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Transient induced molecular negative ions formed in cold electron collisions with polarized molecules*

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Abstract. Using a relatively simple semiclassical model, it is shown that transient, induced molecular negative ions (TIMNI), are produced through a potential barrier interaction between cold electron collisions and polarizable molecules in plasma. Such new negative ions lead to radio-frequency absorption in such discharges. The calculated radio-frequency absorption frequencies are consistent with earlier experimental measurements.

Key words: interaction processes in plasmas • new negative molecular ions

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Introduction

In the last few years we reported on a new type of high-density, low-temperature reflex discharge plasma source. It was optimized both for the electronegative and electropositive gases within the pressure range 1.0 to 100 Pa [12–14]. Due to the enhanced hollow cathode effect by the magnetic trapping of electrons, the electron density n_e is as high as 10^{18} m^{-3}, and the electron temperature T_e is as low as a few tenths of an electron volt, for dissipated power of only tens of watts. Such high electron density and low electron temperature plasmas, coupled with the data reported in the relatively recent work [2, 3, 7, 8, 10, 11] on short-lived molecular negative ions, created in an attractive potential, have stimulated our interest in the interaction of low temperature electrons with polarized molecules. While much of the previous work has some relevance in that it is focussed on explaining dissociative attachment and low energy scattering rates, we are particularly interested in seeing if the existence of short-lived molecular negative ions can explain and/or predict absorption and stimulated emission of radio-frequency radiation in such plasmas.

Initially, we are interested in the mechanism of formation of this type of ions and in obtaining the expression of the transition frequencies. The calculated data are used to explain the absorption and stimulated emission dispersion curves within the radio-frequency range reported by Ionescu *et al*. [4–6]. Should these radio-frequency signatures be associated with what are termed here transient, induced molecular negative ions (TIMNI), then radio-frequency spectroscopy of molecular ions may provide an interesting diagnostic

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and analytic tool, with application in rf wave propagation, plasma chemistry and plasma processing.

Unfortunately, the highly developed calculations of these systems have not yet been applied to this problem so here we use a simple semiclassical approach to predict the mechanism of formation, structure and resonant frequencies of the TIMNIs, focusing on molecular oxygen. We hope that this will stimulate interest in undertaking more precise calculations and additional experimentation.

Transient, induced molecular negative ions (TIMNI)

Classically the adiabatic interaction of the cold electron (charge e and mass m) with the polarizable molecule (polarizability α) can be considered in terms of the interaction potential $V(r) = [(-\alpha e)/(8\pi\varepsilon_0 r^4)]$, the total energy of the system $E_0 = \frac{1}{2} m v_0^2$, where v_0 is the initial velocity of the electron, and the impact parameter b. Considering the momentum and energy conservation equations, the total energy of the system can be written as

$$E_0 = \frac{m v_r^2}{2} + \frac{L^2}{2mr^2} - \frac{\alpha e^2}{8\pi\varepsilon_0 r^4} \quad (1)$$

where r is the distance of the electron from the molecule, assumed here to be a point, and $\vec{L} = (m\vec{v} \times \vec{r})$ is the electron angular moment. The first term on the right side is the radial energy E_r where $v_r(r)$ is the radial velocity, the second term is the centrifugal potential energy $U_c(r)$, and the last term is the potential interaction energy $U_p(r)$. In Eq. (1), the last two terms are collectively the effective potential $U_{\text{eff}}(r)$, i.e.

$$U_{\text{eff}}(r) = \frac{L^2}{2mr^2} - \frac{\alpha e^2}{8\pi\varepsilon_0 r^4} = E_0 \frac{b^2}{r^2} - \frac{\alpha e^2}{8\pi\varepsilon_0 r^4} = \frac{A}{r^2} - \frac{B}{r^4} \quad (2)$$

The electron is moving in an inverse-square-repulsive potential $V_c(r) \propto r^{-2}$, and in an inverse-fourth-power-attractive potential $V(r) \propto r^{-4}$. The first term in Eq. (2) dominates at larger distances, while the second term (the attractive polarization potential) is dominant at smaller distances, producing a maximum in $U_{\text{eff}}(r)$. In general, a potential barrier will exist for any attractive potential $V(r)$ that is a steeper than an inverse square function of r.

The form of the electron trajectory upon approaching the molecule depends on the value of both E_0 and L. The variation of the different terms in Eq. (1) with the distance r between the incoming electron and the molecule is shown in Fig. 1. The axis values refer to a specific calculation for oxygen, as discussed later. Consider, with reference to Fig. 1, the sequence of trajectories for electrons with initial kinetic energies E_0, but with a range of impact parameters corresponding to different values of L. With increasing L the corresponding curve $U_{\text{eff}}(r)$ moves upward. At some values of L, the maximum in this curve becomes equal to E_0, i.e., $U_{\text{eff,max}} = U_{\text{eff}}(r_M) = E_0$, where r_M is the attachment boundary radius. Electrons with energies lower than E_0 and with the same L will evidently be reflected by the potential

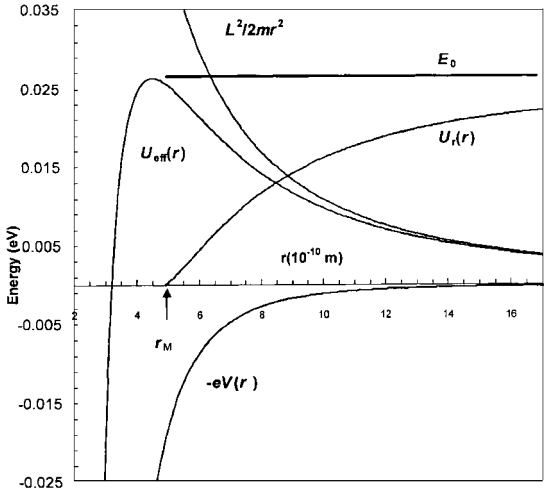

Fig. 1. Example of spatial variation of the terms in Eq. (1); $E_0 \approx U_{\text{eff,max}} = 0.026$ eV.

barrier, while those with the total energy greater than E_0, pass over the potential barrier and pass through the point-like molecule.

The situation that particularly interests us here is when the initial kinetic energy of the electron E_0 is almost equal to the value of $U_{\text{eff}}(r_M)$ at the peak of the potential curve. In this case the electron will spend a considerable time at a radial distance close to r_M. The electron can then be said to "orbit" about the centre of force (the polarized molecule). The angular motion speeds up as r decreases in order to conserve angular momentum, and a large number of revolutions may be made. It is important to note that these are unstable orbits, unlike those when the r dependence of the interaction potential is shallower than an inverse square. Such sticky collisions [9], where both the energy and the angular momentum are always conserved although the form of the energy may change, lead to the formation of transient, induced molecular negative ions, TIMNIs.

Referring to the data of Fig. 1, and considering the radius of the attachment boundary r_M, the classical value of the cross section $\sigma = \pi r_M^2$ is estimated to be of the order of 10^{-15} cm^2. A better quantity to describe the interaction process is the two-body rate coefficient [1] $\beta = \sigma v_0$. For the specific case discussed here, its value is as high as 2×10^{-8} cm^3/s, evidencing a very probable process that can occur within a high density and low electron temperature reflex discharge plasma. Then, according to the classical analysis the free electron moves toward the polarized diatomic molecule up to a minimum distance, remains attached for a short time, forming a TIMNI, and then leaves the molecule on a symmetric trajectory. Both the total energy and the angular momentum of the electron are conserved all the time, though different forms of energy can change. Consequently, the polarized molecules are under the influence of the magnetic field generated by the attached electrons. The attached electron makes tens of thousand of revolutions and the life-time of a TIMNI can be of the order of 10^{-7} s. It is connected with the magnetic field generated by the attached electron, and is different by the life-time of the resonance states involved in rf transitions which is an intrinsic characteristic of the polarized molecules.

The oxygen TIMNI

As shown above, there is a possibility for cold electrons in cold plasmas to move on circular orbits about the polarized molecules. Since the molecule "feels" only the influence of the magnetic field but not its origin, we can analyse the possible magnetic resonances following the methods used in the radio-frequency spectroscopy in the presence of the external magnetic fields. The orbiting electron is considered as a current loop in the form of a circle of radius r that carries a current I. For example, for $r = 5 \times 10^{-10}$ m, and $v = 5 \times 10^{6}$ m/s, the magnetic field at the centre of the loop is as high as 0.3 T. A more convenient way is to analyse the radio-frequency magnetic resonances in polarized molecular plasmas using a quantum mechanics vector model.

The angular momentum of the orbiting electron can be quantified as $L = \sqrt{2mE_0}\cdot b = \sqrt{l(l+1)}\cdot\hbar$, where l is the orbital momentum quantum number. The electron energy and the impact parameters must satisfy the condition

$$b_l = \sqrt{\frac{l(l+1)}{2mE_0}}\cdot\hbar \tag{3}$$

This means that there is an energy range and an impact parameter range for which the electron can form a TIMNI. The upper limit of the electron energy, $E_{0\max}$, is determined by the condition that a solution exists for Eq. (1) and the lower limit of the impact parameter $b_{\min}$ is determined by the condition $b > r_b$, where r_b is the bond length of the molecule.

The radius of the orbit, obtained as the largest real root of Eq. (1), is

$$r_l = \left\{\frac{l(l+1)\hbar}{4mE_0} + \left[\frac{l^2(l+1)^2\hbar^4}{16m^2E_0^2} - \frac{\alpha e^2}{8\pi\varepsilon_0 E_0}\right]^{1/2}\right\}^{1/2} \tag{4}$$

According to formula (4), the electron energy must satisfy the condition $E_0 \le \{[\pi\varepsilon_0 l^2(l+1)^2\cdot\hbar^4]/(2\alpha m^2 e^2)\}$, and for the oxygen plasma ($\alpha_{0_2} = 1.571 \times 10^{-30}$ m^{-3}) the electron energy must be lower than 1.5 eV. This is an encouraging result for our model since in the reflex discharge plasmas, with bulk electron density as high as 10^{18} m^{-3}, the number of electrons within the energy range from 0 to 1.5 eV represents more than 60% of all electrons [7, 12–14].

Considering the oxygen molecule as an example, it is characterized by the electron spin angular momentum $\vec{S}$ the rotational momentum $\vec{K}$ the total angular momentum, $J = \vec{S} + \vec{K}$ (the corresponding quantum numbers are S, K, and J) and by the spin magnetic moment $\vec{\mu}_S$ due to $\vec{S}$. The projections of $\vec{\mu}_S$ along the axis $\vec{J}$ are $\mu_{J_1} = K + 1$, $\mu_{J_2} = K$ and $\mu_{J_3} = K - 1$.

On the other hand, the orbiting electron is considered as an effective current loop that creates a magnetic field in the center of the loop. Therefore, to the orbital angular moment $\vec{l}$ corresponds an orbital magnetic moment $\vec{\mu}_l$ and to the spin angular momentum $\vec{S}$ corresponds a spin magnetic moment. Consequently, the electron has a total magnetic moment $\vec{\mu}_j$.We consider, *a priori*, $l = 1$ and the two values of the magnetic moment μ_j are $\mu_{3/2}$ and $\mu_{1/2}$, respectively.

The magnetic field in the centre of an orbit of radius r is

$$B = \mu_0\mu_j/r^3 \tag{5}$$

where μ_0 is the vacuum permeability. Since $\vec{B} \,//\, \vec{J}$, then the magnetic energy corresponding to a molecular quantum state will be $\mu_0\mu_{J1,2,3}\mu_J/r^3$ where $\mu_{J1,2,3}$ is a function of K. There are two possible electron spin magnetic resonance transitions of the oxygen molecule within the magnetic field created by the attached electron, given by the expressions

$$\begin{aligned} h\nu_{K+1\to K} &= \frac{\mu_0\mu_j}{r^3}\cdot(\mu_{K+1} - \mu_K) \\ h\nu_{K\to K-1} &= \frac{\mu_0\mu_j}{r^3}\cdot(\mu_K - \mu_{K-1}) \end{aligned} \tag{6}$$

The values of the frequencies corresponding to such a spin magnetic resonant transition can be obtained by calculating r using (4) and using known values in Eq. (6). For the oxygen molecule, analyzed in Fig. 1, the expressions obtained theoretically for μ_{K+1}, μ_K, μ_{K-1} from molecular spectroscopy, are

$$\mu_{K+1} = 2\sqrt{\frac{K+2}{K+1}}\times\mu_B;\quad \mu_K = \frac{2}{\sqrt{K(K+1)}}\times\mu_B;$$
$$\mu_{K-1} = -2\sqrt{\frac{K-1}{K}}\times\mu_B$$

where μ_B is the Bohr magnetron. For $j = 3/2$ state ($\mu_{3/2} = 2.582\mu_B$) the corresponding magnetic resonant transitions are

$$\begin{aligned} \nu_{K+1\to K} &= 6.2\left(\sqrt{\frac{K+2}{K+1}} - \sqrt{\frac{1}{K(K+1)}}\right)\ \text{MHz} \\ \nu_{K\to K-1} &= 6.2\left(\sqrt{\frac{1}{K(K+1)}} + \sqrt{\frac{K-1}{K}}\right)\ \text{MHz} \end{aligned} \tag{7}$$

In this manner, doublets both in emission and absorption are to be observed. The transitions correspond to a variation of the magnetic energy that comes out of the change in projection of $\vec{\mu}_j$ onto the magnetic field of the attached electron. The formula (7) predicts magnetic resonance transitions within the radio-frequency frequency range from few MHz ($K + 1 \to K$ transition and $K = 1$) to almost tens of MHz for higher values of K and this is in agreement with the data reported by Ionescu *et al*. [4–6] in a low pressure, direct current glow discharge. The fact that they were evidenced in the region of the cathode head of the Faraday dark space of a low pressure oxygen glow discharge (electron temperature of tens of electron volts) but not in other regions like the negative glow or positive column, and do not change with the discharge current or the oxygen gas pressure exclude other channels like the presence of Rydberg states or ionization waves. We are currently planning to extend this model to other type of polarized molecules and to use the reflex discharge plasma for an experimental analysis of the problems connected with TIMNIs.

Conclusions

This semiclassical model suggests that transient, induced molecular negative ions (TIMNI) are produced through a potential barrier interaction between cold electron collisions and polarizable molecules in plasma. Such new negative ions lead to radio-frequency absorption in such discharges. The calculated radio-frequency absorption frequencies are consistent with earlier experimental measurements. This potentially opens up a new area of radio-frequency spectroscopy in low temperature plasmas making it worthy of further experimental and theoretical study.

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