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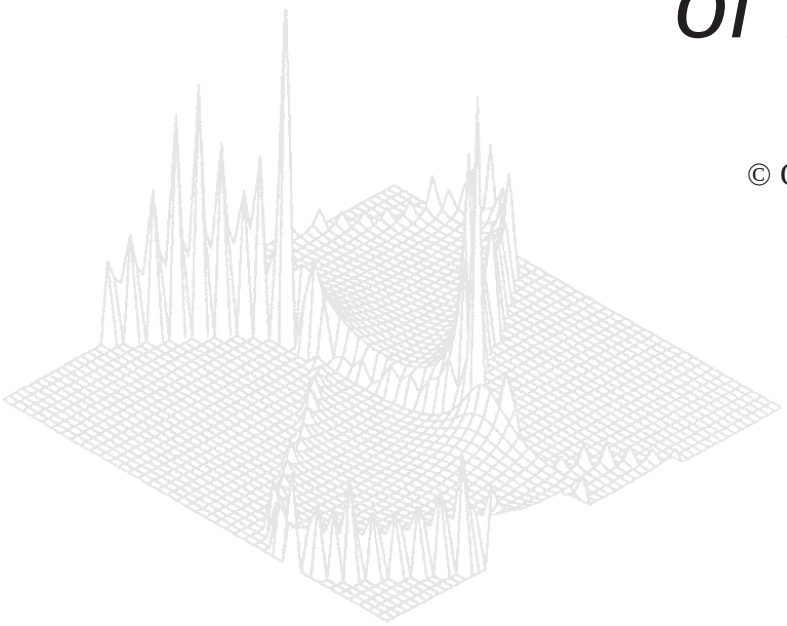

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Influence of Excited Molecules on Electron Swarm Transport Coefficients and Gas Discharge Kinetics*

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Abstract

In this paper we study different effects of excited molecules on swarm parameters, electron energy distribution functions and gas discharge modeling. First we discuss a possible experiment in parahydrogen to resolve the discrepancy in hydrogen vibrational excitation cross section data. Negative differential conductivity (NDC) is a kinetic phenomenon which manifests itself in a particular dependence of the drift velocity on E/N and it is affected by superelastic collisions with excited states. A complete kinetic scheme for argon required to model excited state densities in gas discharges is also described. These results are used to explain experiments in capacitively and inductively coupled RF plasmas used for processing. The paper illustrates the application of atomic and molecular collision data, swarm data and the theoretical techniques in modeling of gas discharges with large abundances of excited molecules. It is pointed out that swarm experiments with excited molecules are lacking and that there is a shortage of reliable data, while the numerical procedures are sufficiently developed to include all the important effects.

1. Introduction

The physics of electron swarms occupies a unique position between classical binary atomic and molecular collision physics and the physics and applications of gas discharges. The interaction between the two disciplines occurs almost exclusively through the physics of swarms. Development of certain applications such as plasma etching and deposition has dictated first the adjustment of the points of interest in swarm physics and, as a result, atomic and molecular collision physics had to modify its interests as well. It appears that one example that does not follow this rule are studies of the influence of electron collisions with the excited molecules. Interest in this topic has increased tremendously in atomic and molecular collision physics, the percentage of papers in this field has increased and the data are becoming more and more reliable (Armentrout *et al.* 1981; Bray and Fursa 1995; Jacka *et al.* 1995), while the experimental techniques for production of well defined excited particle beams have improved and become widespread. Similarly, the needs for plasma modeling have dictated the inclusion of electron-excited state kinetics for some time now.

* Dedicated to Professor Robert W. Crompton on the occasion of his seventieth birthday.

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In this paper we shall describe one possible swarm experiment proposed by R. W. Crompton with a high abundance of excited hydrogen molecules which should help resolve the uncertainties in vibrational excitation cross sections for electron hydrogen collisions. The influence of collisions with excited molecules on a kinetic phenomenon known as negative differential conductivity (NDC) will be shown next by using an example of NDC occurring in methane in an RF field.

In principle, when excited states affect significantly the electron transport in an ionised gas it is necessary to make complex self-consistent calculations. Starting from the assumed densities of excited states, excitation rates are calculated and applied in a system of kinetic equations for excited state population densities. Those equations have to include a large number of levels and a number of collisional processes such as resonant state trapping, intramultiplet collisional quenching, cascading and heavy particle quenching. A special item in the kinetic scheme which is almost always neglected is the collisions of electrons with excited states. Thus the effect of these processes is double, through the effect on the electron energy distribution function (EEDF) and rate coefficients and through the effect on the kinetics of excited states. Once number densities are determined a new series of Boltzmann equation calculations is performed until self-consistent results are obtained. Such calculations have to be performed for a specific system: geometry, pressure, gas composition, current etc. Thus general conclusions are difficult to make but such results are needed to model the absolute emission data from gas discharges at moderate and high current densities. Our work was primarily aimed at testing the available data in an attempt to provide a complete data set for RF discharge modeling in argon (Petrović *et al.* 1992, 1993) and here we shall illustrate the complexity of the procedure, list some of the available data and give some of the results.

Finally, we shall give some experimental examples and results of modeling (and some combined experiments and modeling) which show how excited states affect the kinetics of moderate to high current discharges. Those include the breakdown time delay measurements at long afterglow times, capacitively coupled discharges including the reference GEC cell and inductively coupled plasmas.

On the whole the paper follows the analysis of discharges from the cross sections to application in explaining the experimentally observed effects and absolute emission data. The basic aims are to describe some of the important steps in the procedure to include the effect of excited states, to discuss the availability of the data and the need for more reliable data from swarm physics and gas discharges, to point out the connections between the different disciplines and to call for further effort in swarm physics for studies of transport in the presence of excited particles.

2. Influence of Excited Molecules on Swarm Parameters

By definition swarm experiments are carried out under conditions where the previous history of electron–gas particle collisions does not affect future encounters. Thus the only practical situation for electron–excited molecule collisions is rotational and vibrational excitation, the molecules attaining their rotational and vibrational states by collisions with other molecules, i.e. by thermal collisions. Most measurements at low values of E/N in molecular gases are affected by rotationally excited molecules; rarely, however, have vibrationally

excited molecules played an important role at room temperature. One such case is that of CO_2 at elevated temperatures. Measurements of drift velocities by Elford and Haddad (1980) showed that vibrationally excited CO_2 molecules could affect the effective momentum transfer cross section.

(2a) Vibrational Excitation of Hydrogen

Morrison *et al.* (1987) have shown that the disagreement between the theoretical and swarm derived cross sections for vibrational excitation of hydrogen is far greater than the combined uncertainties. At the same time total momentum transfer and rotational excitation cross sections were in good agreement. The history and the current status of this controversy will be described elsewhere in this volume. Crompton (1984) proposed that an experiment in which a large abundance of vibrationally excited molecules of hydrogen is induced by some means could be used to provide additional data to distinguish between the 'swarm derived' and the 'rest of the world' cross sections for electron induced vibrational excitation of hydrogen. The experiment should be performed with and without vibrationally excited molecules and both sets of the experimental data analysed.

We have performed calculations of transport coefficients in parahydrogen (pH_2) at 77 K with and without superelastic collisions. As an example 50% of the molecules were assumed to be in the $v = 1$ vibrational state. It was assumed implicitly that all the inelastic and momentum transfer cross sections for vibrationally excited molecules are the same as those for the ground state molecules. The resulting drift velocities v_{dr} and D/μ values are shown in Fig. 1. Thermal equilibrium at 77 K is imposed at lowest E/N, an assumption that may be questionable with such a large abundance of excited molecules which would pump energy into the gas. A standard set of cross sections for pH_2 was used (England *et al.* 1988; Petrović 1985).

As expected, the drift velocities are below and D/μ values are above the data for the unperturbed gas. The maximum difference is observed around $1{\cdot}5$ Td ($1\ \text{Td} = 10^{-17}\ \text{V cm}^2$) as can be seen from Fig. 2. In Fig. 3 we show the influence of superelastic collisions (under the assumptions given above) on the electron energy distribution function (EEDF) at 1 Td.

Finally, in Fig. 4, differences between the transport coefficients calculated from the swarm derived and the theoretical (Morrison *et al.* 1987) vibrational excitation cross sections are given for the cases when there is a significant population of vibrationally excited molecules and when this population is zero. Superelastic collisions with excited molecules shift the maximum of the discrepancy to around 1 Td from 25 Td. This is not the result of an increase in mean energy due to superelastic pumping of energy to electrons, as the mean energy at 1 Td in the perturbed gas corresponds to the mean energy at 2 Td in the unperturbed system. Thus the effect is purely the result of the fact that at those energies the superelastic process affects the transport coefficients and, as the superelastic cross section is proportional to the vibrational excitation cross section, the difference between the two sets is observable at those energies which are well below the energies required for vibrational inelastic losses to affect the transport significantly. In addition one should bear in mind that the data for pH_2 have been extrapolated from 6 to 12 Td on the basis of normal hydrogen (nH_2)–77 K data and to 30 Td on the basis of the room temperature nH_2 data (Petrović

1985). Thus superelastic collisions with vibrationally excited molecules would push the maximum of the difference between the two sets well into the region where pH_2 measurements are feasible.

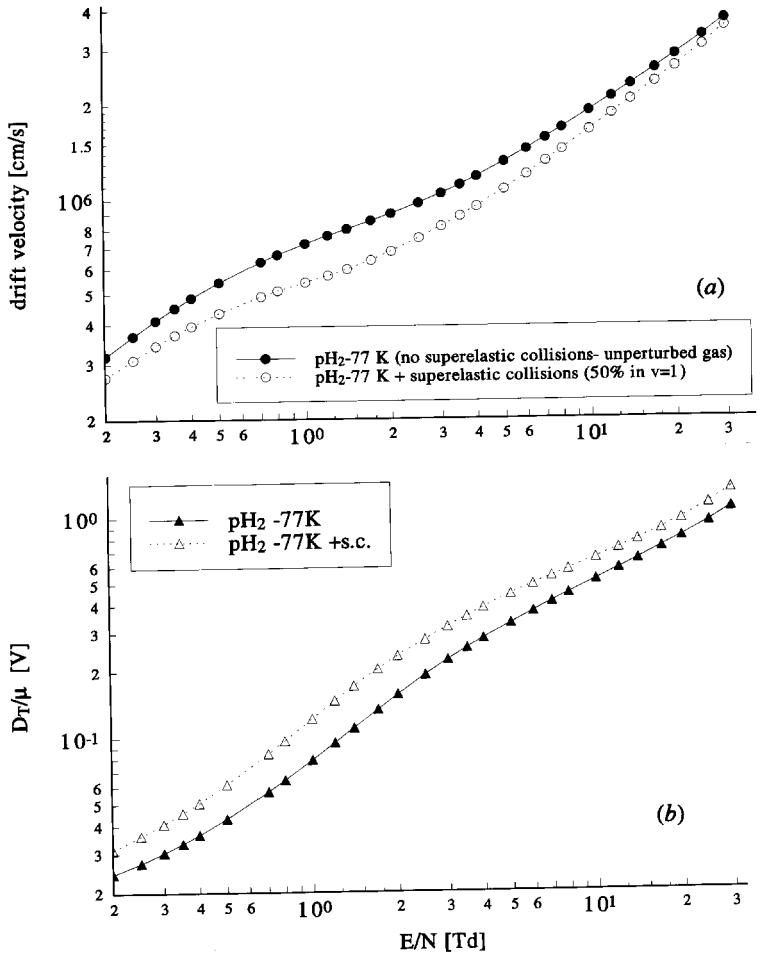

Fig. 1. (*a*) Drift velocity as a function of E/N for pH_2 at 77 K. (*b*) D/μ as a function of E/N for pH_2 at 77 K. Solid symbols are for the unperturbed gas, while open symbols correspond to the gas with 50% of excited molecules.

Another interesting feature is the change in sign of the difference between the two sets. A higher theoretical cross section would, at high E/N, result in higher energy losses but at lower E/N would result in an increased energy gain due to the superelastic process.

The experiment as proposed above would not suffer from the need to extrapolate the rotational excitation cross section to higher energies, as this cross section in the relevant energy range is well established from the experiment with the 'unperturbed' gas. The differences between the swarm data based on the swarm

derived and the theoretical vibrational excitation cross sections are well beyond the experimental uncertainty and larger than the differences in the standard pH_2 experiment. Thus we may conclude that an experiment with pH_2 at 77 K with and without a significant population of vibrationally excited molecules would give a decisive test on the discrepancy between the two existing vibrational excitation cross sections of electron–hydrogen molecule collisions.

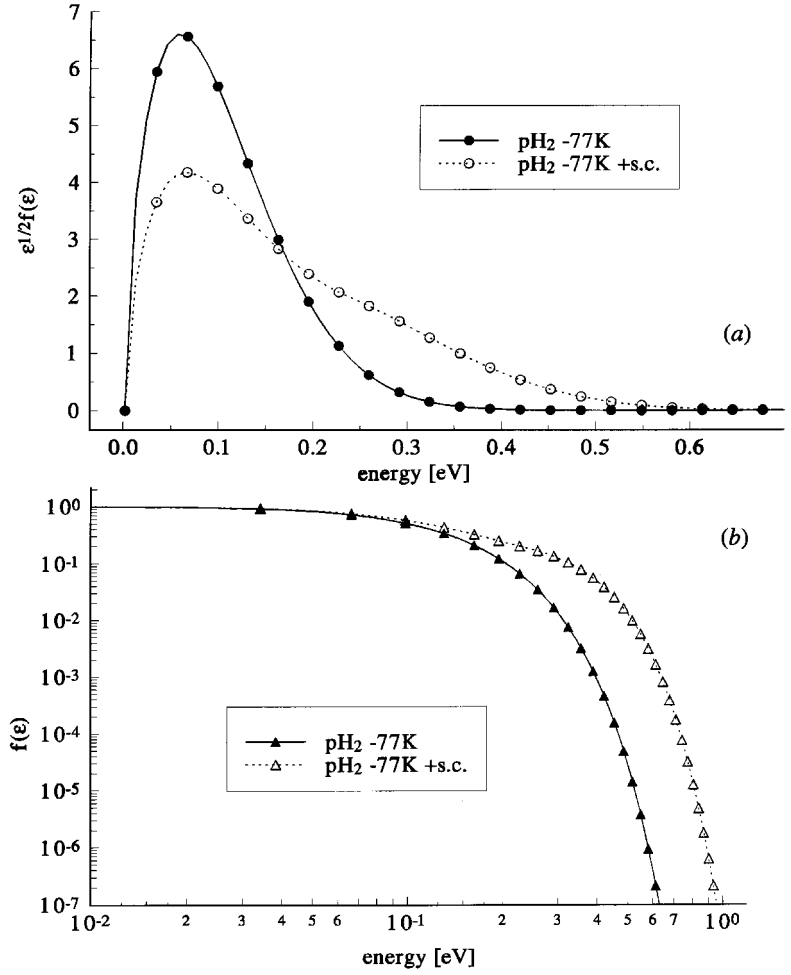

Fig. 2. Electron energy distribution function for pH_2 at 77 K at 1 Td: (*a*) probability density function; (*b*) electron energy distribution function. Solid symbols are for the unperturbed gas, open symbols correspond to the gas with 50% of excited molecules.

The feasibility of such an experiment is another issue. It appears that the first vibrationally excited level of hydrogen is not likely to absorb light efficiently, and thus it cannot be selectively excited by a laser operating at around $2 \cdot 5\ \mu$m. Some complex schemes to populate the level 'from above' are likely to produce numerous higher excited levels with uncertain abundances. The most promising of

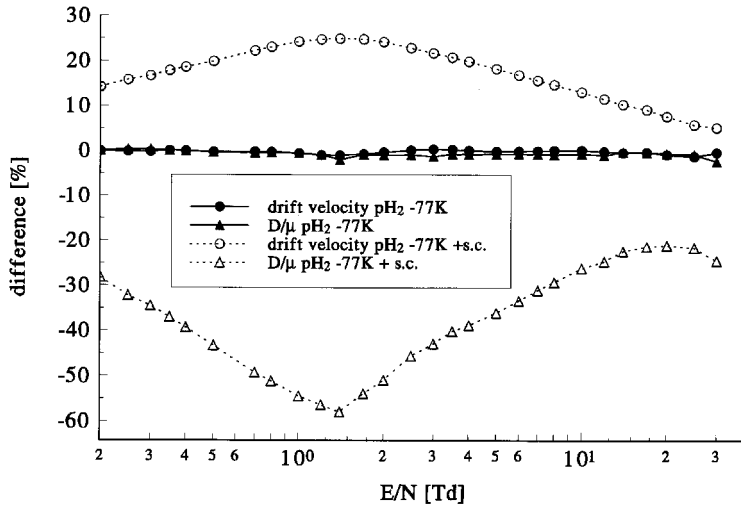

Fig. 3. Difference between the experimental data for unperturbed pH_2 at 77 K and the calculated data for the unperturbed gas (solid symbols) and the gas with 50% of excited molecules (open symbols).

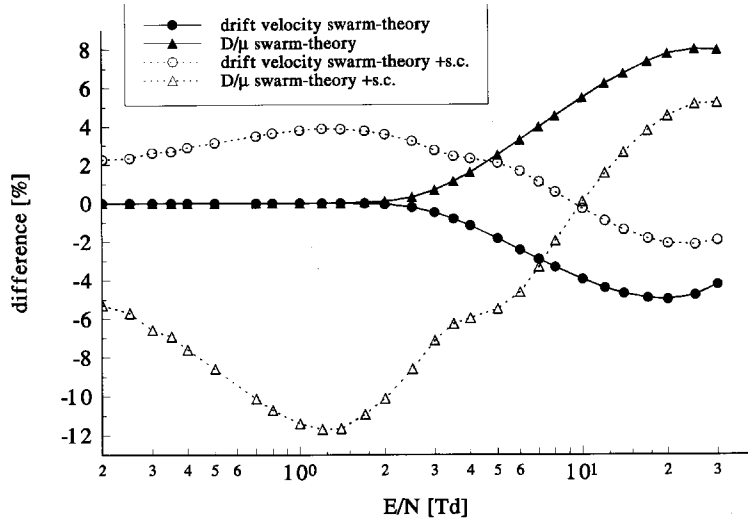

Fig. 4. Difference between the calculated data based on theoretical and swarm derived vibrational cross sections. Results for the unperturbed pH_2 at 77 K are shown with solid symbols and the calculated data for the gas with 50% of excited molecules shown with open symbols.

such schemes would be recombination of atoms on surfaces leading to desorption of vibrationally excited molecules (Čadež *et al.* 1993). Such a scheme suffers from many technical problems but it has been applied with an electron beam technique. Another limitation is due to relaxation of vibrational energy on the walls and

in gas phase collisions (see Capitelli 1986). Nevertheless, even if one were able to prepare an experiment with 100% of the molecules in the first vibrational state, the results would suffer from the assumption that the cross sections for rotational and vibrational excitation of such molecules are the same as those for the ground state molecules. Uncertainties introduced by such an assumption may exceed the requirements for a making distinction between the two sets of results and thus our conclusion is that, for the time being, a swarm experiment with a high abundance of vibrationally excited molecules is an unlikely prospect, even though it would be an experiment that we would like to see more than any other in the study of the physics of gas discharges.

(2b) Negative Differential Conductivity under the Influence of Excited Molecules

Negative differential conductivity (NDC), i.e. the reduction of the drift velocity with increasing E/N, has been studied recently for two reasons. First, the phenomenon itself is interesting for fundamental reasons as it also represents a difficult test of the validity of kinetic theories of electron transport (Robson and Ness 1988). The second reason is its importance in some applications such as opening diffuse discharge switches (Hunter *et al.* 1985).

Petrović *et al.* (1984) and Robson (1984) have established a set of conditions for the occurrence of NDC which until recently covered all the known examples. These authors gave a set of driving mechanisms that either favour NDC or work against it. One surprising result of that study is that NDC could be expected in a very wide range of situations, especially at very low E/N once electrons depart from thermal equilibrium with the background gas and start significant rotational or vibrational excitation. It was suggested by Petrović *et al.* (1984) and recently confirmed by Jelenak *et al.* (1995) that the primary reason for the failure of NDC to occur in most cases where it can be expected is the influence of superelastic collisions on the EEDF. In this paper the influence of excited states on NDC will be discussed for a rather unusual example of NDC in RF fields.

The NDC for RF fields can be predicted on the basis of the DC field effect. The first observation of this effect for the RF case was by Nakajima *et al.* (1990), although it was not discussed in terms of NDC. Recently Jelenak *et al.* (1995) have reported RF NDC and Bzenić and Petrović (1995) studied it in terms of relaxation of momentum and energy as a function of E/N and frequency. Independently, a similar effect was studied by Robson and White (1995). In this paper we show calculations for methane based on the cross sections by Ohmori *et al.* (1986). Similar effects can be expected for silane and other gases and gas mixtures where NDC occurs (Petrović *et al.* 1984). The calculations are based on the Monte Carlo simulation code developed specifically for the time varying electric fields (Bzenić *et al.* 1995). At $\nu = 10^5$ Hz [ν is the frequency and $E/N(t) = E_0/N\cos(2\pi\nu t)$], the time dependence of the drift velocity (Fig. 5*a*) has two symmetric peaks at points where dc E/N gives the maximum of the drift velocity. At $\nu = 10^6$ Hz the profile is asymmetric and at the point where the field drops from higher values the maximum almost completely disappears (Fig. 5*b*). Increasing the population (shown as percentage of the total population) of vibrationally excited molecules of methane (again under assumption that other processes for excited molecules are not affected) reduces the effect of NDC. The overall behaviour is frequency dependent and the detailed influence of excited states can be seen from the time

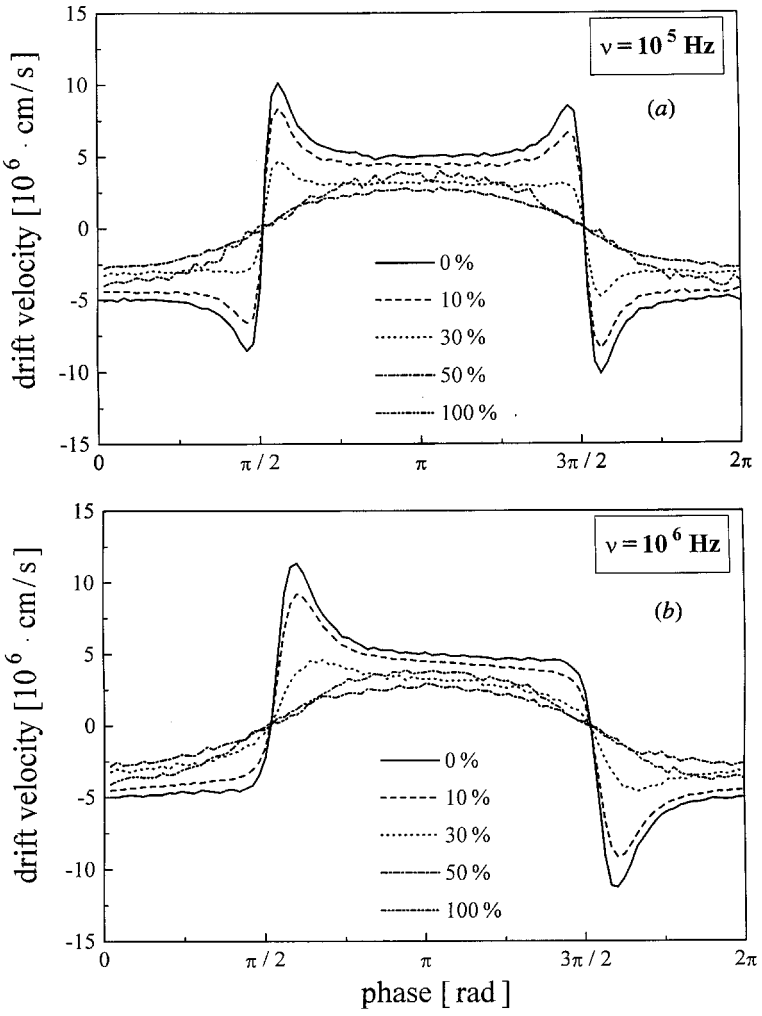

Fig. 5. Drift velocity as a function of time within one period for $E/N_0 = 50$ Td and (*a*) $\nu = 10^5$ Hz and (*b*) $\nu = 10^6$ Hz for electrons in methane with different abundances of vibrationally excited molecules.

resolved EEDF. In Fig. 6*a* we show the time resolved EEDF for the unperturbed case and in Fig. 6*b* the EEDF for methane with a 30% population of molecules in the first vibrationally excited state. One should note that the corresponding temperatures are exactly the same as those measured in RF discharge plasmas (Makabe 1994). The difference between the two EEDF (see Fig. 6*c*) reveals that, similar to the dc case in H_2, the unperturbed EEDF is larger at low energies and the EEDF is affected by superelastic collisions at energies above the mean energy. From Fig. 6*c* one can see that the excited states through superelastic collisions affect the distribution function more, during the period when the value of E/N is falling, as can be expected. The overall effect of excited molecules is strongly dependent on frequency and E/N and, even though NDC is reduced at frequencies larger than inelastic collision rates, some sign of NDC persists in

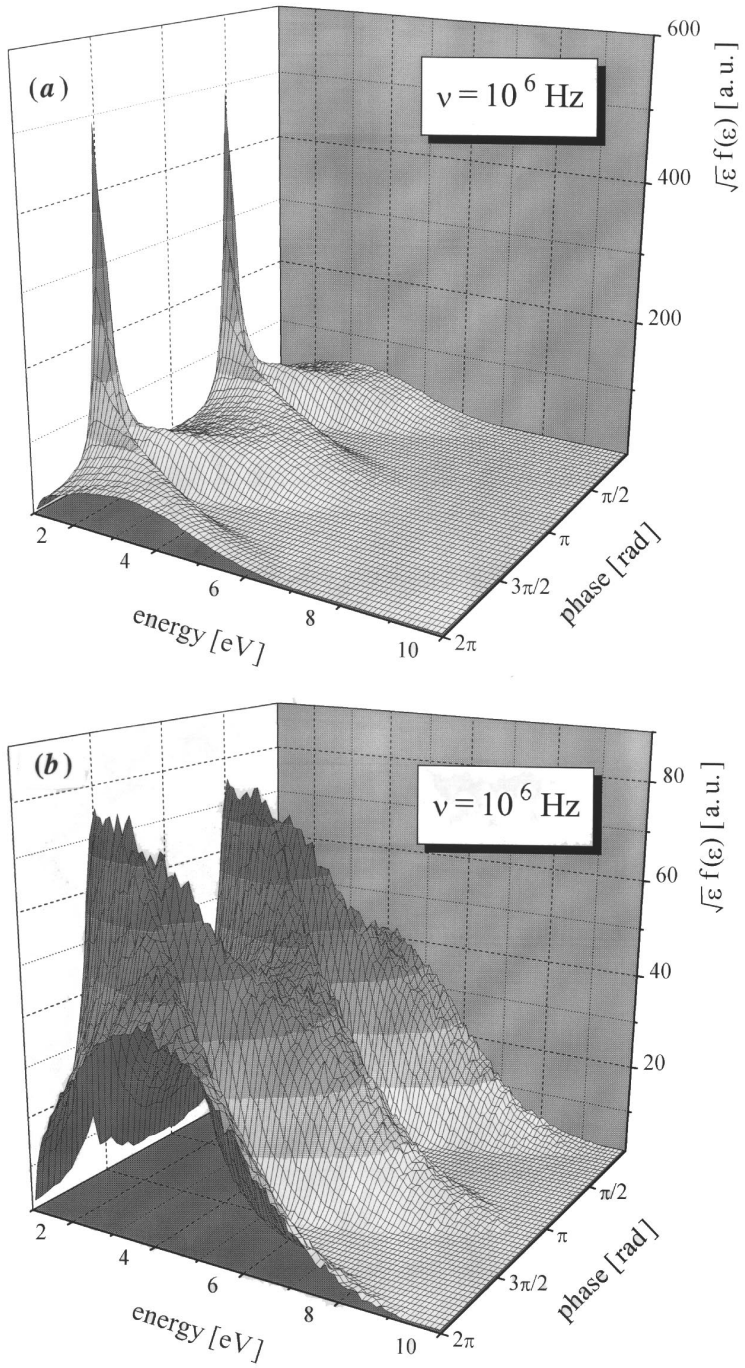

Fig. 6. (*a*) Electron energy distribution function as a function of time within one period for $E_0/N = 50$ Td and $\nu = 10^6$ Hz for electrons in methane with no vibrationally excited molecules. (*b*) Same as (*a*) but for $\nu = 10^6$ Hz and for 30% of vibrationally excited molecules. (Next page) (*c*) Contour plot of the difference between (*a*) and (*b*) where positive values indicate that the unperturbed EEDF is larger.

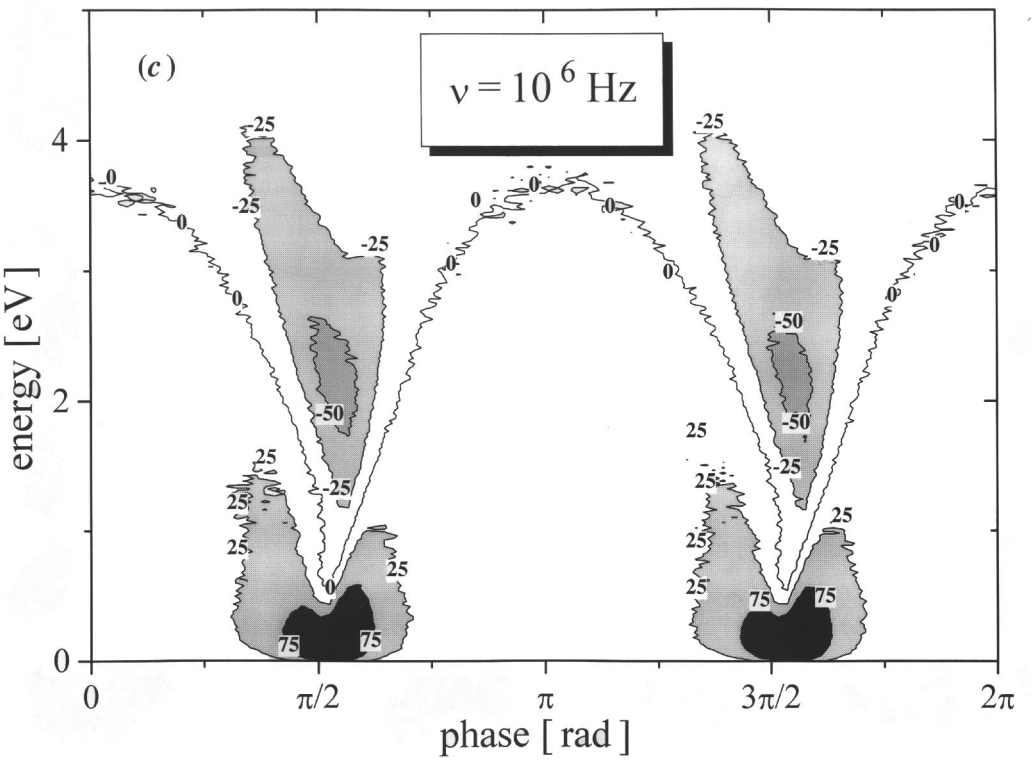

Fig. 6. (*Continued*)

the waveforms until very high frequencies equal to momentum transfer collision rates. The convolution of voltage and current gives the power in RF discharges and any presence of the NDC deformed drift velocity waveforms will affect a determination of the power absorbed by the discharge.

One should bear in mind that the basic criteria for NDC have collision rates for inelastic losses and superelastic gain as a difference in all terms (Ness and Robson 1988, Vrhovac and Petrović 1996). Thus the superelastic rate that decreases with E/N results in a decrease of NDC, just like the increasing inelastic collision rate. The opposite behaviour will favour the NDC (Petrović *et al.* 1984; Robson 1984) but is difficult to obtain under normal circumstances.

3. Modeling of Excited State Kinetics in Argon

While we apply theoretical and numerical techniques developed in swarm physics to model swarm experiments, we rarely encounter the need to treat collisions with excited states except for the thermal populations. In low pressure glow discharges similar theoretical techniques are applied but non-equilibrium populations of some excited states with high threshold energies may correspond to large effective temperatures. In this section we shall discuss some examples where large populations of excited states included into transport theory or simulations affect significantly the EEDF and the calculated transport data.

(3a) Calculation of the Electron Energy Distribution Function, Rate Coefficients and Excited State Number Densities

Swarm parameters and the EEDF are often used to model the gas discharges operating at elevated currents, i.e. when electron excitation produces a large population of excited states. Calculations for such conditions should include effects of the following processes involving excited states on the EEDF and overall kinetics:

(*a*) superelastic collisions;
(*b*) stepwise excitation and ionisation;
(*c*) low threshold inelastic processes from excited states for atomic gases; and
(*d*) Penning ionisation in the presence of impurities or for mixtures (chemi-ionisation, pooling reactions, etc.).

The numerous studies in the literature (Karoulina and Lebedev 1992; Ferreira and Ricard 1983; Vlček and Pelikan 1989) that have been performed for rare gases are mostly based on incomplete data sets, even when educated and semi-educated guesses were used. The results of calculations give conclusions which range from 'almost no effect' to 'very important' and the excited to ground state number density ratio onset of the effect varies from 10^{-10} to 10^{-4} cm^{-3}. In the case of molecules, a large number of vibrational and rotational level populations with all the details of V–V, V–R and V–T relaxation (where V denotes vibrationally excited states, R rotationally excited states and T the translational kinetic energy), dissociation and ionisation have to be followed, leading to even more complex schemes which have been studied (in great detail) by Capitelli and his coworkers (see Capitelli 1986).

We have performed simplified calculations for molecules such as silane and methane. Calculations performed for argon were however the most detailed (both in the number of processes and number of excited levels included) in the literature. Rare gases are an excellent example for illustrating the influence of excited states on transport parameters needed for gas discharge modeling (due to the absence of inelastic processes at low energies and prominent metastable levels of the lowest excited state).

In the case of argon, process (*c*) above was included in Boltzmann calculations by Judd (1976). For electron-excited state collisions, only ionisation of 4s levels was included by using the calculations of Vriens (1973). It was concluded that for excited state densities above 10^{-4} of the ground state population the excitation rates are significantly reduced. However, it was noted that inclusion of superelastic collisions reduces the overall effect. One should also note that the large effects observed by this author are the result of the large assumed density of the metastables. A detailed analysis of the influence of superelastic collisions (process *a*) of electrons with argon metastables was carried out by Bretagne *et al.* (1987). These authors also included Penning ionisation (process *d*) but the metastable densities (N^*) that were selected $N^*/N(0) = 4 \times 10^{-9} - 4 \times 10^{-10}$ were lower than those adopted in other similar papers. Nevertheless, there was a significant effect on the EEDF and consequently on the collisional rates. Ferreira *et al.* (1985) have put together a model for argon which included collisional coupling between the radiative and metastable levels, resonance radiation trapping, and stepwise excitation and ionisation from metastables. The rate coefficients for the

metastable to resonant state collisionally induced transitions were based on an estimate, while the cross sections of Hyman (1978, 1979) were used for stepwise excitation and ionisation.

In our calculations we have included:

- direct electron excitation from the ground state (up to 80 different coupled equations for the levels, states or bunched levels);
- electron excitation and quenching from excited states (4s and 4p);
- radiative transitions;
- collisional quenching (two and three body, pooling);
- collisional intramultiplet coupling;
- diffusion of excited states; and
- resonant level trapping (both Doppler and collision induced profiles).

A general problem in such calculations is the lack of data. Even the radiative transition probability tables are incomplete, parent gas quenching for all but the most popular, low level, metastables are in short supply, while electron induced quenching and heavy particle intra multiplet coupling data are practically nonexistent in all but one or two cases. The shortage of data was compensated for by extrapolations from the data for other states and for other gases, neon in particular. The effect of some impurities was also studied.

The calculations consisted of solving the Boltzmann equation as well as the set of coupled differential equations for the time evolution of excited states. These equations were followed until a steady state was reached. A standard two term code for solving the Boltzmann equation was used (1970) and a specially written code was used for the set of coupled equations based on Fehlberg's modification of the Runge–Kutta method (Hairer *et al.* 1987). In calculations using the Boltzmann equation the rate coefficients processes (a) and (c) were included with an assumed initial population of excited states. As our primary concern was the modeling of RF discharges operating in the moderately low pressure range, the conditions were selected to obtain a realistic value of metastable concentrations corresponding to the conditions found in RF argon discharges (Makabe *et al.* 1992; Tochikubo *et al.* 1994) at pressures between $0{\cdot}5$ and 1 Torr and close to the minimum sustaining voltage. The value of $1{\cdot}5 \times 10^{11}$ cm^{-3} was selected for the excited state number density in the initial calculation of the rate coefficients for electron induced quenching and stepwise processes.

Apart from affecting the energy distribution function superelastic collisions (process a) contribute directly to the quenching of excited states. The cross sections can be obtained from the ground state excitation cross sections by applying the principle of detailed balancing. The rate coefficient for the superelastic process and consequently its contribution to quenching is relatively small for all but thermal electrons, which is in agreement with the results by other authors (Lymberopoulos and Economou 1993). Over the entire energy range covered in our calculations the superelastic collisions do not make a significant contribution to the loss of excited states, the rates are more than two orders of magnitude smaller than the rates for coupling between metastable and resonant levels.

The dominant loss of excited states induced by electron collisions is therefore due to transitions between the different levels of the 4s state of argon. Experimental data for this process are of relatively low accuracy. The data were obtained for

plasmas with very low energies close to thermal and vary significantly. The most detailed study of electron induced quenching of metastables by collisional coupling to resonance states was made (by Baranov *et al.* 1981) using the absorption technique in the argon discharge afterglow for electron temperatures between 500 and 3000 K. These authors fitted their data and obtained the temperature dependence of the rate coefficients and the cross sections for deexcitation of the resonant and metastable states at very low energies. Analytical forms of the electron scattering cross sections were used to extrapolate the cross sections to very high energies, far from the range of experimental data which covered only energies close to the threshold. Thus their cross sections should be viewed as less reliable than their rate coefficients. The large scatter of the experimental points (see Fig. 7) indicates the rather large uncertainty in the data which cannot be easily and directly obtained from the experiment. Scheller *et al.* (1988) have determined the rate of quenching of argon metastables most probably $^3P_2$, to be $1 \cdot 2 \times 10^{-7}$ cm^3 s^{-1} for an estimated electron energy of 1 eV.

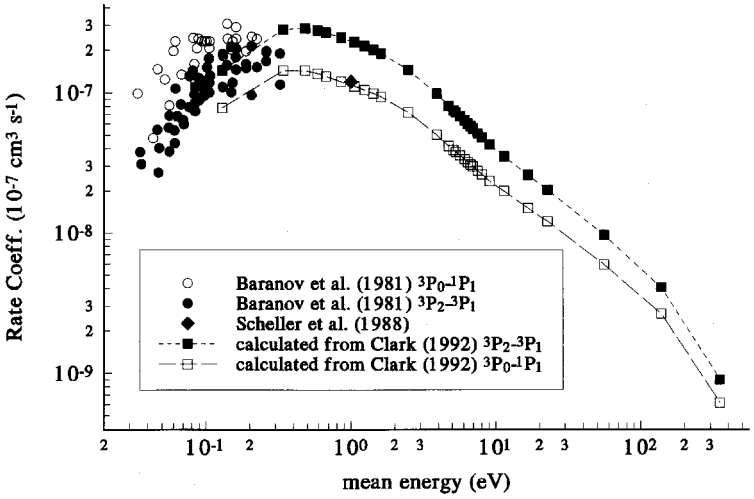

Fig. 7. Rate coefficients for electron induced collisional quenching of argon metastables.

There are no direct measurements of electron collision induced transitions within the 4s state available. In our calculations we have used the data of Clark *et al.* (1989) and Clark (1992), who used the first order many body theory (FOMBT) to calculate the cross sections for electron induced transitions between the 4s levels. While this theory may fail to represent such transitions very accurately these calculations are very valuable since they are the only ones available and are part of a complete set of electron excitation cross sections for most excited levels.

Apart from the electron transitions between the 4s levels, electrons can induce excitation to higher levels, ionisation and may also be scattered elastically. The total cross section for electron scattering from metastable argon atoms has been measured by Celotta *et al.* (1971). These cross sections are a factor of 2 larger than the calculations of Robinson (1969) for elastic scattering. This process may be of interest, however, only when very accurate transport coefficients are

required for low energies, below 0·5 eV and with metastable densities larger than 10^{-5} of the ground state population density, which is normally not the case.

Excitation cross sections for the 4s-4p transition have been determined by Mityureva (1985) in a gas cell type electron beam apparatus by the measurement of the emitted radiation. These results are of limited accuracy since optical emission from only one 4p level has been used, and also there is great difficulty in determining the absolute density of metastables (cascading has been assumed to make a negligible contribution to the upper state). Because of these problems we used mainly the theoretical results in our comparisons. The often quoted Born cross sections calculated by Hyman (1978) have been used in our calculations together with the FOMBT results of Clark and Csanak (1989). As an example of a large number of semi-empirical formulae we included the formula due to Behnke *et al.* (1985) with parameters obtained from fits to the experimental data for emission from argon discharges. A comparison of the cross sections with the measurements of Mityureva (1985) is inconclusive. The only relevant rate coefficient result is the one point (1 eV) by Scheller *et al.* (1988) where quenching of 4s metastables by transitions to both resonant 4s levels and to 4p levels occurs. It appears that the cross sections of Hyman are too large in the threshold region and that a modification similar to that done by Behnke *et al.* is required. The data of Clark and Csanak are also in reasonably good agreement.

Data for the cross sections for transitions from the 4s state to higher levels are lacking except for the calculations by Hyman (1978) and Clark (1992). In the calculations presented here we show only the results based on the latter set.

Ionisation from the 4s state is a very important process in gas discharges but still there is only a limited supply of experimental data. The well known measurements of the cross section by Dixon *et al.* (1973) have not been published yet in final form, though numerous theoretical papers compare those data with calculations (Hyman 1979; Ton-That and Flannery 1977; Clark *et al.* 1989). In addition to the theory several forms of semi-empirical formulae exist which have been used to fit the experimental gas discharge data (Vriens 1964, 1973; Vriens and Smeets 1980). Bearing in mind the importance of this process in the overall ionisation balance, it is essential to have more experimental cross section and ionisation rate data. Ionisation from the 4p and other higher levels is much larger than that for the 4s state and should be considered in the ionisation kinetics if a sufficient population of higher states exists.

(3b) Results of Calculations

Having included all those processes in the solution of the Boltzmann equation and population kinetics equations we have performed calculations for low pressure (0·01–100 Torr) discharges in argon. One example of the calculated rate coefficients is given for the electron induced collisional coupling (quenching) of the 4s state. The results of Baranov *et al.* (1981) and Scheller *et al.* (1988) are compared with our calculations based on the cross sections of Clark (1992). The agreement is reasonably good, bearing in mind the large uncertainty in the experimental data. The very wide scatter shown in the Fig. 7 is the best that we can do at the moment, which may be sufficiently good for the discharge modeling when many different processes compete, but current development of experimental techniques and the importance of modeling of plasmas for processing justify further efforts

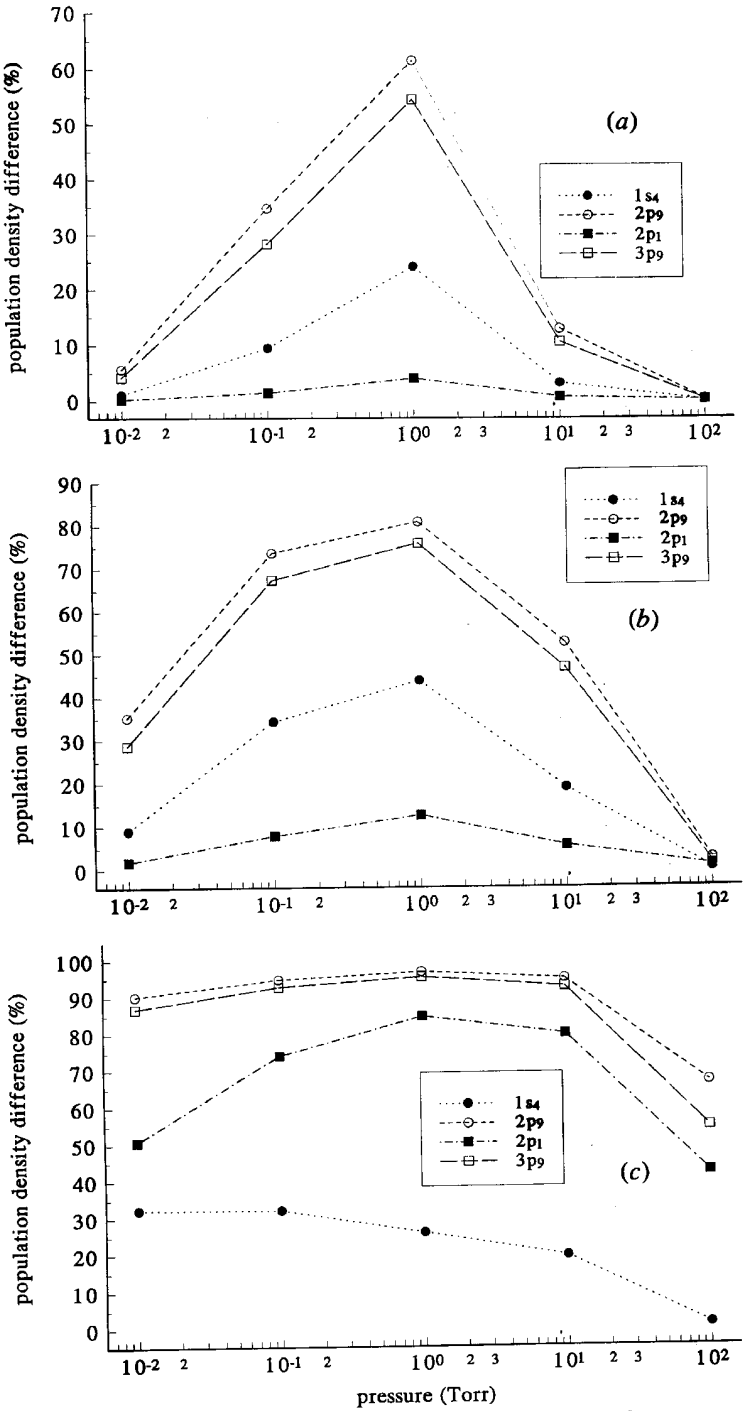

Fig. 8. Percentage difference between the population densities, with and without the inclusion of electron induced transitions in the kinetic model: (*a*) $n_e = 10^8$ cm^{-3}; (*b*) $n_e = 10^9$ cm^{-3}; and (*c*) $n_e = 10^{11}$ cm^{-3}.

in measuring both the cross sections and the rate coefficients. The same is true for other stepwise processes from the 4s and higher excited states.

The calculations for the argon excited state populations have to be performed for each value of E/N and pressure. The best way to visualise the data is to fix all the input parameters and vary the input for just one process while observing the percentage difference of the excited level population densities. In Fig. 8 we show the change of population of several levels due to electron induced collisional coupling of excited levels, where detailed data for the excitation of all the higher states from 4s are included as well as the data for 4p state excitation and ionisation. Three different levels of electron number densities were chosen from relatively low $n_e = 10^{-8}$ cm^{-3} (Fig. 8*a*) to moderate 10^{-11} cm^{-3} (Fig. 8*c*). In all the cases chosen as examples, the maximum effect is observed at around 1 Torr. At low values of n_e the effect is localised around 1 Torr, while at higher concentrations it extends from the lowest to the highest pressures. Modeling of absolute line intensities requires taking into account electron induced collisional coupling of excited states. A similar magnitude of effect is obtained for the influence of 4p intramultiplet coupling by heavy particle collisions, collisional quenching of 5s and 3d states and cascading from higher excited states, except that the pressure dependence is somewhat different since it increases with pressure reaching a maximum at or above 10 Torr. The resonance radiation trapping effects are huge but confined to the two lowest resonant levels. Other states are affected very little, which is unexpected but reasonable since even with a very pronounced trapping of resonant levels nearby metastable level populations are quite larger. Higher resonant levels have many parallel decay channels through other excited states so trapping can affect significantly only their own number density but not the overall kinetics.

One should bear in mind that some processes may have a different influence on different level populations, so simplified kinetic schemes are not likely to give guidance as to which channels should be included. Modeling of the complete excitation kinetics is required for accurate results.

Another way of presenting results is to generate effective excitation coefficients from number densities of excited levels. In Fig. 9 we show the effective excitation data for two 4p levels $2p_1$ (Fig. 9*a*) and $2p_9$ (Paschen notation) (Fig. 9*b*). The former gives the $750 \cdot 4$ nm line and the latter the $811 \cdot 5$ nm line, both frequently used in plasma diagnostics. In the case of the $2p_1$ level there is almost no excitation through intramultiplet collisional coupling, and both cascading and transitions from other excited states by electron collisions are much smaller than electron excitation from the ground state. The situation is completely different for the $2p_9$ level, where electron induced transitions from other excited states and cascading dominate over direct electron excitation. The calculations have been performed for $p = 1$ Torr and $n_e = 10^8$ cm^{-3} and the conclusions change if those parameters change. In any case the kinetics of the two levels for the selected conditions (which are typical) will be quite different, which will be shown later.

In concluding this section we may state that complex modeling of complete excited state kinetics requires the inclusion of all relevant processes for the specific conditions and is particularly important if absolute line intensities from plasmas are to be modeled. There is a shortage of reliable data, especially for stepwise electron induced processes, for heavy particle induced intra multiplet coupling

and for higher excited state collisional quenching. Electron transport coefficients and EEDF used in modeling are affected by the collisions with excited states in a significant way through the processes described above.

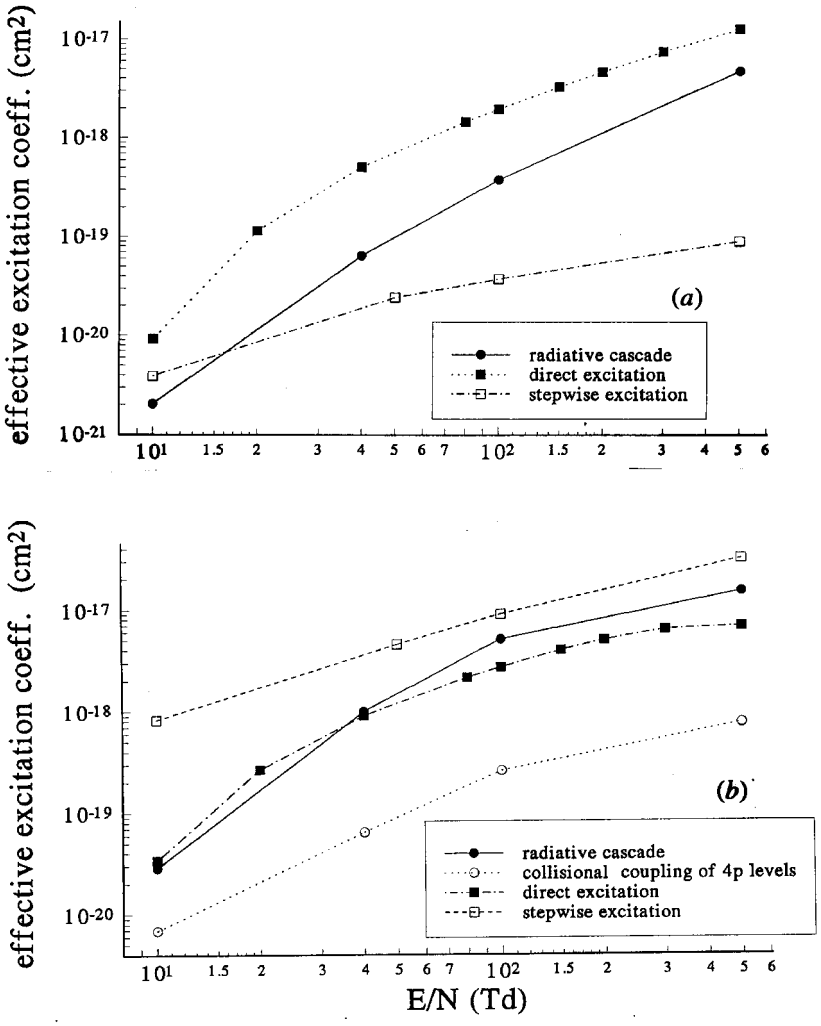

Fig. 9. Effective excitation coefficients for a pressure of 1 Torr and $n_e = 10^8$ cm^{-3} in argon: (a) $2p_1$ level and (b) $2p_9$ level.

4. Gas Discharge Kinetics with an Abundance of Excited Molecules

There are numerous examples of gas discharges where the effects of excited states have been noticed but very few have been obtained in experiments where absolute measurements allow quantitative comparisons between the predictions of the models and the experimental data.

The effect of excited states on the breakdown probability has been studied over a long period of time and the most recent explanation is that the long

afterglow dependence of the breakdown time delay, the so-called 'memory effect' is due to the kinetics of the atoms remaining from the dissociation of molecules in the discharge (Marković *et al.* 1994). After recombining, atoms of nitrogen produce enough excess energy to create a secondary electron and thus can affect the breakdown and ionisation kinetics in general. One should keep in mind that the atoms resulting from the dissociation of stable molecules should be regarded in a similar way to the excited molecules.

(4a) Modeling and Diagnostics of RF Discharges

Measurements of the spatial distribution of emission from discharges aimed partly at verifying the procedures for actinometry and the determination of the sheath widths (Radovanov *et al.* 1990; Djurović *et al.* 1994; Tochikubo *et al.* 1990) has revealed that the onsets of emission in the sheaths are ordered so that the highest threshold transitions are the closest to the electrode. The phenomenon was explained as the result of the combined effect of a significant component of excitation due to γ electrons, while the main discharge sustaining mechanism is electron reflection from the moving sheath boundary. In this case the threshold for the process, and the shape of the cross section close to the threshold determine the onset of emission.

The explanations proposed in the literature (Radovanov *et al.* 1990; Petrović *et al.* 1995; Tochikubo *et al.* 1990) were able to explain most of the observed cases except for the behaviour of the $811 \cdot 5$ and $750 \cdot 4$ nm lines in argon. Both the onset of emission and the overall spatial profile were different, while the excitation threshold and the cross section energy dependence were practically the same. In particular, the $811 \cdot 5$ nm line had a very broad profile extending into the sheath and middle of the discharge unlike profiles of other lines. Tochikubo *et al.* (1990) have suggested that stepwise processes may play a role in the arrangement of the onsets of emission. Petrović *et al.* (1995) were able to prove by particle in the cell (PIC) (Birdsall 1991) simulations that the $811 \cdot 5$ nm line profile corresponds to the profile of stepwise excitation through the 4s state whereby the effective threshold is reduced. In Fig. 10 we show the results (Petrović *et al.* 1995) for the simulation of spatial profiles for model argon in a symmetric RF discharge at $0 \cdot 25$ Torr operating at 13 MHz. The $811 \cdot 5$ nm line has a much broader profile and a different onset. The conditions are such that the $2p_1$ level, giving rise to $750 \cdot 4$ nm radiation, is populated mostly through ground state excitation while the stepwise excitation dominates for the $2p_9$ level which decays through $811 \cdot 5$ nm emission.

Recently the effect of inelastic losses due to electron-excited state collisions on metastables in RF discharges has been investigated. Independently of our work (Petrović *et al.* 1992), Lymberopoulos and Economou (1993) have included superelastic collisions, stepwise excitation and electron induced coupling of metastable and resonant states. They use their calculated rate coefficients for stepwise excitation and the data of Ferreira *et al.* (1985) for electron induced coupling between the metastable and resonance levels, which is the dominant quenching channel for very low electron energies. On the other hand Tochikubo *et al.* (1994) have performed both experimental and theoretical studies of the effect of excited states on RF discharge kinetics. For typical capacitively coupled RF plasmas at between $0 \cdot 1$ and 2 Torr in argon it was found that the metastable densities

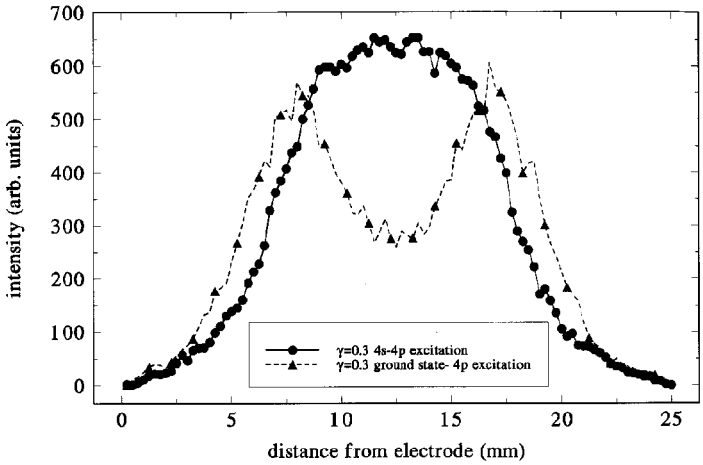

Fig. 10. Spatial distribution of emission in relative units for a capacitively coupled discharge in argon at 0·25 Torr at 13 MHz. The line with triangles corresponds to the direct excitation of the $2p_1$ level, i.e. 811·5 nm emission. The line with circles corresponds to the stepwise excitation from the 4s state of the $2p_9$ level, i.e. 750·4 nm emission.

are of the order of $0{\cdot}5 \times 10^{11}$ cm^{-3} and the stepwise ionisation and metastable–metastable pooling reactions contribute to the overall ionisation balance as much as the direct ionisation.

The work of Tochikubo *et al.* (1994) shows the effect of electron–excited molecule collisions on the overall gas discharge kinetics much more directly than our previous discussion of the onset of emission in RF discharges. By adding small amounts of nitrogen to a capacitively coupled discharge these authors were able to determine the absolute density of metastable states through the emission of the second positive band of nitrogen. A discharge model containing most of the processes described above was able to predict the space–time resolved emission and excited state density profiles and a very good quantitative agreement with the experiment was achieved.

The latest growth area in gas discharge physics is undoubtedly the study of non-equilibrium inductively coupled plasmas (ICP) operating at low pressures. Characteristics of these discharges are large electron and excited state number densities, while relatively low fields mean that the average electron energies are low throughout the discharge. Under such conditions the EEDF will be strongly affected by superelestic collisions, while stepwise processes will play a determining role in the overall kinetics especially for the ionisation and excitation of ionic lines. This effect was very clearly shown by Okigawa *et al.* (1996). These authors made measurements of absolute emission intensity from an ICP at very different gas flows while keeping other conditions fixed as much as possible. In Fig. 11 we reproduce their results for the $3p_5$ level number density and in Fig. 12 we reproduce their data for the $A^+(4p^4D_{7/2})$ level of the argon ion which are excited with thresholds of 14·57 and 35·05 eV respectively. The population of the atomic level was reduced significantly, by 30% when the gas flow was increased from 10 to 100 sccm, while the population of the excited state of ion was reduced by almost

two orders of magnitude. The increased flow of gas has reduced the population of metastables in the discharge and consequently the ionic state, which can only be produced through excitation of metastables, can no longer be excited by the relatively low energy electrons.

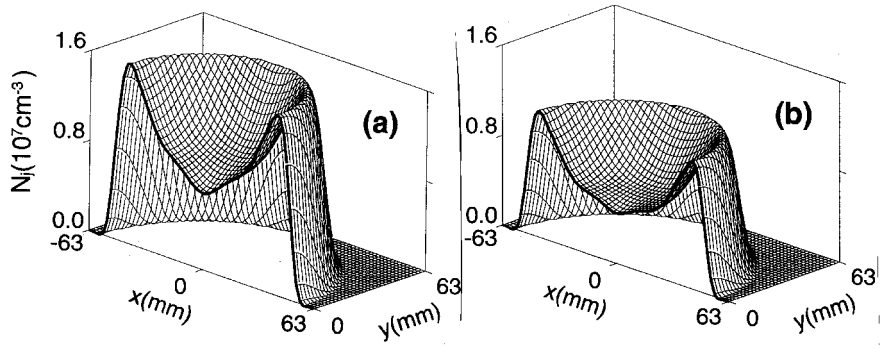

Fig. 11. Spatial density of the excited $3p_5$ level of argon in ICP at 0·5 Torr: (*a*) 10 sccm flow rate and (*b*) 100 sccm flow rate. [Reproduced from Okigawa *et al.* (1996).]

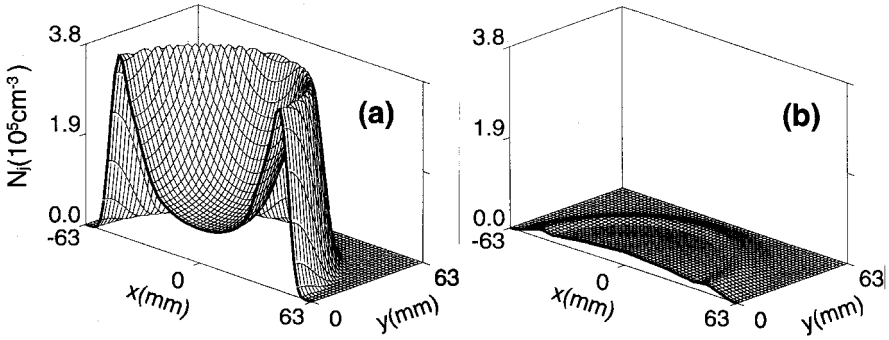

Fig. 12. Spatial density of the excited $A^+(4p^4D_{7/2})$ level of the argon ion in ICP at 0·5 Torr: (*a*) 10 sccm flow rate and (*b*) 100 sccm flow rate. These data show a dramatic drop in emission at an increased flow rate due to the loss of metastables which are necessary to produce emission of the high threshold ionic line. [Reproduced from Okigawa *et al.* (1996).]

All these examples show that it is important (at least for gas discharge modeling purposes) to understand the overall kinetics of excitation and energy deposition, as well as ionisation kinetics, and it is encouraging that models (which include calculations of EEDF and swarm parameters as discussed above) give good quantitative agreement with experiments.

5. Conclusion

In our discussion of the application of the 'excited molecule' pH_2–77 K experiment it was concluded that such an experiment would shift the range where the two sets of cross section data produce quite different results to lower E/N where there are less uncertainties and the overall sensitivity to the vibrational excitation cross section would be increased. Unfortunately, technical difficulties

make this experiment difficult to perform at the moment and there are some limitations in principle. The NDC effect is expected to be affected by electron collisions with excited molecules: in general NDC will be reduced both in DC and in RF discharges. However, the theory of NDC includes the possibility that NDC could be induced by superelastic collisions if the collision rate coefficient for this process increases with E/N.

When modeling the emission from gas discharges, such as RF plasmas in argon for processing, it is necessary to include a complete set of processes in the kinetic scheme. The electron–excited molecule collisions enter the kinetics twice making it nonlinear, once through calculation of the EEDF and rate coefficients and once through the kinetics of the excited states. For normal conditions it is quite possible that two levels with similar thresholds may have completely different kinetics, one through excitation of ground state and the other through other excited states. This leads to completely different spatial profiles of emission and possibly even temporal dependences. The presence of excited molecules strongly influences the capacitively coupled RF discharges, but the models are able to give good quantitative agreement provided that all the important processes are included. Inductively coupled plasmas with their high density of low energy electrons and excited molecules will be prime candidates for stepwise excitation and ionisation.

We may conclude that the application of the swarm data and calculation techniques for gas discharge modeling dictates the need to study further the role of excited molecules on swarm properties and that kinetic schemes coupled with EEDF calculations provide a reasonably good basis for modeling purposes. Swarm experiments, for such conditions, are unfortunately still lacking and increased activity in this direction may be one of the most important future interests in swarm physics.

It appears that the uncertainties in the available data are not the limiting factor in modeling RF discharges at present but with the improvement of numerical techniques the need may arise for more accurate input data. The biggest problem in any case is the shortage of data. There is another important warning concerning the available data. One should analyse carefully the source of data before applying them because in the analysis of most experiments some processes are neglected with the consequence that the results obtained are effective results. A more detailed model may include the same effect twice. A typical example of such a problem is the cascading which is already included in most rate coefficient and cross section data.

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