured spectra can be attributed to the unresolved observation of the fine structure components. The fit gave a Gaussian width of (3.2 ± 0.9) pixels corresponding to (22 ± 0.06) pm. This can serve for an estimation of an upper limit of the ion temperature of $k_B T_e = (0.1\text{–}0.32)$ eV.

The H_β transition was identified in the spectra measured in first order. It was not observed in second order because of its low intensity. The intensity ratio of the H_α and H_β transitions was determined to be 15 ± 5 with a relatively high uncertainty due to the low intensity to noise ratio of the H_β transition. By assuming a Maxwell–Boltzmann distribution of the level population, an electron temperature of $k_B T_e = (0.30\text{–}0.43)$ eV was deduced. Since the electron density of

the present plasma was small, the assumption of a Maxwell distribution was somewhat questionable. Nevertheless, only a slightly higher temperature of $k_B T_e = (0.32–0.48)$ eV was found when a coronal model was applied [16]. In both cases, radiation transport was neglected in the calculations so that the temperature given represents an upper limit.

Figure 4 shows two scanned spectra in the vacuum ultraviolet spectral range where the emission of the L_α and L_β transitions can easily be seen. Strong emission of bands and lines were also observed in this wavelength region which will be discussed later. The intensity ratio of the L_α and L_β transitions was measured with a higher accuracy to be 16.5. For an optically thin plasma, the corresponding temperature of a Boltzmann level population is 62 eV. This excessive energy may indicate that this model is not applicable possibly because of the large distance of the energy levels. For these series of transitions to the ground state, a coronal model may be more suitable which gave an upper estimate of the electron temperature of $k_B T_e = 1.6$ eV. Nevertheless, this temperature is also factors higher than the above estimated temperatures. It has been reported recently [12, 17] that stationary inverted Lyman populations have been achieved in similar plasmas and the H atom temperature determined from the width of the Balmer α line is very high, >15 eV. The data support an internal chemical source of free energy.

In summary, the data indicate that the electron temperature of the present plasma was not higher than $k_B T_e = 0.5$ eV. On this basis, it was astonishing that the Lyman α and Lyman β transitions appeared in the spectra since an excitation energy of 10.2 eV and 12.1 eV is required, respectively. The same holds for the Balmer series as well. The Lyman alpha energy is a factor of about 20 above the measured thermal energy. The amount of electrons in the Maxwell tail that had enough energy to enhance the Lyman transition was 11 orders of magnitude lower than the total number of electrons which was measured to be $n_e = 2 \times 10^9$ cm^{-3} [12].

Figure 5 shows the spectra of figure 4 together with emission spectrum of the Werner bands of molecular hydrogen taken from [18]. The experimental spectra in this reference have a coincidence of 95% with theoretical results showing a high level of confidence. About 12 000 transitions were taken into account in the production of the latter spectra. The relative intensities are presented as stated in [18], and the lines were convoluted with the measured apparatus profile. Not only the vibrational but also numerous rotational transitions were identified in the spectra of the cell. Similar to atomic emission, electronic transitions in low quantum numbers were preferred by the molecules in the plasma of the cell. However, the relative intensities of the spectrum in figure 5(*b*) differed significantly from those of the spectrum of Roncin *et al* in the range around 110 nm. This part of the spectrum belongs to a Werner band with $v'' = 0$ and 1, respectively. The similar deviation in intensity at 110 nm has been discussed previously [19].

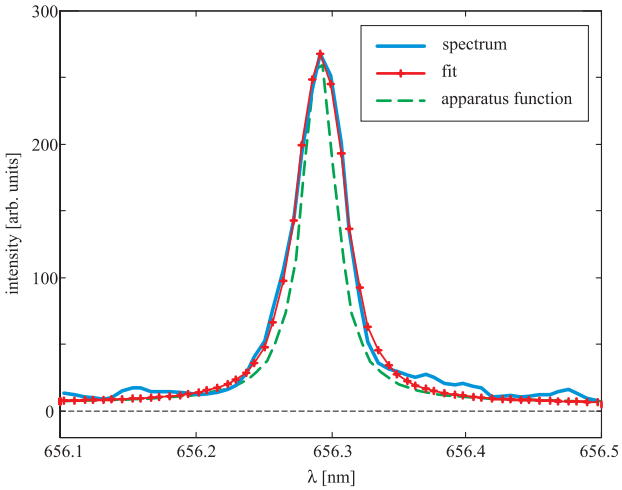

Figure 3. H_α emission measured in the second order together with the best fit and the apparatus function.

4. Discussion

The emission of VUV radiation, and in particular, Lyman series and Werner band emission was observed from a low

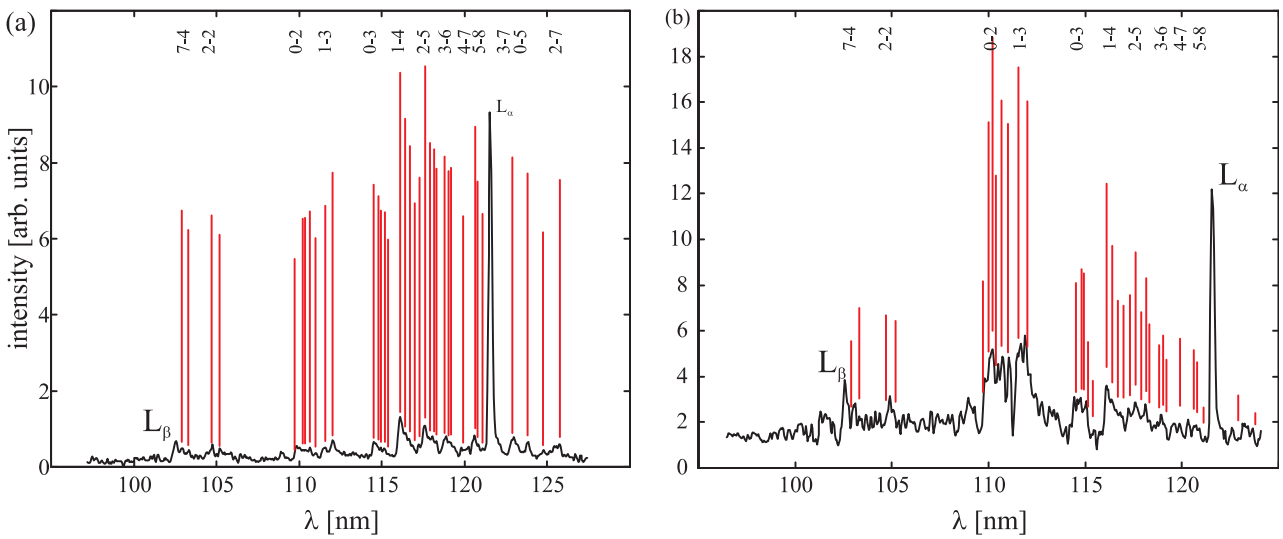

Figure 4. Examples of spectra of the atomic hydrogen L_α and L_β transitions and rotational–vibrational transition of molecular hydrogen belonging to the Werner band system.

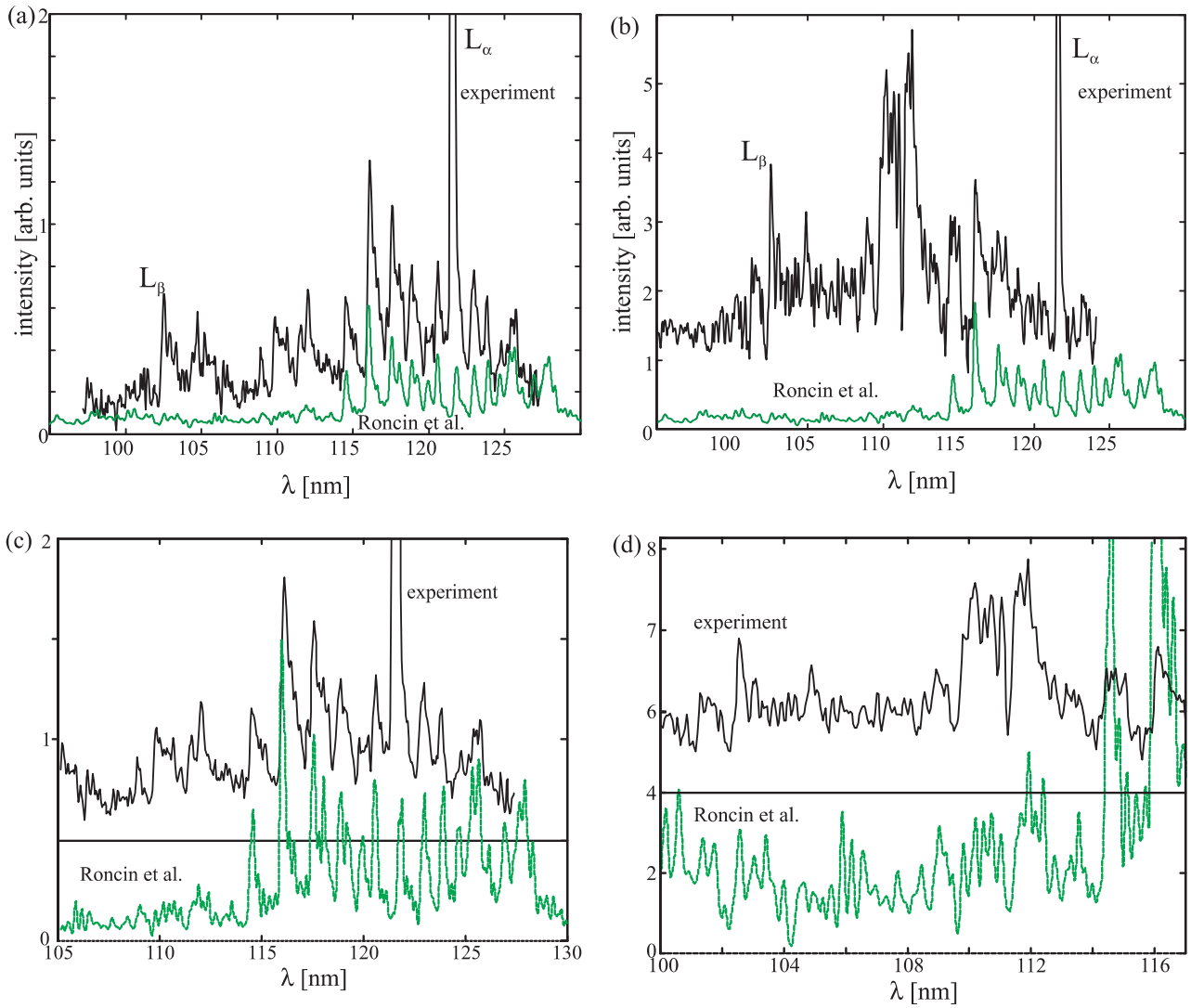

Figure 5. The measured molecular hydrogen spectra of figures 4(*a*) and (*b*) are compared with synthetic emission spectrum (intensity-scaled) after [18] in (*a*), (*c*) and (*b*), (*d*), respectively.

density plasma of quite moderate temperature similar to that in fluorescence tubes for general lighting. Such a plasma of an incandescently heated cell should not emit VUV radiation. The spectra showed that the plasma was far from thermal equilibrium. It was unlikely that the cell components, such as the heater and titanium mesh contributed to a non-Maxwellian free-electron velocity distribution. And, if the velocity distribution of free electrons determined the population of the electronic levels, it must have been an unusual one because of the preference for emission from a few specific electronic states of low quantum number.

Without the combination of K_2CO_3 and hydrogen, only blackbody radiation from the tungsten coil was observed at lower wavelengths. Based on the VUV emission, the plasma was predominately a hydrogen plasma. The ionization of atomic hydrogen requires 13.6 eV. In the cases where plasma was observed, no possible chemical reaction of the tungsten filament, the titanium screen, K_2CO_3, and low pressure hydrogen at a cell temperature of 750°C could be found which accounted for the generation and sustaining of the plasma and observed spectra. In fact, no known chemical reaction releases enough energy to form an atomic hydrogen plasma of sufficient free electron and excitation temperature.

The enthalpy of formation ΔH_p of potassium hydride is -14.13 kcal mole^{-1} [20]. Thus, the formation of potassium hydride releases only 0.59 eV per atom. But, potassium hydride decomposes in this temperature range (288–415°C). Thus, it cannot account for any emission of the hydrogen plasma.

The reduction of K_2CO_3 by hydrogen calculated from the heats of formation is very endothermic [21].

$$\begin{aligned} H_2 + K_2CO_3 &\rightarrow 2K + H_2O + CO_2 \\ \Delta H &= +122.08\,\text{kcal mole}^{-1} H_2. \end{aligned} \tag{1}$$

The reaction absorbs 2.5 eV per hydrogen atom.

The most energetic reaction possible with oxygen is the reaction of hydrogen to form water which releases 1.48 eV per atom of hydrogen; whereas, the energy of Lyman emission is greater than 10.2 eV per atom.

The dissociation of molecular hydrogen on the filament produces atomic hydrogen which may recombine to release

4.45 eV. Since atomic hydrogen is neutral, no contribution from the electric field of the filament was possible. Thus, excitation with energies of 4.45 eV or less was possible by the transport of thermal energy from the filament due to hydrogen dissociation followed by recombination. But this reaction is not sufficiently energetic to support the observed VUV emission.

Chemical energy may have been transported from regions outside of the annular region where most of the emission was observed. Dense and cold plasmas may have been created close to surfaces such as the titanium mesh due to chemical reactions. In such non-ideal plasmas with electron densities close to solid density and temperatures below 0.5 eV, the potential energy of the electrons becomes comparable to their kinetic energy, and energy levels of bound electrons in atoms such as hydrogen are altered such that excitation and ionization energies are lowered [22]. This also applies to other elements of the plasma such as potassium. The electronic energy levels of the different species are further distorted when interacting with each other. The dissociation of molecules and ionization of both the molecules and atoms may become more probable with more species. However, the lowering of the ionization and excitation energies by the state of 'non-ideality' in dense plasmas is only about 1 eV even for potassium. Thus, the most energetic chemical source possible, dissociated atomic hydrogen, could not have provided more energy than the Frank-Condon energy of 4.45 eV during recombination. Thus, a state of 'non-ideality' of the plasma cannot explain the energetic processes of at least 10 eV. Furthermore, the electron density measured using a Langmuir probe was $n_e = 2\times10^9$ cm^{-3} [12], 15 orders of magnitude less than solid density which eliminates any possibility of non-ideality in these plasmas.

The measured electron temperature, 0.5 eV, was over an order of magnitude too low to account for the hydrogen plasma. The filament electric field as the energy source of the excitation was also eliminated. The emission occurred even when the electric field was set and measured to be zero. The results cannot be explained by electric field acceleration of charged species since the estimated external field of the incandescent heater was extremely weak, about 1 V cm^{-1}. The electron mean free path at the operating pressure range of 0.1–1 mbar was about 0.1 cm corresponding to a mean energy from the acceleration of electrons in the field of about 1 V cm^{-1} of under 1 eV. Thus, electron collisional excitation of Lyman emission or hydrogen ionization by a so-called 'run-way-situation' of the velocities of free electrons is not probable.

Temperature dependent electric fields also arise due to the greater mobility of electrons compared to ions. The generated voltage U for a plasma with a similar ion and electron temperature T is given by

$$U = \frac{kT}{2e}\ln\frac{m_x}{m_e} \qquad (2)$$

where m_x is the mass of the ion such as the potassium ion or a proton, m_e is the electron mass, and e is the electron charge. From equation (2), the maximum voltage corresponding to the potassium ion is also of the order of 1 V.

Excitation of hydrogen in one region of the cell with transport to produce excited state emission from the centre of the cell was eliminated as a possibility. Emission was observed from the gas in the annular space between the central filament and the outer titanium mesh. Since the lifetimes of H ($n = 2$) and H ($n = 3$) are each approximately 10^{-8} s and the average velocity of the fastest hydrogen atoms was $<10^{-5}$ m s^{-1}, the excitation must have been local [23].

Multi-collisional processes may be possible [24], but very dense, high-pressure plasmas are required, and given an electron energy of 0.5 eV, about 30 concerted electron collisions would be required within 10^{-8} s—a definite impossibility.

Multiphoton absorption with excitation to intermediate virtual levels may be possible [25–27], but extraordinary power of the order of GW are required from pulsed lasers [28].

Resonant energy transfer from excited Ne_2^* excimer formed in high pressure microhollow cathode dicharges to hydrogen atoms in the ground state is possible to give predominantly Lyman α and Lyman β emission [24, 29, 30]. However, the formation of this plasma resulting in Ne_2^* excimers and excited Ne* atoms required a field of over 10^4 V cm^{-1} and a power density of several hundred kilowatts per cm^3. Whereas, the field in the heated cells was on the order of 1 V cm^{-1}, and power was only applied to the filament, and the pressure was 1000 times lower. Thus, this mechanism does not provide a source of energetic excited states that may resonantly transfer energy to atomic hydrogen.

The titanium-mesh and tungsten filament were present in all experiments. The emission was not observed with the cell alone, with hydrogen alone, or under identical conditions wherein Na_2CO_3 replaced K_2CO_3. When the power was interrupted, the emission decayed in about 2 s. Decay was recorded over a time greater than 10 000 times the typical duration of a discharge plasma afterglow [31]. This experiment showed, that plasma emission was occurring even though the voltage between the heater wires was set to and measured to be zero for a time duration which was surprisingly extended. Since the thermal decay time of the filament for dissociation of molecular hydrogen to atomic hydrogen was similar to the plasma afterglow duration which required the presence of K_2CO_3 the emission was determined to be due to a reaction of K_2CO_3 with atomic hydrogen. The minimum temperature requirement of the tungsten wire for emission also demonstrated the emission reaction's dependence on atomic hydrogen.

A source of energy other than that provided by the electric field or known chemical reactions must be considered for explaining our experimental findings.

5. Conclusion

The generation of the Lyman and Balmer series and the Lyman Werner bands of molecular hydrogen requires energies significantly greater than 10 eV. The formation of a hydrogen plasma by the cell loaded with K_2CO_3 on titanium and operated in hydrogen required a minimum temperature. The heat from the filament and possibly the weak dipole field from the filament may sustain the hydrogen plasma; but, the latter is not essential because hydrogen lines were emitted during times when this voltage was set to zero. Furthermore, given the observations, free electrons could not excite these states. In the case that the free electrons should have been thermalized, their temperature was too low to contribute to excitation

or ionization even from the tail of the velocity distribution. Longer range fields (of the order of mm) were only about a $1\ \mathrm{V\ cm^{-1}}$. In addition to electron collisional excitation, known chemical reactions, resonant photon transfer, and the lowering of the ionization and excitation energies by the state of 'non-ideality' in dense plasmas were also rejected as the source of ionization or excitation to form the hydrogen plasma.

The emission from a plasma was observed at low temperatures (e.g. $\approx 10^3$ K) from atomic hydrogen and potassium. The release of energy from hydrogen was evidenced by the hydrogen Lyman and Balmer emission which identified the presence of a hydrogen plasma. The persistence of emission following the removal of all of the power to the cell indicates that unknown chemical power source is present. The implication is that a new plasma and light source for the vacuum ultraviolet has been discovered.

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