PHYSICAL REVIEW E **84**, 055401(R) (2011)

Electrical Breakdown in Water Vapor

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(Received 22 July 2011; published 10 November 2011)

In this paper investigations of the voltage required to break down water vapor are reported for the region around the Paschen minimum and to the left of it. In spite of numerous applications of discharges in biomedicine, and recent studies of discharges in water and vapor bubbles and discharges with liquid water electrodes, studies of the basic parameters of breakdown are lacking. Paschen curves have been measured by recording voltages and currents in the low-current Townsend regime and extrapolating them to zero current. The minimum electrical breakdown voltage for water vapor was found to be 480 V at a pressure times electrode distance (pd) value of around 0.6 Torr cm (∼0.8 Pa m). The present measurements are also interpreted using (and add additional insight into) the developing understanding of relevant atomic and particularly surface processes associated with electrical breakdown.

DOI: 10.1103/PhysRevE.84.055401 PACS number(s): 52.80.Dy, 51.50.+v, 52.20.−j

I. INTRODUCTION

The electrical breakdown of water is of both fundamental and technological significance. There has been a recent increase in activity in the study of discharges created in water [1,2], with water electrodes [3] or in contact with water. This has been partially driven by the increasing applications of such discharges in plasma medicine, nanoscience, and environmental remediation [4–7]. It is therefore of immediate interest to determine how discharges are created in water [8–10]. Currently it is thought that discharges can only be formed in water vapor resulting from an induced phase change in the water. Therefore a starting point must be to have accurate knowledge of the electrical properties of water vapor and in particular its breakdown potential.

The theory of the initiation of electrical breakdown in gas was first formulated by Townsend, who considered the atomic and surface processes that would lead to a sustained current across a gap between two oppositely charged electrodes following a single ionizing event in the gas filling that gap. This theory predicts that the breakdown voltage (V_b), scales with the product pd, where d denotes the interelectrode gap length and p the pressure. pd is proportional to the number of collisions that one particle makes while covering some distance. A plot of the breakdown voltage dependence on pd is known as a Paschen curve and is unique to each gas or gas mixture. Another standard scaling parameter is E/N (E is the electric field and N is the gas number density), usually given in units of townsends ($1\ \text{Td} = 10^{-21}\ \text{V m}^2$) and which is proportional to the mean energy gained between collisions. Paschen curve measurements provide a stringent test of the understanding of the underlying processes in electrical breakdown.

Interestingly, to our knowledge there have been only two previous measurements of the Paschen curve for water vapor, which cover a very limited range of conditions at high pd (i.e., at low E/N) [11,12] and fail to identify the conditions for a minimum breakdown potential. As described here, more recent advances in experimental techniques now allow the first precise determination of this breakdown potential in the region of its minimum value. The present measurements can also be interpreted using, and add additional insight into, the new understanding of relevant atomic and particularly surface processes associated with electrical breakdown [13–16].

In this paper measurements of the Paschen curves for dc breakdown of water vapor over a full range of pd covering the minimum and the left-hand side of the Paschen curve are presented. Measurements have been made, under conditions where the Townsend theory is valid, for several electrode gaps and for several procedures of obtaining water samples. The principal problems in obtaining accurate measurements of the electrical breakdown potential are addressed by careful vapor and electrode preparation and simultaneous measurements of the current-voltage characteristics and the spatial profiles of the initial light emission from initiation of the subsequent discharge.

II. EXPERIMENTAL SETUP

The discharge chamber consists of two parallel plate electrodes 5.4 cm in diameter, a copper cathode, and a quartz anode covered by a transparent, conductive platinum film. These are placed inside a quartz cylinder, which fits tightly enough to prevent long-path breakdown while allowing a pump to evacuate the chamber to a pressure of $<10^{-6}$ Torr. The pump was then throttled and water vapor was allowed to flow through the chamber to maintain pressures (p) ranging from 0.03 to 20 Torr as measured using a capacitance manometer with an uncertainty $<0.2\%$.

The distance between the electrodes is adjustable and measurements have been performed for electrode separations (d) of between 0.5 and 3.1 cm. This chamber construction views allows both the axial and radial profiles of the discharge light emission to be recorded.

The electrical circuitry provides highly reproducible and reliable measurements of the temporally evolving voltage-current (VI) characteristic of the discharge. The breakdown voltage at any pd condition is then determined from the low-current limit of the discharge, i.e., by extrapolating the discharge voltage to zero current in voltage-current (VI) characteristics. High reproducibility of measurements is

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achieved by cathode conditioning in a hydrogen discharge prior to the measurements [17,18] as tested by repeated measurements under identical conditions. Therefore the overall uncertainty in determination of breakdown voltages could be determined from the instrumental sensitivity of the current and voltage measurements, and the statistical fluctuations in the repeated measurements. Measurements conducted with increasing and decreasing pressure are indistinguishable.

There are several key issues in the experimental measurement of electrical breakdown potentials in gases. One is making sure discharge operates in the Townsend regime and not in higher current regimes or in streamer breakdown regime. Here this is achieved by observing the light emission from the gap region and more specifically the axial emission profile. Axial profiles in the Townsend regime of the discharge exhibit an exponential increase in intensity (electron density) from the cathode towards the anode. The increase in current will lead to a gradual change in the axial profile due to the space charge, which is first revealed as the flattening of the (otherwise exponential) profile close to the anode and later as formation of a peak in the glow between two electrodes. The axial discharge profiles were recorded in the visible region of the spectra using an intensified CCD (ICCD) camera (Andor iStar DH720-18U-03). All the emission profiles are taken with the same camera sensitivity.

The other main issues with water vapor stem from gases dissolved in the liquid water, condensation on surfaces, and hydration of charged particles in the gas phase. It is thus necessary to ensure that the water vapor is devoid of any dissolved oxygen [19] and other volatile constituents. Previously repeated pump-freeze-thaw procedures have been used [12,19,20], by applying a sudden reduction of pressure to achieve freezing. However, in this case freezing is avoided mainly because a constant flow of gas is maintained. Water vapor is introduced into the discharge chamber from a container through a pressure regulating valve at a slow flow rate. The flow was chosen to achieve stable pressure and continuous pumping of the vapor from the liquid source and it was always below 10 sccm (Standard Cubic Centimeter per Minute). This produces an initial period of boiling water in the container which then becomes still. Extended pumping of the sample is applied prior to each set of measurements. Water vapor is maintained at a moderate pressure in the chamber for periods of 1–2 h in order to saturate the chamber walls. During measurements, ambient temperature in the vicinity of the discharge chamber was measured and found to remain constant at 297 ± 2 K. The procedure of preparing samples was tested by making measurements with and without extended pumping of the sample. Although differences were less than the scatter of repeated measurements under identical conditions, the water sample preparation described above was used for all reported measurements. Measurements were performed with two types of water samples: bidistilled, deionized water and ordinary tap water. Bidistilled water had a measured conductivity of $<0.005\ \mu\text{S/cm}$, with specified chlorine and organic carbon concentrations <0.5 mg/l.

III. RESULTS AND DISCUSSION

Figure 1 shows typical axial discharge visible emission profiles at a range of *pd* values for the two types of water samples. Axial profiles are produced from two-dimensional images of the discharge taking into account that no constrictions or filamentations occurred. The different lines show data for a number of *pd* values, each corresponding to a different E/N. The signal outside the discharge region is due to scattered light and is higher when overall emission intensity is larger. All the axial profiles, except that for the lowest *pd* value (0.2 Torr cm), exhibit an increase in emission intensity from the cathode towards the anode as characteristics of a Townsend discharge. Under those conditions normal and abnormal glows would have a peak in the gap between two electrodes. At the lowest *pd* and correspondingly highest E/N there is a marked difference in the axial emission profile with the intensity growing towards the cathode. This phenomenon has been observed before in hydrogen and hydrogen-containing molecules [21–25] and is associated with the excitation by fast neutrals.

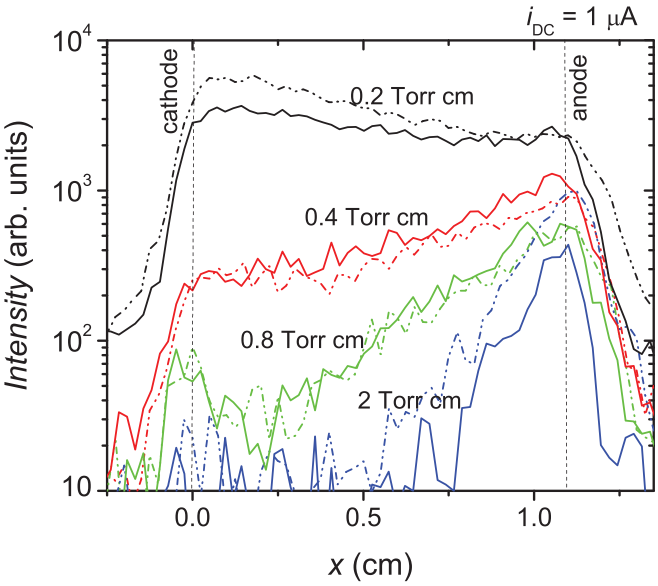


FIG. 1. (Color online) Axial profiles of the visible discharge emission in water vapor from bidistilled, deionized water (solid lines) and tap water (dashed lines) for $d = 1.1$ cm. All profiles are taken in low-current limit, at 1 μA. The corresponding E/N are 0.2 Torr cm/23 kTd; 0.4 Torr cm/4 kTd; 0.8 Torr cm/2 kTd; 2 Torr cm/850 Td.

In Fig. 2 the measured breakdown voltages as a function of pressure times interelectrode gap (the Paschen curve) for bidistilled and tap water for a 1.1-cm gap are presented. The data show that there are no measurable differences in the breakdown voltages for the two types of water samples. These conclusions are also supported by the similarity in the axial emission profiles for both samples in Fig. 1. This also was found at larger electrode gaps, indicating that the tap water impurities do not affect the value of the dc breakdown potential. This can be explained since some of the dissolved impurities are not volatile and also the breakdown is dominated by ionization through the high-energy electrons. The ionization potentials of water and any impurities have similar shapes, magnitudes, and thresholds and thus the breakdown is not very much affected by impurities, unlike measurements of low-energy attachment [19]. Thermal attachment of any

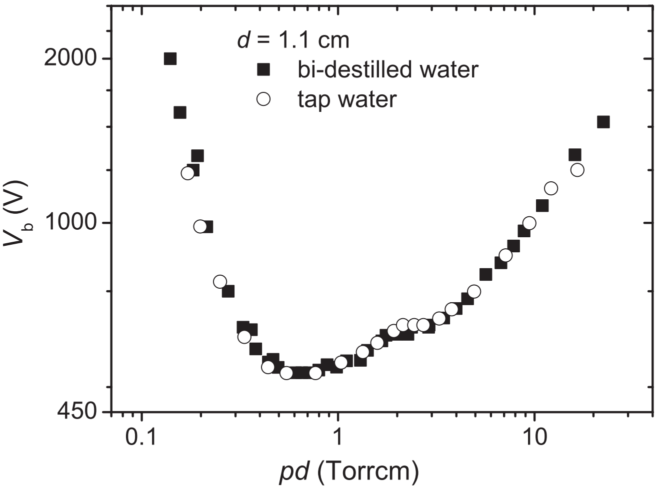
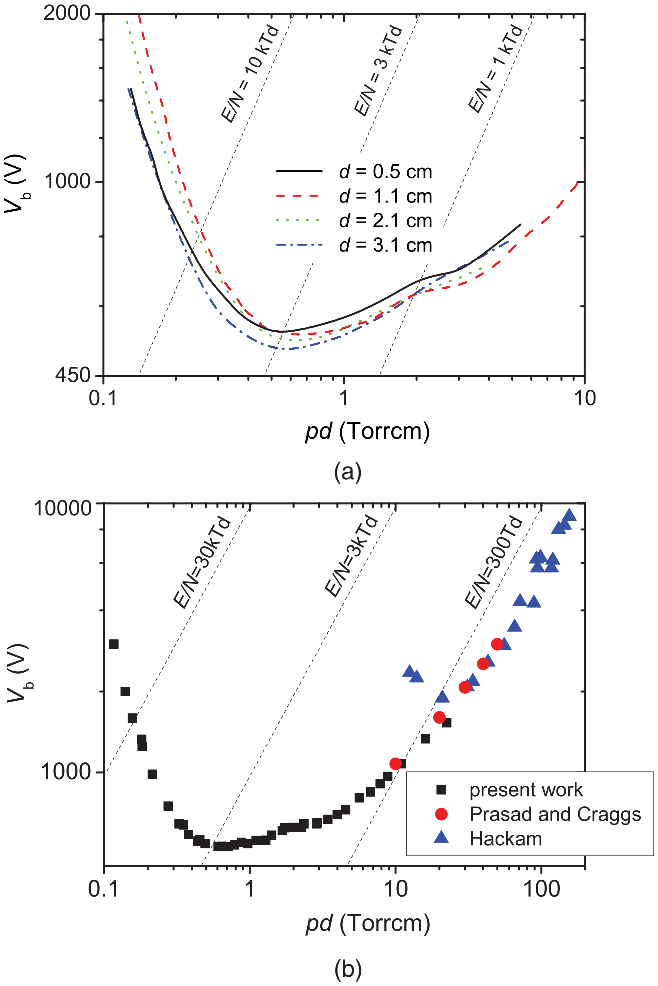


FIG. 2. Breakdown voltage vs pd in water vapor from bidistilled, de-ionized water (solid squares) and tap water (open circles) for $d = 1.1$ cm.

impurity will show as water itself has no attachment at low energies [19].

In Fig. 3(a) the Paschen curves measured for different electrode gaps are presented. The characteristic E/N values are also shown on the plot. All the curves agree well within the experimental uncertainties on the left-hand side and around the minimum. The maximum pressure that could be achieved and therefore the maximum pd value was limited by the vapor pressure of water at the room temperature (around 20 Torr). An option to reach high pd is to increase the interelectrode gap but this would require an apparatus with much larger electrode radii. This is required to maintain a diameter-to-gap ratio that would limit the radial charged particle losses to an acceptable level for the one-dimensional Townsend theory to be valid.

On the right-hand side, the Paschen curves obtained for $d = 0.5$ and $d = 1.1$ cm manifest an inflection point around 2 Torr cm, i.e., corresponding to vapor pressures of 4 and 1.8 Torr, respectively. Repeated measurements confirm the existence of this inflection point for these smaller electrode gaps and its absence for the larger gaps. The explanation for inflection could not be found in the surface-related phenomena since the cathode is treated in the same fashion before every measurement. The pressures at which they are observed are well below the vapor pressure of water at room temperature (around 20 Torr). In any case this explanation would scale with p and not with pd and would be effective for all values of d. Likewise three-body collision, pressure-dependent processes can be excluded as these would not scale with pd but also with p. Presence of inflection at higher pressures and absence at lower pressures could be consistent with the proximity of the dew point. This explanation, however, would also scale with p and not with pd and would be effective for all chosen d. We therefore conclude that at higher vapor pressures additional phenomena, other than those considered in the Townsend theory, are present that satisfy pd scaling and lower the breakdown voltage. Although an interesting phenomena, which is worthy of further study, this inflection is a minor perturbation on the measured Paschen curve.



(a)

(b)

FIG. 3. (Color online) (a) Paschen curves of water vapor for different interelectrode distances. (b) Comparison of our data for $d = 1.1$ cm (squares) with the experimental data of Prasad and Craggs (circles) [11] and Hackam (triangles) [12]. In [11] the cathode was made of platinum, while the electrode gap was not stated. In [12] measurements were made with a stainless steel cathode with an electrode gap $d = 0.5$ cm.

Figure 3(b) compares the present measurements with those from the only other two previous measurements of the Paschen curves for water vapor [11,12]. The data of Prasad and Craggs [11] is in excellent agreement with our data where there is overlap in pd values and then continues smoothly to higher pd values. On the other hand, the Paschen curve of Hackam [12], while in excellent agreement at the highest pd values with both an extrapolation of our results and the data of Prasad and Craggs, displays a minimum at a voltage of ~1800 V and pd of the order of 20 Torr cm.

In the present measurements, discharge emission measurements allow us to identify the nature of the breakdown, i.e., to ascertain the low-current Townsend regime. However, in our experiments we do observe a higher current streamer breakdown at the highest pd under some conditions. This suggests that Hackam's data at the flat minimum and the region to the left of it may have been obtained for streamer breakdown and so does not represent the onset of Townsend's electrical breakdown.

IV. CONCLUSION

Measurements of the Paschen curve in water vapor have been made. The electrical breakdown minimum voltage for water vapor was found to be 480 V and occurs at a *pd* value of around 0.6 Torr cm (0.8 Pa m). There is generally good agreement between the curves measured for electrode gaps ranging from 0.5 to 3.1 cm and gas pressures ranging from 0.03 to 20 Torr. No significant differences were observed between measurements made with water vapor produced from bidistilled, deionized water and regular tap water in either the Paschen curves or in the recorded discharge emission profiles.

A small inflection in the otherwise smooth Paschen curve for electrode gaps smaller than 1 cm, i.e., at vapor pressures above 2 Torr was observed. We conclude that at higher vapor pressures additional phenomena, other than those considered in the Townsend theory, are present that appear to satisfy *pd* scaling and lower the breakdown voltage for a narrow range of conditions.

In general the present results connect very smoothly to the two previous data sets [11,12] taken at higher *pd* values. However, there is a distinct deviation in a narrow range of *pd* with one set of the data [12] predicting a much higher breakdown voltages and *pd* value of the minimum of the Paschen curve. It is argued here that in that case streamer breakdown may have been observed.

To our knowledge this is the first Paschen curve obtained in water vapor at the low *pd* values associated with the minimum breakdown voltage and left side of the Paschen curve in gases. The measurements also provide the first axial emission profiles in this high E/N regime and a strong effect associated with the excitation of hydrogen emission by fast neutral atoms in hydrogen-containing gases [21–25] has been observed.

ACKNOWLEDGMENTS

The work was supported by Projects No. ON 171037 and III 41011 of the MES of Serbia.

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