

Chemistry design from the ground up

First step:

Here, we construct the most basic chemistry set necessary to get a stable simulation. The absolute minimum is the feed gas, electrons, and one type of ion. If the feed gas is ionized dissociatively, we may need to add other neutrals.

Example A Oxygen:

O₂ as feed gas, electrons, O₂⁺ as ion.

Example B CF₄:

CF₄ as feed gas, electrons, CF₃⁺ as ion, F as by-product of dissociative ionization, CF₃ as product of neutralization at walls.

As reactions, we include some basic reactions for the feed gas - elastic collisions, vibrational excitation (only for the energy balance), and the chosen ionization channel. Reactions for the other species are ignored, as we assume only very small densities for them at this stage.

Note: Elastic collisions and vibrational excitation do not produce any species (unless vibrationally excited states are explicitly included), but they play an important role in determining the shape of the EEDF and collisional energy losses.

We also should not forget to include reactions at surfaces; a must is the neutralization of charged particles at surfaces. We let ions return as their neutral counterpart¹, while electrons are fully absorbed. In a first approximation, we ignore effects such as secondary electron emission or the reflection of electrons at surfaces. The interaction of neutrals with surfaces is a bit trickier, as it depends much more on the surface; in general, reactive neutral species can stick to walls and react with species sticking to the walls. For our CF₄ case, F can for example be absorbed by the wall and then form F₂, which returns to the gas phase. On the other hand, the CF_x radicals can form polymers at the wall; from these sites, F can return as CF₄. The CF_x radicals themselves, can return as CF_{x+1} from fluorinated sites, but will simply stick to polymerized sites. So which surface reaction dominates depends on the surface composition, which can also be different on different wall materials. This can be modelled by a surface site model, which is, however, beyond the scope of this tutorial. To demonstrate the effect of neutral losses at surfaces, we will let all neutral species except CF₄ stick to the walls with a probability of 0.1 in the CF₄ case and neglect it entirely in the O₂ case.

We test this basic chemistry in a simple ICP setup at 50 mTorr varying the power from 100-1000 W. With our basic chemistry, both gases like typical electropositive gases as can be seen in figure 1; the electron density is a linear function of the power, whereas the electron temperature is essentially constant. Due to the dissociative ionization of CF₄, we also have small amounts of F as a direct product of it and CF₃ due to the recombination of CF₃⁺ at surfaces. Note, how the neutral particles have much higher densities (two orders of magnitude) than the ions, although they are produced by the same process. However, they are lost on a larger time scale due to the smaller loss probability at surfaces and slower diffusion.

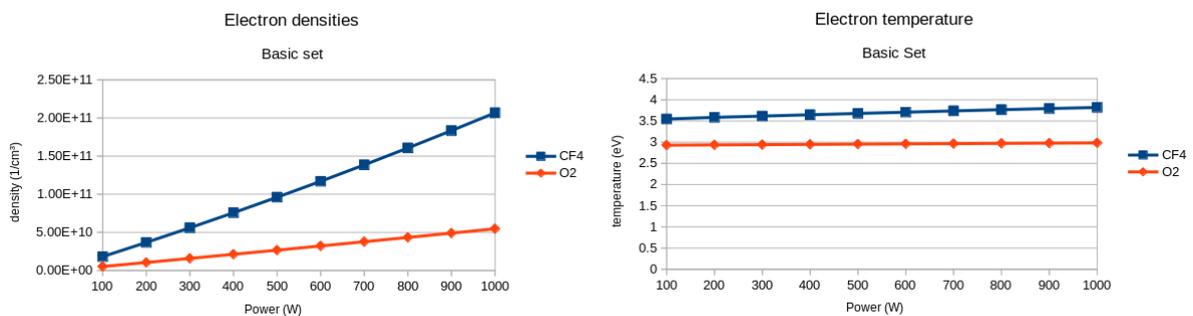


Figure 1: Electron density and temperature as a function of power for the basic CF₄ and O₂ chemistry sets.

¹ In some cases, this is not possible as the neutral counterpart does not exist. A well known example is H₃⁺. If supported by the simulation, they should return as an adequate pair (e.g. H₂ + H). In a first approximation, they can also return as the closest existing neutral (e.g. H₂). As the neutral densities are usually much larger than the ion density, this should introduce only a negligible error.

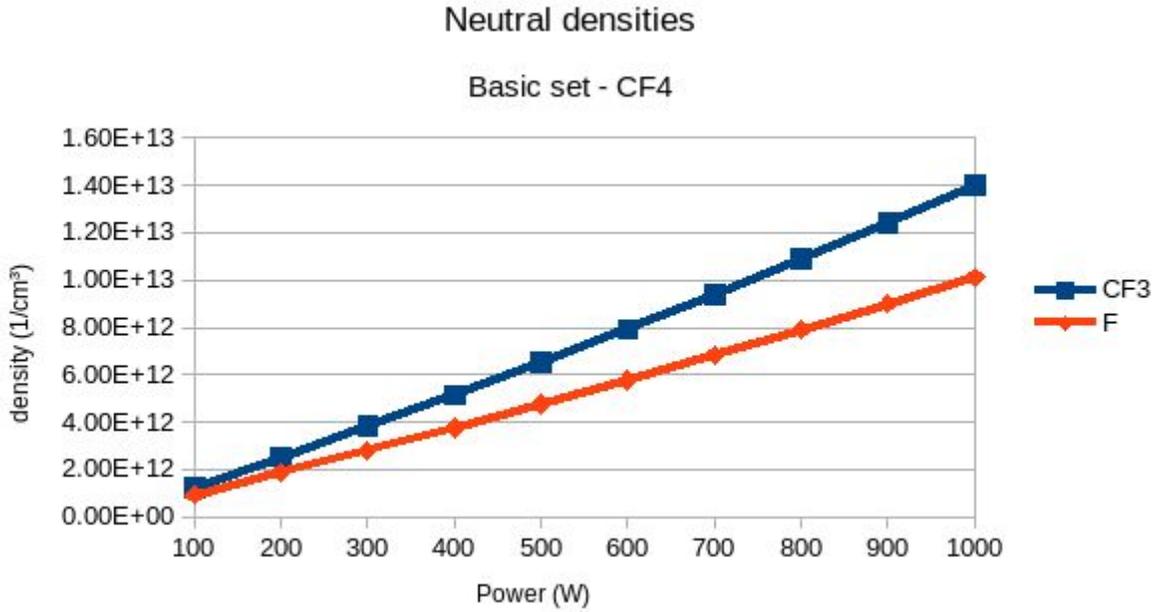
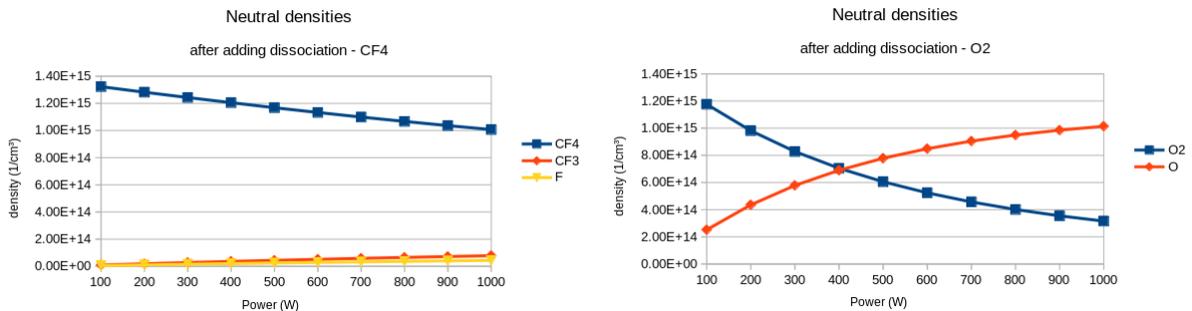


Figure 2: Neutral densities as a function of power in the CF₄ basic set.

The effect of neutral dissociation

Next, we will add the neutral dissociation of the feed gas; after all, producing significant amounts of neutral radicals is the reason for plasmas in molecular gases. For the CF₄, we first only add the CF₄ → CF₃ + F pathway, for O₂ the dissociation in two O.

As figure 3 shows, in the CF₄ case, we are still in the regime of a rather small degree of dissociation, while the O₂ is highly dissociated at the high end of our power range². Note, how the densities change linearly in the CF₄ case over the entire power range, while in O₂ a saturation effect is observed. In figure 4, we do not observe a significant change in the electron density; in case of O₂, however, we do see a significant increase in the electron temperature as a function of power; this happens, because the electron temperature self-consistently reaches a value where charged particle losses and gains are balanced. As we do not have included the ionization of O yet, the electron temperature increases to counter the significant loss of O₂ and therefore ionization channels.



² Keep in mind, that we neglected the loss of atomic O at surfaces.

Figure 3: Neutral densities as a function of power in CF_4 and O_2 after adding dissociation of the feed gas.

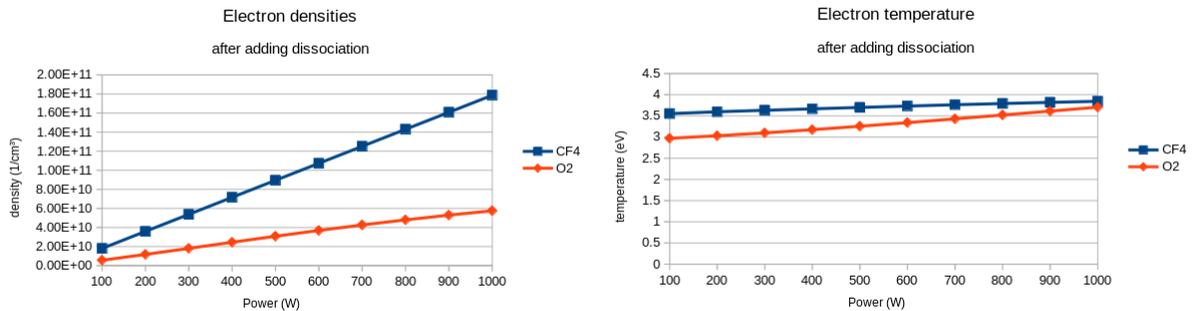


Figure 4: Electron densities and temperature as a function of power in CF_4 and O_2 after adding the dissociation of the feed gas.

Note: It is entirely possible to have a stable simulation producing species densities in agreement with experiments although important ionization channels are missing. In this case, the electron temperature increases self-consistently to achieve larger ionization rates. Vice versa, if loss channels for charged species are missing, the electron temperature decreases.

Keep in mind: Do not only rely on species densities, also check the electron temperature. If it is uncharacteristically high, you are likely missing important ionization channels; if it is uncharacteristically low, you are likely missing loss channels.

As the neutral dissociation fragments reach now significant densities, especially in the O_2 case, we will now introduce the ionization of these species. We add the $\text{CF}_3 \rightarrow \text{CF}_3^+$ and the $\text{O} \rightarrow \text{O}^+$ channel, respectively. As figure 5 shows, this leads to an increase in the electron density in both cases, with a larger effect in O_2 . Also note, how the electron density now increases slightly faster than linear in the O_2 case due to the significant change in the plasma composition. Furthermore, the electron temperature now remains constant. The effect on the neutral densities is negligible in the O_2 case, whereas we see a small decrease at high powers in the CF_4 case; this is related to higher neutral temperatures.

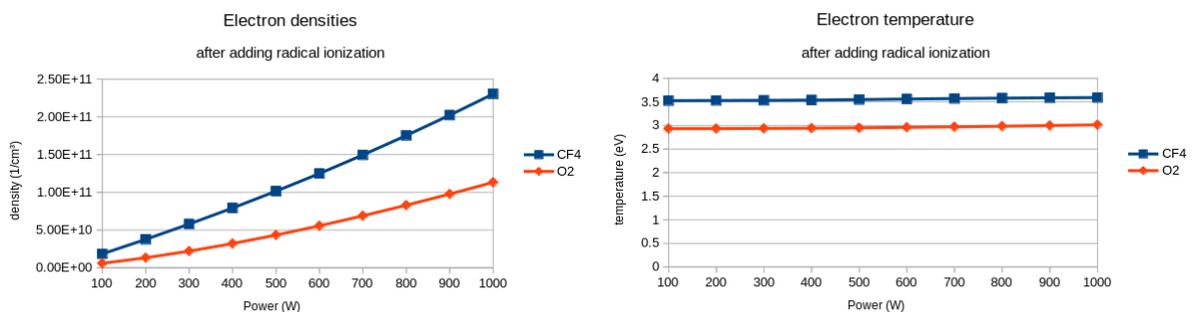


Figure 5: Electron densities and temperature as a function of power in CF_4 and O_2 after adding the ionization of radicals.

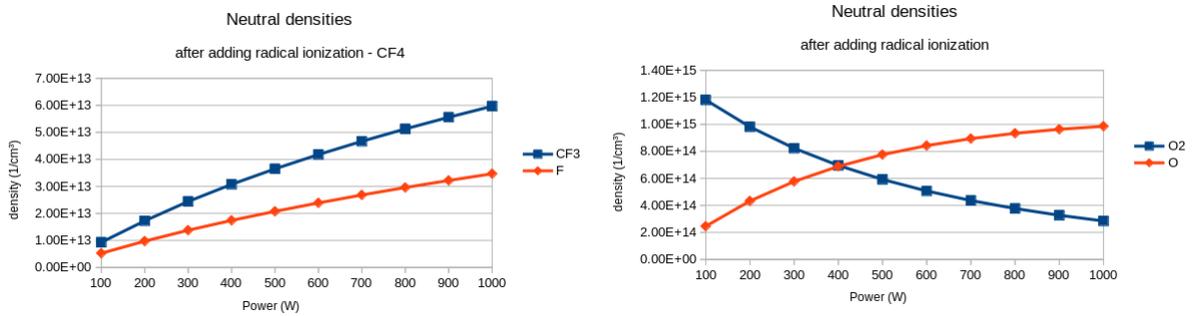


Figure 6: Neutral densities as a function of power in CF_4 and O_2 after adding the ionization of radicals.

Negative Ions

Another characteristic of molecular gas discharges is the presence of negative ions. We will add F^- and CF_3^- to our CF_4 set and O^- to the O_2 set. In the latter case, we will neglect O_2^- due to the expected low density. We will also deactivate the calculation of temperatures for all negative ions, as they are quite notorious for introducing instabilities in the sheath regions due to the combination of low densities and high electric fields. Apart from the production of negative ions via dissociative attachment, we also include the ion-ion recombination for all possible negative ion - positive ion combinations.

Always include ion-ion recombination when introducing negative ions to a chemistry!

Note: Before adding a species to a chemistry, it is worthwhile to approximate the density analytically. Consider the mentioned O_2^- ions. They are produced by a three-body process $\text{E} + \text{O}_2 + \text{M} \rightarrow \text{O}_2^- + \text{M}$. M is an arbitrary third body; its presence is necessary to fulfill both conservation of momentum and energy. The rate of such processes is highly dependent on the pressure; in this case, it is a linear function of the third body density. Thus, we can express the particle balance for O_2^- (gains = losses) roughly as:

$$k_{\text{att}} n_e n_{\text{O}_2} n_{\text{M}} = k_{\text{rec}} n_{\text{O}_2^-} n_{\text{ions}}$$

with the rate coefficients for k_{rec} and k_{att} for recombination and attachment, respectively. For a rough approximation, we set $n_e = n_{\text{ion}}$ and $n_{\text{O}_2} = n_{\text{M}}$, which yields:

$$n_{\text{O}_2^-} = n_{\text{M}}^2 k_{\text{att}} / k_{\text{rec}}$$

Typical values are $k_{\text{att}} = 10^{-32} \text{ cm}^6/\text{s}$ and $k_{\text{rec}} = 10^{-7} \text{ cm}^3/\text{s}$. With $n_{\text{m}} = 10^{15} \text{ cm}^{-3}$ at our conditions, we get an estimated density of 10^5 cm^{-3} , which is negligible compared to the plasma density of about 10^{10} - 10^{11} cm^{-3} .

Important: In general, the particle balance also includes diffusive losses and in case of neutrals the production at the surfaces. In case of negative ions, diffusive losses can be neglected, as they are trapped in the plasma bulk due to their large mass and the positive

plasma potential.

Figure 7 shows how both discharges transition from an electronegative to an electropositive plasma as a function of power, as we deplete the particles capable of producing negative ions (CF_4, O_2). Note, how both densities deviate from the linear behaviour as a function power. The electron density increases slightly more than linear, whereas the negative ion density first increases less than linear and, in the case of O_2 , reaches a maximum around halfway through our power range. Furthermore, the summed densities of electrons and negative ions are somewhat larger than the electron density in the previous case; this is a result of the diffusion being slowed down by the heavy and rather cold negative ions.

In terms of electron temperature shown in figure 8, we do not see a large change in the O_2 case, but a jump from about 3.5 eV to slightly over 4 eV in the CF_4 case. The electron temperature is still almost constant, but shows the opposite behaviour than without negative ions on a small scale: it shows a small decrease instead of a small increase. This behaviour is caused by the reduced electron density due to attachment; as the electron density decreases, the electron temperature must increase to balance electron losses and gains.

In case of the CF_4 case this has a substantial influence on the neutral densities. In Figure 9 we observe an increase of roughly a factor of 2, despite the smaller electron density. This cannot be explained by a change in the gas temperature alone. Rather, the rate coefficient for the neutral dissociation of CF_4 is very sensitive in this electron temperature range. Between 3-4 eV, this rate coefficient increases by a factor of about 5.

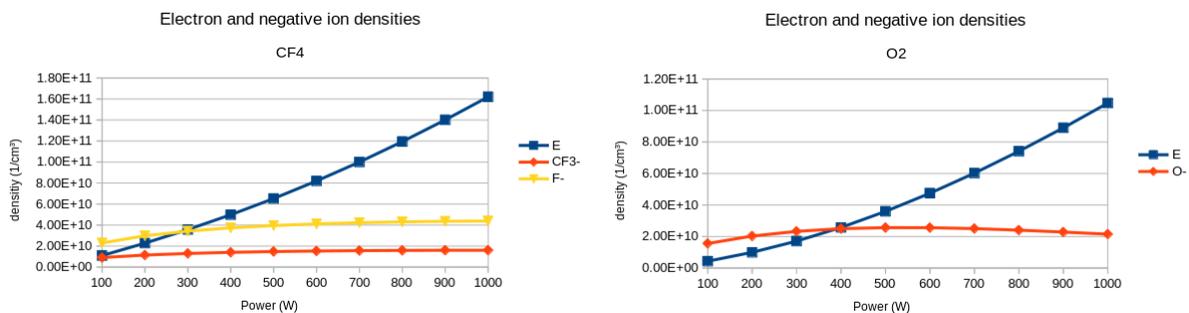


Figure 7: Electron and negative ion densities as a function of power in CF_4 and O_2 .

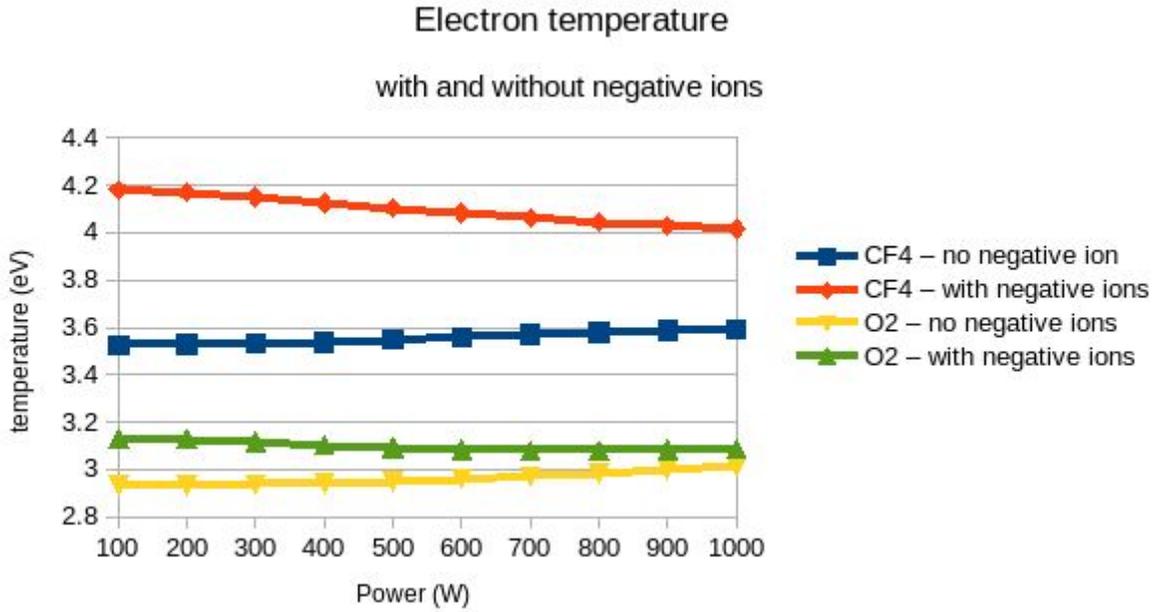


Figure 8: Electron temperatures in CF_4 and O_2 with and without negative ions.

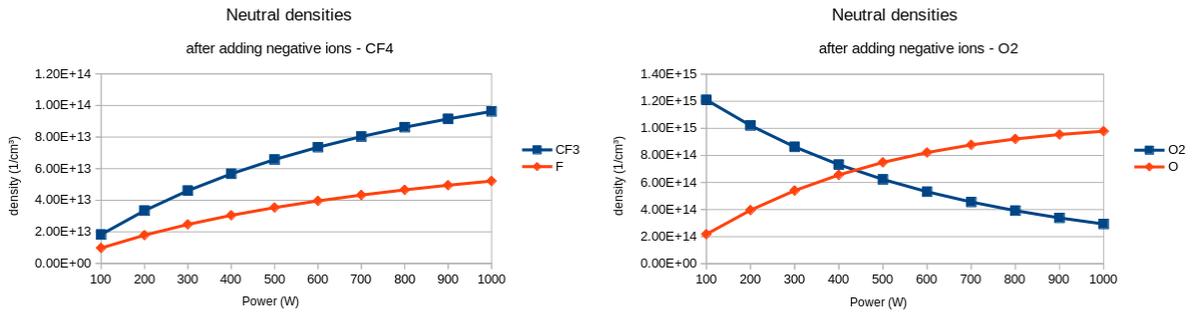


Figure 9: Neutral densities in CF_4 and O_2 after adding negative ions.

Note: The behaviour of molecular gases can drastically change at different degrees of dissociation. Usually, they turn from being electronegative to electropositive the higher the degree of dissociation. This can have a large impact on the dependence of species densities and other parameters as a function of power, pressure etc. For example, the electron temperature is largely independent from the power in noble gases; in molecular gases, it can significantly change due to changes in the plasma composition and electronegativity, which in turn affects the rate coefficients and finally species densities.

Keep in mind: Always check your chemistry for the entire range of plasma parameters, you want to investigate.

Adding missing species

After understanding the impact of the main electron processes and different types of species, we will now fill the CF_4 chemistry with the missing neutral species down to C and the accompanying positive ions. As reactions, we add the dissociation of one F from the CF_x

molecule, the ionization channel to the positive ion counterpart, and the dissociative attachment to F^- , where available. In O_2 , there are no additional dissociation products left. Excited states will be discussed later.

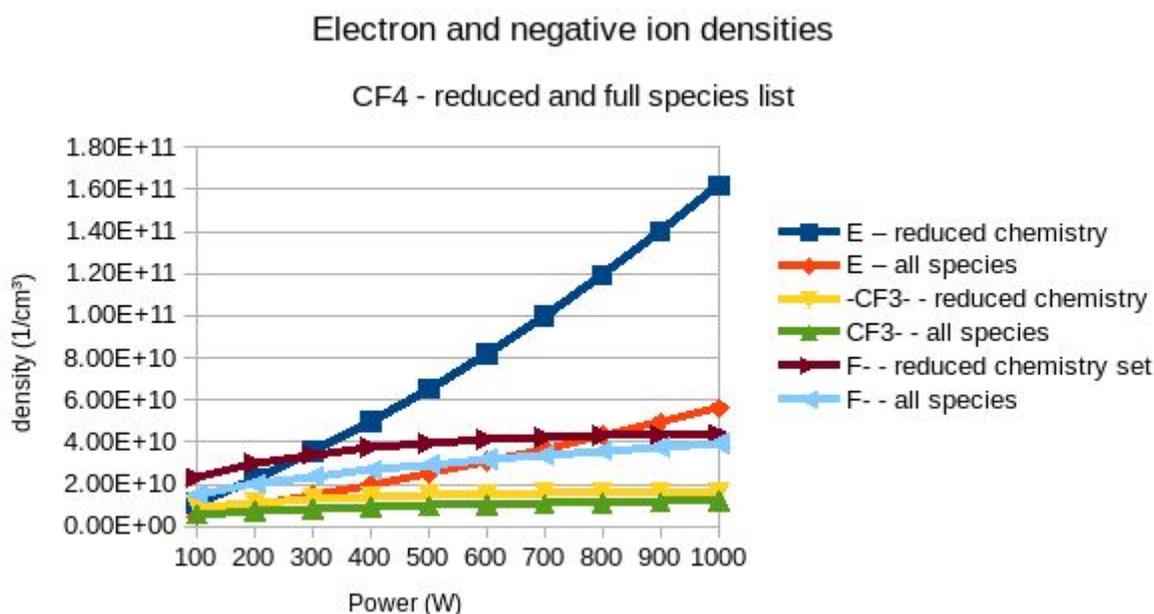


Figure 10: Electron and negative ion densities in CF_4 with a reduced and the full species list.

As figure 10 shows, we see a significant difference in the negatively charged particles densities, despite the rather low degree of dissociation - their sum is smaller and the transition to an electropositive discharge happens at a much higher power (700 W instead of 300 W). A detailed explanation for this is beyond the scope of this tutorial. Likely candidates are additional dissociative attachment channels (CF_3 and CF_2), a reduced gas temperature (effectively increasing particle density and electronegativity) and additional electron energy loss channels by the newly introduced species.

Additional reactions and species

So far, we have constructed chemistry sets including relevant ions and ground state neutral particles, as well as basic electron collisions and ion-ion recombination reactions. We will now have a look at the effects of heavy particle reactions and some additional electron collisions. Note, that we do not have examples for all types of reactions, as their efficiency depends on the process parameters and not all showed a significant influence under our chosen parameters.

Charge exchange collisions

In charge exchange collisions, the charge from a positive ion is transferred to neutral particle. There are two types: symmetric and asymmetric. In symmetric charge exchange collisions, the charge is transferred from an ion to its neutral counterpart, e.g. from O^+ to O.

Obviously, these kind of reactions do not change species' densities directly. They do, however, contribute significantly to the neutral gas heating and can therefore change the densities indirectly. They can also influence the shape of the IEDFs at surfaces.

In asymmetric charge exchanges, the charge is transferred from an ion to a different neutral, sometimes in combination with dissociation or transfer of atoms from one collision partner to the other. A well known example for this is $H_2^+ + H_2 \rightarrow H_3^+ + H$. Apart from contributing to the neutral gas heating, these collisions also directly change the relative ion densities, as can be seen for our O_2 case in figure 11.

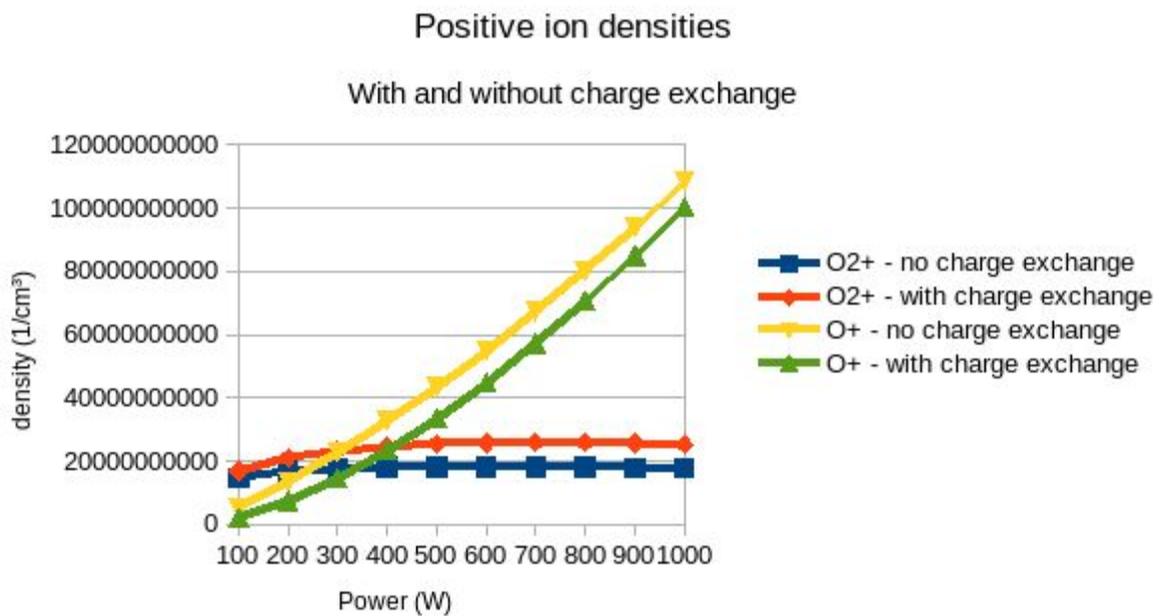


Figure 11: Positive ion densities as a function of power in O_2 with and without charge exchange collisions.

Dissociative recombination

The recombination of atomic ions is negligible under low pressure conditions, as this is actually a three-body process. However, this is not the case for the dissociative recombination of molecular ions, such as $e + O_2^+ \rightarrow O + O$, which are quite efficient. As they give an additional electron loss channel, they can influence both electron density and temperature and indirectly other parameters. They can be negligible at very low pressures and in highly dissociated plasmas, but when in doubt, they should be included.

Electron detachment

Negative ions cannot only be destroyed by ion-ion recombination, but also by electron detachment; in this process the excessive electron is stripped from the ion by an electron or a neutral particle, for example $e + O^- \rightarrow e + e + O$. This reaction reduces the electronegativity of discharges, as can be seen in figure 12, where we added the detachment of O^- by electrons and O to the reaction set. The direct influence on the neutral

density is usually negligible, but the reduced electronegativity can influence the electron temperature and other species' densities indirectly.

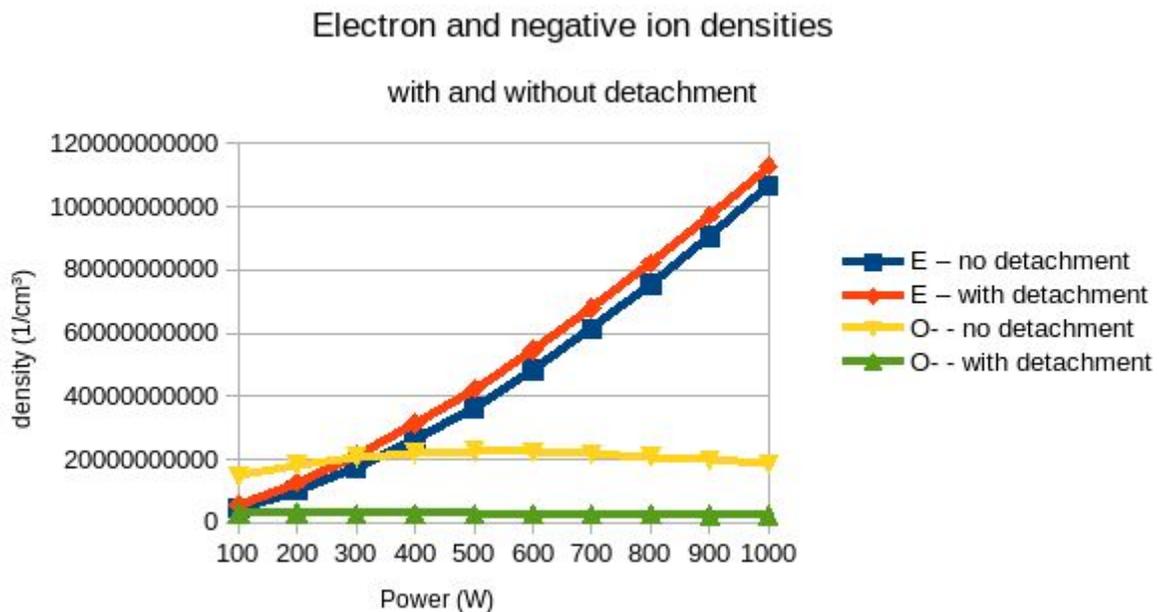


Figure 12: Electron and negative ion densities in O_2 as a function power with and without electron detachment.

Dissociative ion-ion recombination

Ion-ion recombination usually refers to the reaction $X^+ + Y^- \rightarrow X + Y$. However, it is possible that one of the ions get dissociated in the process, for example $XY^+ + Z^- \rightarrow X + Y + Z$. Such reactions are for example known for a couple of fluorocarbons. They have the effect of further reducing the density of negative ions, while the influence on the neutral densities is rather negligible.

Wall recombination of radicals

In the comparison of the CF_4 chemistry with radical losses at the walls and the O_2 chemistry without, we have already seen how the interaction of neutrals with walls influence the density of dissociation products. However, neutral particles cannot only be lost at walls, they can also form there. For example, O can recombine to O_2 , F to F_2 , CF to CF_2 etc. Note, that this can introduce new species to a chemistry such as F_2 in CF_4 discharges. If the amount of reactive species is large enough, wall recombination can have a significant impact on the plasma composition with all its side effects (different electronegativity, changes in electron temperature etc.)

Radical recombination in the gas phase

Radicals cannot only recombine at walls, but also in the gas phase. These processes are highly dependent on the pressure, as they are usually three-body processes; hence, they do not have a significant influence in our O_2 example. The rate coefficients can vary strongly depending on the involved species; a rough thumb of rule is, the larger the involved species, the higher the rate coefficient. So the recombination of two atomic species is less likely than the recombination of one atomic with one molecular species which is less likely than the recombination of two molecular species. Before deciding, whether to add these reactions, you should compare its expected rate with the one of the opposing dissociation reaction. In general, these reactions have the same effect as losses and recombination at the wall: Reducing the degree of dissociation with all its side effects. Please also note, that such reactions can form neutral particles larger than the feed gas, such as C_2F_4 in CF_4 discharges.

Other neutral-neutral reactions

There is a plethora of other possible neutral-neutral reactions, typically a transfer of specific atoms from one molecule to another. Going into detail here is beyond the scope of this tutorial. As these reactions can alter the neutral composition of the plasma significantly, they should be thoroughly researched. A rather well known example is silane; the dissociation yields primarily SiH_2 which is then quite efficiently converted to SiH_3 by reactions between neutrals. Also note, that in mixed discharges, such reactions can produce new species such as COF_x in CF_4/O_2 discharges.

Excited states

So far, we have neglected excited states and only dealt with neutrals in their ground state. However, excited states can have a significant impact on the discharge. Possible effects include:

- Many rates including neutrals are higher for the excited species, so they can have a significant influence despite their smaller densities.
- Excited species can also induce or accelerate surface processes.
- Fluorescent states emit photons, which can also induce surface processes.
- Excited states can ionize neutrals, if the excitation energy is higher than the ionization energy of the collision partner (Penning - ionization).
- Through collisions with electrons, excited states can affect the shape of the EEDF, electron temperature, and rate coefficients.

In our O_2 case, the metastable O_2 states can, for example, detach electrons from negative ions quite efficiently in contrast to ground state O_2 . As figure 13 shows, this leads to a reduced density of O^- . Note, that we also included wall losses and recombination of O in this model to achieve sufficient densities of metastable O_2 . When deciding whether to include excited states or not, you should get a comprehensive overview of possible reactions they can induce and estimate their rates in comparison with the ground state reactions. When in doubt, include them.

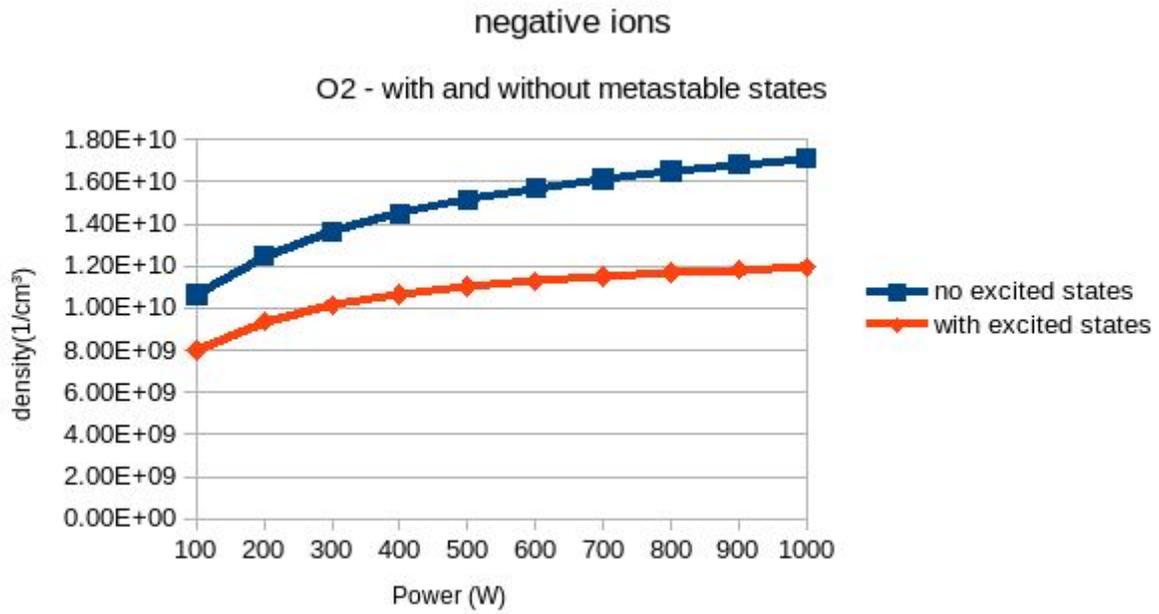


Figure 13: negative ion density as a function of power in O₂ with and without metastable states.

Contact us:

Website: www.quantemol.com

QDB: www.quantemolDB.com

Sales – sales@quantemol.com

Support – support@quantemol.com

Information – info@quantemol.com

Phone: +44 (0) 20 8133 5103

Quantemol Ltd
 320 Angel
 City Road
 London
 EC1V 2NZ