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CHMWTR: A Plasma Chemistry Code for Water Vapor

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The CHMWTR code tracks the evolution of 21 ionic and neutral species in a water vapor plasma excited by a slowly varying electric field. This report discusses the physics of water vapor breakdown, and describes the assumptions and methods used in developing the code. The code results are used to determine the breakdown field in water vapor under typical conditions. The conductivity of the plasma is also computed. Since this is an interim report, it concludes with task areas for further study and development.

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Contents

I. Introduction 1

II. Overview of Water Plasma Chemistry 2

III. Model Equations 3

IV. Reactions 6

V. Remarks on Numerical Solution 10

VI. Simulation Results 11

VII. Summary and Task Areas 14

VIII. Acknowledgements 15

References 16

I. INTRODUCTION

This interim report describes the physics of electrical discharges in water vapor, and describes a computer code designed to model such discharges. The code is called CHMWTR, in analogy with the NRL legacy code CHMAIR, which was written to model air plasmas. The CHMWTR code is written using the commercial software package *Mathematica*. The primary task of the code is to solve for the composition and temperature of the water vapor plasma excited by an applied electric field.

On Earth, water vapor occurs naturally only as a minor constituent of air. In contrast, CHMWTR treats a gas of pure water vapor. The interest in drawing an electrical discharge in such a gas arises from the possibility of creating an underwater vapor channel using a laser [1]. Once the vapor channel is created, it might guide an electrical discharge along its axis, raising the possibility of creating a guided underwater discharge. The CHMWTR model can be applied in this scenario provided the model is started after the channel expands enough to be treated as an ideal gas. The CHMWTR model might also be of astrophysical interest, *e.g.*, in connection with the atmospheres of icy moons in the outer solar system [2]. Furthermore, the framework can be easily adapted to other scenarios.

An electrical discharge is the process of gas breakdown (ionization and dissociation) driven by an applied electric field. When the discharge length is long, the breakdown is preceded by streamer formation [3]. A streamer is a traveling ionization front driven by field enhancement at the tip of a plasma column aligned parallel to the applied field. When streamers coalesce, a leader is formed which propagates in a similar way. When the leader finds ground, or even before, strong ohmic heating, and therefore avalanche ionization, sets in. This can lead to a high degree of gas breakdown.

The process of the breakdown of a gas by avalanche ionization is highly nonlinear. This is due not only to the nature of the avalanche process, but also to the exponential dependence of the ionization rate on the electron temperature. This high degree of nonlinearity, on the one hand, makes the breakdown problem a difficult one to solve. On the other hand, it leads to the possibility of identifying a well defined *breakdown field*. This is because, due to the high nonlinearity, a field slightly below the breakdown field will barely perturb the gas, while a field slightly above the breakdown field will lead to the establishment of a fully ionized plasma. Predicting the breakdown field under varying conditions is a primary purpose of the

CHMWTR code. Another purpose is to evaluate the conductivity of the plasma at various times during the breakdown.

Avalanche ionization must always start with at least one free electron. Although a discharge may be drawn using the small number of background free electrons that are always present, greater control is afforded by pre-ionizing the gas using a laser. Ultra-short pulse lasers can provide this pre-ionization in the form of a long narrow column (meters in length, sub-millimeter in diameter) due to the fact that such pulses can propagate in a self-guided mode. This self-guided mode, called an optical filament, results from a balance of Kerr self-focusing and plasma defocusing [4]. The intensity at the core of such a filament is such that multi-photon ionization creates a plasma filament wherever the optical filament exists. The plasma created by an ultra-short pulse optical filament is weakly ionized and cold. The gas temperature is barely perturbed due to the fact that the optical pulse is too short to couple energy to the plasma via collisions.

CHMWTR is designed to be a pure chemical rate equation code, *i.e.*, there is no attempt to rigorously incorporate effects resulting from finite spatial derivatives. However, it is envisaged that the code will be coupled to a quasi-static transmission line model of the type proposed by Lampe *et al.* [5]. This model assumes that the discharge propagates at a constant speed, v, which allows a one dimensional problem in (z, t) to be formulated as an effective zero-dimensional problem in the variable $t - z/v$. The output of this type of calculation is the voltage waveform required to drive the discharge at the velocity v.

II. OVERVIEW OF WATER PLASMA CHEMISTRY

Upon photo-ionization by a mJ class ultra-short pulse laser filament, water vapor becomes a weakly ionized plasma consisting of electrons and H_2O^+. If no further excitation is applied, frequent encounters between H_2O^+ and H_2O lead to rapid formation of the hydronium ion, H_3O^+. The electrons either recombine with hydronium in a reaction such as

$$e + H_3O^+ \rightarrow H_2O + H, \tag{1}$$

or attach to the hydroxyl radical, forming OH^-. If, on the other hand, an electric field is applied, ohmic heating has the potential to lead to catastrophic breakdown of the gas. This process is dominated by avalanche ionization, and eventually, thermalization of the plasma

TABLE I: Neutral Species in CHMWTR

s	Formula	Ionization Energy (eV)	Dissociation (eV)	e^- Affinity (eV)	p^+ Affinity (eV)
2[a]	H_2O	12.60	5.10	-	7.38
3	H_2	15.43	4.48	1.09	4.38
4	OH	13.02	4.40	1.83	6.16
5	O_2	12.07	5.11	0.46	1.04
6	H	13.60	-	0.76	2.65
7	O	13.62	-	1.45	5.03

[a]The species index $s = 1$ is reserved for electrons

by electron-ion collisions. In the highest state of excitation, the plasma consists of e^-, H^+, and $O^{(n+)}$, where n is an integer varying over the charge states of oxygen that exist in the plasma. One expects $n \leq 6$ due the fact that the K shell electrons have binding potentials of several hundred electron volts.

The neutral species tracked by CHMWTR are displayed in Table I, along with ion energetics data, mostly taken from NIST (http://webbook.nist.gov/chemistry/form-ser.html). Most of the species have significant electron affinites, making it necessary to track negative ions. The fact that H_2O has the highest proton affinity explains the predominance of the hydronium ion in many scenarios. The ionic species tracked by CHMWTR are displayed in Table II. At present, CHMWTR allows for multiple ionization of oxygen up to $O^{(3+)}$.

III. MODEL EQUATIONS

The fundamental assumption of CHMWTR is that a fluid model describes gas breakdown. This requires that the distribution function for any species be Maxwellian. Furthermore, it is assumed that the translational, rotational, and vibrational degrees of freedom of all heavy particles are in thermodynamic equilibrium. The energy of the plasma is therefore characterized by a gas temperature, an electron temperature, and the potential energy of all the excited, ionized, or dissociated species that constitute the plasma at some instant.

TABLE II: Ionic Species in CHMWTR

s	Formula	Ionization/Detachment (eV)
8	H_2O^+	-
9	H_2^+	-
10	OH^+	-
11	O_2^+	-
12	H^+	-
13	O^+	35.12
14	$O^{(2+)}$	54.94
15	$O^{(3+)}$	-
16	OH^-	1.83
17	H^-	0.76
18	H_2^-	1.09
19	O^-	1.45
20	O_2^-	0.46
21	H_3O^+	-

Although the present version does not track the electronically excited states, it is envisioned that excited states will eventually be incorporated into the model. A vibrational model, perhaps patterned after what is used in CHMAIR, may also be included in the future.

Let the chemical species be indexed by an integer s. Let each species have density n_s, mass m_s, and charge q_s. Heavy gas particles ($m_s > m_e$) have temperature T_g, and electrons have temperature T_e. The gas energy density is Θ_g, and the electron energy density is Θ_e. The equations of state are

$$P_s = n_s k T_s \tag{2a}$$

$$\Theta_e = \frac{3}{2} n_e k T_e \tag{2b}$$

$$\Theta_g = T_g \sum_{s \neq e} c_{vs} m_s n_s \tag{2c}$$

Here, c_{vs} is the specific heat at constant volume for species s [14]. The equations describing

the evolution of particle number have the form

$$n_s'(t) = C_s(t) - D_s(t) \tag{3}$$

where C_s is the rate of creation of species s and D_s is the corresponding rate of destruction. In order to compute C_s and D_s, the reactions describing the plasma chemistry have to be analyzed. The list of reactions in CHMWTR is given in Table III. Forming C_s and D_s from this data is discussed below. The equations describing the evolution of energy density are

$$\Theta_e'(t) = Q_\Omega + Q_{eg} - \eta Q_R + \sum_r H_{er} \tag{4}$$

$$\Theta_g'(t) = -Q_{eg} - (1-\eta) Q_R + \sum_r H_{gr} \tag{5}$$

Here, Q_Ω is ohmic heating, Q_{eg} is thermalization by electron collisions with heavy particles, Q_R is radiative cooling, H_{er} is the electron heating due to reaction r, and H_{gr} is the gas heating due to reaction r. The weighting factor η determines how much of the radiative cooling affects the electrons. CHMWTR currently assumes that radiative cooling is weighted by partial pressure. Once Θ_e and Θ_g are found, T_e and T_g are known via the equations of state.

The ohmic heating term Q_Ω plays a crucial role as the source of plasma excitation. CHMWTR uses the formula

$$Q_\Omega = \frac{n_e e^2 E^2}{m_e \sum_{s \neq e} \beta_s n_s} \tag{6}$$

where E is the applied electric field, which may vary in time provided the frequency is small compared to the electron collision frequency. The variables β_s are rates (cm^3/s) for electron collisions with species s. They are given by

$$\beta_s = \frac{4}{3}\sqrt{\frac{8kT_e}{\pi m_e}}\bar{Q}_s \tag{7}$$

where $\bar{Q}_s$ is the cross section for electron collisions with species s. For ions, this is

$$\bar{Q}_s = \frac{32}{\pi}\left(\frac{\pi m_e}{8kT_e}\right)^2 \left(\frac{q_s e}{4\pi\epsilon_0 m_e}\right)^2 \ln\Lambda \quad \text{(ions)} \tag{8}$$

with Λ the Coulomb logarithm. For electron-neutral collisions the cross section is assumed constant.

The thermalization term Q_{eg} becomes important when the plasma is highly ionized so that electrons can rapidly heat the heavy particles. It is given by

$$Q_{eg} = 3k(T_g - T_e)n_e \sum_{s \neq e} \frac{m_e}{m_s} \beta_s n_s \tag{9}$$

The crucial observation is that the rate of thermalization is reduced by the mass ratio, m_e/m_s, relative to the electron collision frequency.

The radiative cooling term Q_R allows heat to escape the system, which prevents the temperature from eventually diverging under excitation by a constant applied field. CHMWTR uses a simple LTE model for an optically thin plasma:

$$Q_R = \frac{4\sigma_{SB} T_g^4}{\ell_1} \tag{10}$$

Here, σ_{SB} is the Stefan-Boltzmann constant, and ℓ_1 is the mean free path of a photon, which is estimated based on table 5.2 in Ref. [6]. This model has the property that Q_R tends to be very small until the plasma does in fact reach LTE, so that the errors made during the non-equilibrium phase are unimportant.

The reaction terms H_{er} and H_{gr} are due to the heat of reaction, and the change in electron density. For instance, in reaction 1 from Table III, an electron must use 12.6 eV to ionize a water molecule. This energy has to come from the reservoir represented by Θ_e. If it is assumed the new electron is born at rest, no further accounting is necessary. On the other hand, in reaction 4, an electron is absorbed by the gas. The energy represented by Θ_e is reduced not only by the 4.34 eV heat of reaction, but also by the loss of an electron, which on average carries an energy Θ_e/n_e. This accounting is discussed further below.

IV. REACTIONS

Even in a gas with only two elements, a very large number of reactions are possible, and in practice, a computer model can only account for some fraction of them. In a gas breakdown problem, it is expected that impact ionization is the most important process. The full list of reactions currently included in the CHMWTR code is presented in Table III. The impact ionization and dissociation rates for molecules were taken from Refs. [7] and [8] (1-6,11-16), with 3-body recombination obtained from detailed balance (34). Reactions pertaining to oxygen were gathered from CHMAIR [9–11] (29-33,35,36). A report on flame

ignition modeling [12] was used to gather rates for certain neutral re-arrangements (17-20). The UMIST database for astrochemistry (www.udfa.net) was used to obtain rates pertaining to hydronium recombination (7-10). The ionization rates for atoms and atomic ions were taken from [13], with 3-body recombination rates obtained from detailed balance (21-28).

Given the data in Table III, the creation and destruction rates for each species have to be formed. The *net* creation rate for some species s, due to a reaction r, is of the form $\mathcal{N}_{sr}\alpha_r(T)\Pi_r$, where $\alpha_r(T)$ is a temperature-dependent rate coefficient, Π_r is the product of the densities of the reactants, and $\mathcal{N}_{sr}$ is the net number of particles of species s produced during one encounter. CHMWTR uses a piecewise construction for $\alpha_r(T)$, with each term having the form

$$\alpha_r(T) = c_0 T^{c1} e^{-c_2/T} \tag{11}$$

Here, T may be either T_e or T_g, depending on r. Table III displays the fitting constants c_0, c_1, and c_2 for each reaction. The units of c_0 are $\mathrm{cm}^{3(b-1)}/\mathrm{s}$, where b is the number of bodies before the encounter. In some cases more than one set of constants are given for a particular reaction, which means that the total rate is the sum over the rates given by each set of constants. Each term only contributes in the temperature range indicated (if no range is indicated, the formula is applied at all temperatures).

As an example, consider the reaction described in Eq. (1), which is listed as reaction 9 in Table III. Assign the species labels according to the indices in tables I and II (for electrons $s = 1$). If reaction 9 were the only reaction, then one would have

$$C_2(t) = C_6(t) = D_1(t) = D_{21}(t) = \alpha_9[T_e(t)]n_1(t)n_{21}(t) \tag{12}$$

with all other creation and destruction rates vanishing. In other words, the reaction creates water and hydrogen, and destroys electrons and hydronium, all at the rate given by $\alpha_9\Pi_9 = \alpha_9 n_1 n_{21}$. In order to add additional reactions, one simply adds their contributions to the various C_s and D_s. CHMWTR implements a scheme to automate much of this process.

In addition to creation and destruction rates, the heating terms H_{er} and H_{gr} also have to be determined from Table III. These are given by

$$H_{er} = \alpha_r \Pi_r \left(\eta_r \epsilon_r - d_r \frac{\Theta_e}{n_e} \right) \tag{13}$$

$$H_{gr} = \alpha_r \Pi_r \left((1-\eta_r) \epsilon_r + d_r \frac{\Theta_e}{n_e} \right) \tag{14}$$

where ϵ_r is the heat of reaction, η_r is the portion of the heat of reaction that goes to electrons, and

$$d_r = \begin{cases} |\mathcal{N}_{1r}| & \mathcal{N}_{1r} < 0 \\ 0 & \text{otherwise} \end{cases} \tag{15}$$

accounts for the absorption of kinetic energy in recombination or attachment.

TABLE III: CHMWTR Reactions

Index	Formula	Heat (eV)	c_0 $\text{cm}^{3(b-1)}/\text{s}$	c_1	c_2 (eV)	Range (eV)
1	$e + H_2O \rightarrow e + e + H_2O^+$	-12.6	2.48E-11	1.5	0	
			3.00E-8	0.23	18.6	
2	$e + H_2O \rightarrow e + e + H + OH^+$	-18.1	2.39E-9	0.61	18.8	$T_e < 21.7$
			1.20E-8	0.20	26.2	$T_e > 21.7$
3	$e + H_2O \rightarrow e + e + H^+ + OH$	-17.0	3.97E-10	1.05	20.2	$T_e < 13.7$
			9.06E-9	0.25	34.2	$T_e > 13.7$
4	$e + H_2O \rightarrow H^- + OH$	-4.34	6.87E-13	2.08	-0.09	$0.09 < T_e < 0.544$
			1.63E-10	0.79	3.32	$0.544 < T_e < 1.72$
			2.96E-9	-1.39	6.34	$T_e > 1.72$
5	$e + H_2O \rightarrow H + H + O^-$	-8.0	1.96E-11	0.77	4.11	$T_e < 2.17$
			4.82E-10	-1.19	7.76	$T_e > 2.17$
6	$e + H_2O \rightarrow H + OH^-$	-3.27	5.20E-12	0.81	3.73	$T_e < 1.72$
			1.11E-10	-1.27	7.05	$T_e > 1.72$
7	$H_2O^+ + H_2O \rightarrow H_3O^+ + OH$	2.37	2.1E-9	0	0	
8	$OH^+ + H_2O \rightarrow H_3O^+ + O$	2.37	1.3E-9	0	0	
9	$H_3O^+ + e \rightarrow H_2O + H$	6.22	1.74E-8	-0.5	0	
10	$H_3O^+ + e \rightarrow OH + H + H$	1.11	4.15E-8	-0.5	0	
11	$e + OH \rightarrow e + e + OH^+$	-12.95	1.99E-10	1.78	13.8	
12	$e + OH \rightarrow e + O + H$	-4.4	2.08E-7	-0.76	6.91	
13	$e + OH^+ \rightarrow e + O + H^+$	-5.01	1.63E-4	-2.04	15.1	

continued...

TABLE III: CHMWTR Reactions (continued)

Index	Formula	Heat	c_0	c_1	c_2	Range
14	$e + H_2 \rightarrow e + e + H_2^+$	-15.43	1.03E-8	1.61	17.9	
15	$e + H_2 \rightarrow e + H + H$	-4.48	2.51E-7	-0.8	10.9	
16	$e + H_2^+ \rightarrow e + H^+ + H$	-2.65	1.79E-7	-0.87	6.92	
17	$H + H + H \rightarrow H_2 + H$	4.48	1.55E-34	-1.0	0.0	
18	$H + H + H_2 \rightarrow H_2 + H_2$	4.48	1.55E-34	-1.0	0.0	
19	$O + OH \rightarrow H + O_2$	0.72	3.74E-11	0.28	0.0	
20	$H + H + OH \rightarrow H_2O + H$	5.10	4.61E-34	-2.0	0.0	
21	$e + H \rightarrow e + e + H^+$	-13.6	7.78E-9	0.41	13.6	$T_e < 20$
			1.31E-7	-0.24	32.57	$T_e > 20$
22	$H^+ + e + e \rightarrow H + e$	13.6	6.38E-31 -	1.09	0.0	$T_e < 20$
			1.07E-29	-1.74	18.97	$T_e > 20$
23	$e + O \rightarrow e + e + O^+$	-13.62	1.57E-8	0.43	14.75	$T_e < 28$
			2.65E-7	-0.15	39.87	$T_e > 28$
24	$O^+ + e + e \rightarrow O + e$	13.62	2.59E-30	-1.07	1.13	$T_e < 28$
			4.39E-29	-1.65	26.25	$T_e > 28$
25	$e + O^+ \rightarrow e + e + O^{(2+)}$	-35.12	5.87E-9	0.41	36.84	$T_e < 28$
			9.31E-8	-0.14	63.20	$T_e > 28$
26	$O^{(2+)} + e + e \rightarrow O^+ + e$	35.12	9.72E-31	-1.09	1.72	$T_e < 28$
			1.54E-29	-1.64	28.08	$T_e > 28$
27	$e + O^{(2+)} \rightarrow e + e + O^{(3+)}$	-54.94	2.02E-9	0.45	55.94	$T_e < 28$
			3.04E-8	-0.08	82.22	$T_e > 28$
28	$O^{(3+)} + e + e \rightarrow O^{(2+)} + e$	54.94	3.35E-31	-1.05	1.00	$T_e < 28$
			5.04E-30	-1.58	27.28	$T_e > 28$
29	$e + O_2 \rightarrow e + O + O$	-5.11	5.72E-10	0.50	8.4	
			1.30E-10	1.50	8.4	
			3.83E-9	0.50	4.5	

continued...

TABLE III: CHMWTR Reactions (continued)

Index	Formula	Heat	c_0	c_1	c_2	Range
			1.70E-9	1.50	4.5	
30	$O_2 + O_2 \rightarrow O + O + O_2$	-5.11	5.8E-9	-0.83	5.12	
31	$O_2 + O \rightarrow O + O + O$	-5.11	1.3E-8	-1.00	5.12	
32	$O + O + O_2 \rightarrow O_2 + O_2$	5.11	8.6E-34	-0.33	0.0	
33	$O + O + O \rightarrow O_2 + O$	5.11	1.9E-33	-0.50	0.0	
34	$H_2O^+ + e + e \rightarrow H_2O + e$	12.6	4.92E-30	-1.27	6.00	
35	$e + O_2 \rightarrow e + e + O_2^+$	-12.1	1.27E-9	1.36	11.41	$T_e < 6.0$
			1.77E-8	0.57	18.69	$T_e > 6.0$
36	$O_2^+ + e \rightarrow O + O$	6.99	2.1E-8	-0.5	0.0	

V. REMARKS ON NUMERICAL SOLUTION

CHMWTR integrates the system of differential equations describing the water vapor breakdown using *Mathematica*'s general purpose solver, `NDSolve`. Although the algorithm works well in general, the gas breakdown problem under consideration has some pathologies that can lead to a failure of the algorithm at late times during the plasma evolution. The difficulty lies in the fact that the starting assumptions are eventually violated. Two of the assumptions in question are that (i) the model is practical at any temperature, and (ii) the density of any species is high enough to be treated as a fluid. The first assumption tends to violated if the applied field is above the breakdown field, the second if it is below.

If the applied field is higher than the breakdown field, then the temperature will become very great, and the system of differential equations will become stiff because of the rapidity of certain processes. As a result, *Mathematica* will start using very short time steps in the integration, and the maximum number of steps may be exceeded. One can increase the maximum number of steps, but the simulation time might become longer than is practical. It is possible that techniques for solving stiff systems of equations would mitigate this particular difficulty.

If the applied field is below the breakdown field, then the electron density will eventually drop precipitously. This leads to a problem in computing the electron temperature, due to division by a small number. The software will at some point report an error message announcing that the integration had to be stopped due to an error tolerance being exceeded. Unfortunately, *Mathematica* tends to report this error too late. The user has to intelligently study the output to identify the point at which the integration really failed. There will usually be an abrupt change in electron temperature at this point. A useful rule of thumb is that the electron density should satisfy $n_e \gg 1$ cm^{-3} at all points where the solution is valid.

VI. SIMULATION RESULTS

In this section, CHMWTR is used to study a scenario in which water vapor with temperature and pressure of 1000 K and 138 kPa, is excited by an applied electric field. The initial gas is composed of 10^{19} cm^{-3} of H_2O, 10^{16} cm^{-3} of H_2O^+, and 10^{10} cm^{-3} of all other heavy particles (electron density is given by charge neutrality). The initial electron temperature is taken as 1 eV. The choice of plasma density corresponds to what is typically achieved by femtosecond filaments in air. The choice of temperature and pressure is at this point somewhat arbitrary. Further study is needed to determine the range of parameters that might occur in an underwater vapor channel, assuming that is the final application.

We consider three simulation runs. In run 1, the gas is allowed to relax without being subjected to any applied field. In run 2, an electric field pulse is applied, but is limited in amplitude to prevent full breakdown. In run 3, a somewhat larger electric field pulse is applied so that full breakdown is achieved. The electric field pulse has the form

$$E(t) = E_0 \begin{cases} t/t_{\text{rise}} & 0 < t < t_{\text{rise}} \\ (t_{\text{rise}} + t_{\text{fall}} - t)/t_2 & t_{\text{rise}} \le t < t_{\text{rise}} + t_{\text{fall}} \\ 0 & \text{otherwise} \end{cases} \tag{16}$$

where in all cases $t_{\text{rise}} = 5$ ns and $t_{\text{fall}} = 1$ μs.

The results from run 1 are illustrated in Fig. 1. Fig. 1(a) shows that the conductivity falls from 200 mho/m at the beginning, to less than 1 mho/m after 100 ns. The electron and gas temperatures are shown in Fig. 1(b). The electron temperature falls from 11600 K to 500 K in a few ns. The electron temperature actually falls below the gas temperature

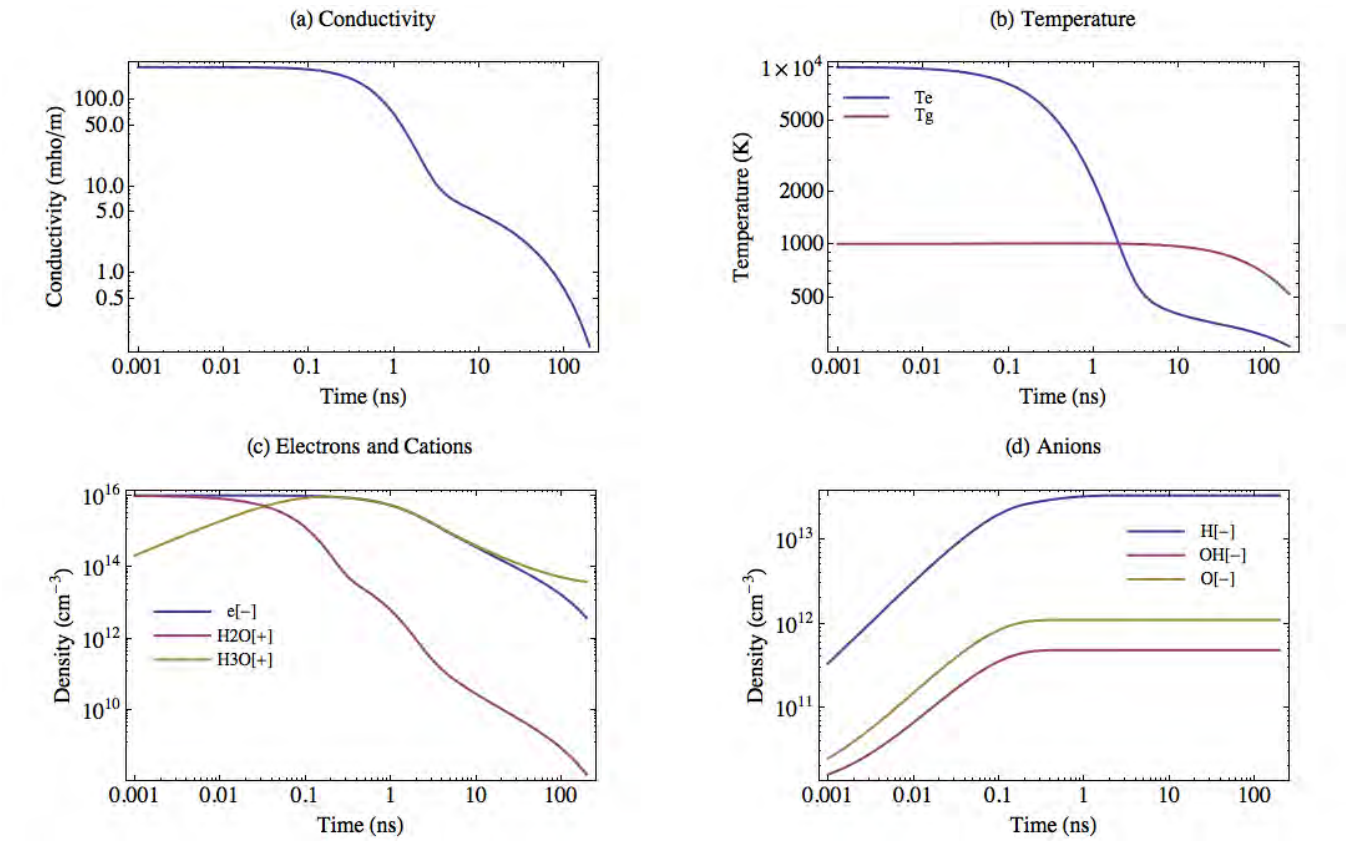

FIG. 1: Water vapor plasma with no applied field ($E_0 = 0$).

due to cooling mechanisms such as ionization and dissociation. The fall in gas temperature is entirely due to the radiation model. The density of electrons and the most important cations are shown in Fig. 1(c). Within a few hundred ps, hydronium becomes the dominant cation. Within a few ns, the hydronium mostly recombines, and the electron density falls correspondingly. As the plasma density drops, a variation between the hydronium and electron densities becomes visible. This difference is due to the presence of anions, as shown in Fig. 1(d). In the present model, the dominant anion, H^-, is only produced by dissociative attachment (reaction 4). In reality, three body attachment processes might also affect the anion density. Also, since the present model does not include ion-ion recombination, the anions tend to persist indefinitely once they are formed.

The results from run 2 are illustrated in Fig. 2. The peak field is $E_0 = 13$ kV/cm. As the field approaches its peak value (t = 5 ns), the conductivity only rises slightly, and then falls precipitously as before. One may conclude that 13 kV/cm is below the breakdown field. During the rise-time of the electric field, the electron temperature rises to about 40000 K

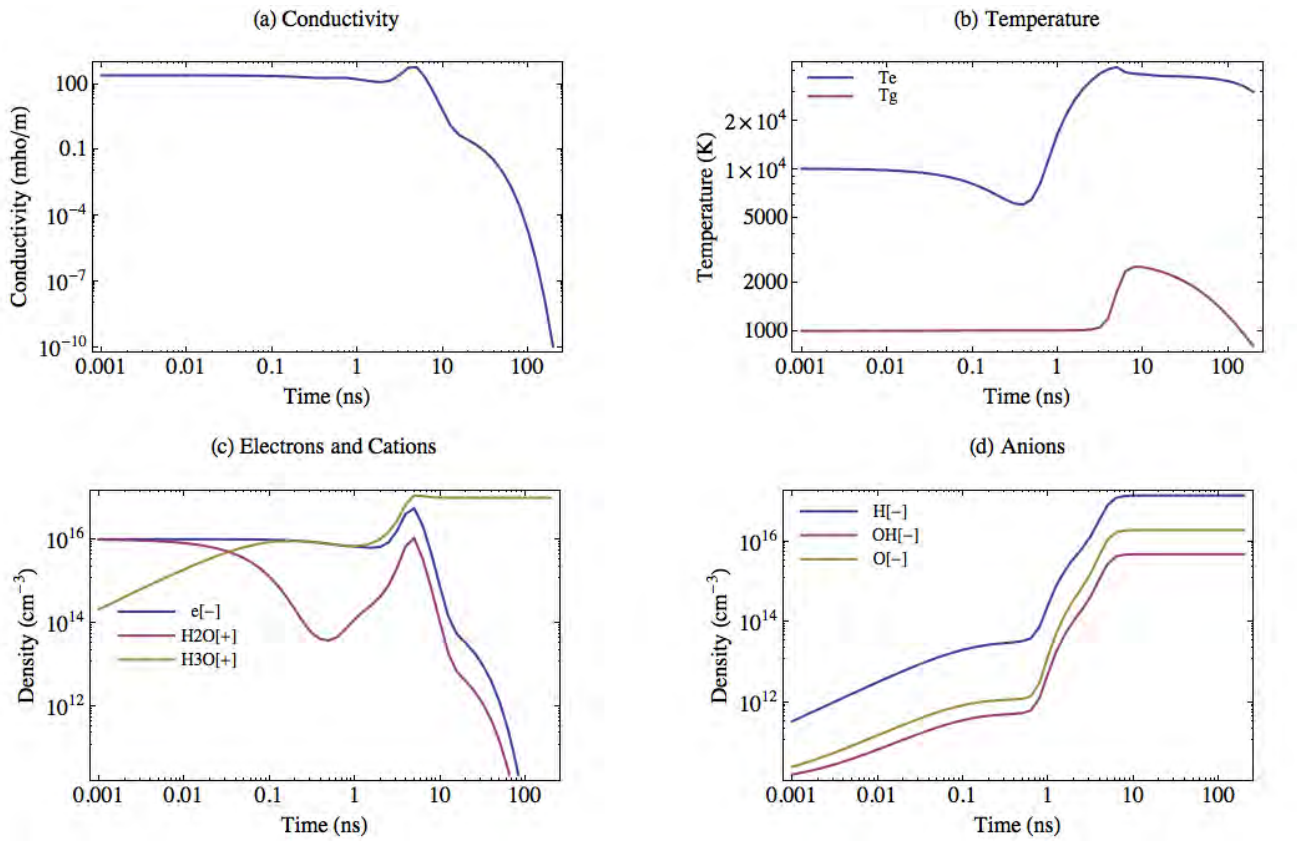

FIG. 2: Water vapor plasma excited by an electric field pulse with $E_0 = 13$ kV/cm.

as a result of ohmic heating. The gas temperature rises to about 2500 K, probably as a result of exothermic reactions involving hydronium, which reaches a density of 10^{17} cm^{-3}. The hydronium does not recombine because the excess negative charge is bound in H^-, as illustrated in Fig. 2. This situation persists because CHMWTR does not currently include ion-ion recombination.

The results from run 3 are illustrated in Fig. 3. The peak field is $E_0 = 14$ kV/cm. In this case, the conductivity is increased by almost two orders of magnitude from its initial value. Thus, one may conclude that 14 kV/cm is above the breakdown field. As the field increases, the conductivity first increases marginally, and then precipitously falls. The reduction in conductivity between 10 and 100 ns is due to a corresponding fall in the electron density and temperature during this time. The reason for this behavior appears to be that electron energy is being put into dissociation. This tends to lower the electron temperature, which reduces the ionization rate. Evidence of dissociation during this interval is seen in the steady increase in the densities of the dissociated products O_2 and H_2, as shown in Fig. 3(c). Once

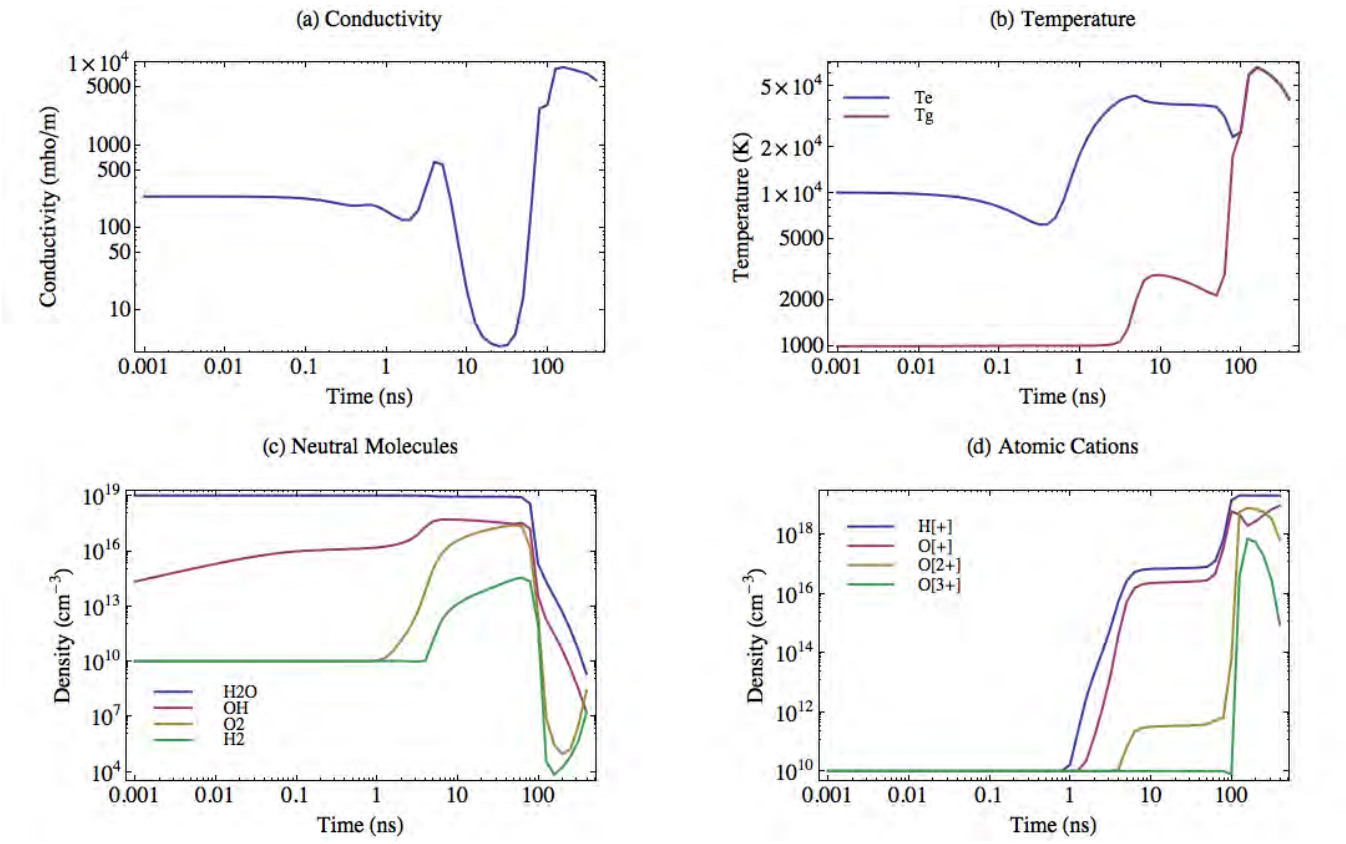

FIG. 3: Water vapor plasma excited by an electric field pulse with $E_0 = 14$ kV/cm.

this dissociation phase is over, the plasma becomes fully ionized, and an equilibrium plasma temperature is established. The plasma temperature reaches 65000 K, at which point the plasma is composed mostly of electrons, protons, and twice ionized oxygen atoms. Fig. 3 shows the densities of the atomic cations. Late in time, the plasma begins to radiatively cool as the applied field diminishes.

VII. SUMMARY AND TASK AREAS

The CHMWTR code can be used to track the evolution of the 21 most important plasma species that develop in electrically excited water vapor. For a water vapor plasma with a temperature of 1000 K and pressure of 138 kPa, CHMWTR predicts that the plasma is only weakly perturbed for a field of 13 kV/cm, but is fully broken down for a field of 14 kV/cm. This high sensitivity to the applied field is a characteristic of the highly nonlinear nature of the breakdown process. One may conclude from these results that the breakdown field is

about 14 kV/cm. The conductivity of the plasma rises from an initial value of about 200 mho/m to nearly 10000 mho/m in the fully broken down plasma.

As mentioned above, this is an interim report. Some of the task areas for future CHMWTR development are as follows:

1. Incorporate additional anion reactions, such as ion-ion recombination, three body attachment, etc..
2. Incorporate explicit vibrational physics.
3. Identify and add important excited states.
4. Investigate whether dissociative ionization of OH, H_2, and O_2 should be incorporated.
5. Incorporate hydronium formation in encounters with H_2^+.
6. Investigate whether additional neutral species such as H_2O_2 and HO_2 should be incorporated.
7. Improve the radiation model to avoid spurious gas cooling prior to breakdown.

Once the CHMWTR model is deemed complete, the following additional task areas can be engaged:

1. Map out a numerical Paschen curve for water vapor.
2. Couple CHMWTR to a transmission line model, and investigate the prospects for guiding long discharges in an underwater vapor channel.

VIII. ACKNOWLEDGEMENTS

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[14] It is understood that c_{vs} includes only the effects due to translational, rotational, and vibrational degrees of freedom. CHMWTR treats higher energy excitations explicitly