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The influence of excited states on the kinetics of excitation and dissociation in gas mixtures containing methane

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Abstract

In this paper, we extend the calculations for rare gas discharges, which aim to establish the influence of excited states on the kinetics of electron-induced excitation, to rare gas–methane mixtures and pure methane which are often used in diamond-like film deposition. In particular, we address the effect of non-thermal vibrational populations on the rate coefficients in methane-containing gas discharges using the procedure applied previously for pure silane. Furthermore, we investigate the kinetics of electronically excited levels of rare gases and methane in the presence of a significant population of excited states. These states may contribute to the overall ionization, excitation and dissociation rates through stepwise processes, superelastic collisions and energy transfer processes.

The influence of superelastic processes on the development of the negative differential conductivity (NDC) is discussed on the basis of the momentum transfer theory, and it is shown that the NDC is reduced when significant populations of excited states are present. This is of importance for calculations of the transport coefficients for a.c. electric fields where NDC leads to a complex temporal dependence of the drift velocity and thus directly affects the power deposition in the discharge.

Finally, we present the rate and transport coefficients calculated for methane in r.f. fields based on the Monte Carlo simulation for time-dependent fields. A good agreement with the effective field approximation and earlier Boltzmann calculations is found.

Keywords: Diamond-like films

1. Introduction

Developments in diamond-like film deposition are at an early stage, similar to developments in other fields of plasma applications in microelectronics and surface modification, and are based on empirical achievements rather than an understanding of the underlying physical phenomena. Therefore there is a need to develop models which give good quantitative agreement with simple, precisely defined, experiments, such as those performed in the GEC reference cell which has yet to be applied for diamond deposition from gases and mixtures.

Initially, complex models are required to reproduce all the important features of the discharges in pure methane, other hydrocarbon gases and their mixtures, usually with hydrogen and argon. The success of these models provides confidence in the proposed mechanisms that sustain the discharge. The complexity of molecular ion kinetics has been achieved in such models. However, electron kinetics, which are often developed for low current minimum sustaining conditions, must be made more complex to cover all the details of higher power operation even when quasi-symmetric operation is achievable.

The modelling of gas discharges used for diamond-like film deposition requires a good knowledge of the basic kinetic processes leading to dissociation [1,2]. Apart from excitation to repulsive states, which is one of the major dissociation channels, the most important non-intrusive diagnostics technique is optical emission spectroscopy [3].

In this paper, we discuss separately some of the features of electron kinetics, namely the influence of excited states mostly through superelastic collisions. Calculations have been performed in pure methane to indicate the importance of vibrationally excited molecules in the development of the electron energy distribution function (EEDF) and rate coefficients. In

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methane–argon mixtures, similar effects are obtained due to the presence of argon metastables, which in pure argon are sufficiently abundant to affect the electron kinetics [4,5].

The effect of the negative differential conductivity (NDC) is of great importance in electron kinetics in pure methane. We study the influence of the excited states on the NDC. In addition, we show how the NDC affects the drift velocity development in a.c. electric fields. The r.f. Monte Carlo simulation code is also applied to calculate the rate coefficients as a function of the a.c. phase for different E/N and ω/N values, indicating the influence of the frequency on the modulation and the rate and transport coefficients in methane.

At this point it is worth mentioning that calculations of a similar type, including the self-consistent calculation of the vibrational state densities, have been performed for hydrogen, nitrogen and other gases including silane by Capitelli et al. [6]. Calculations of the effect of metastables on discharges in argon have been made by Judd [7], Ferreira et al. [8], Bretagne et al. [9] and Jovanović et al. [10].

2. The influence of excited states on the kinetics of ionization and dissociation by electron impact in methane

In this section, we discuss the influence of the non-equilibrium temperatures (populations) of excited states on the EEDF in methane. It has been observed that vibrational levels in silane [11] and even in methane [12] may have increased populations and that collisions of electrons with such molecules may have an important influence on the EEDF both for d.c. and a.c. electric fields.

We have performed calculations on the basis of two-term Boltzmann equation solutions using two different codes to include the superelastic collisions through time relaxation (ELENDIF [13]) and iterative (GISBE [14]) procedures. The basic sets of cross-sections were those selected by Morgan [15] in a recent compilation and, for simplicity, the set of Ohmori et al. [16] was used giving essentially the same results. We did not attempt to use the experimental transport data to obtain the best fit or to obtain the cross-section set that fitted the transport data most satisfactorily. Our aim was to show the influence of different processes on the overall excitation, dissociation and ionization kinetics, and thus the two cross-section sets mentioned above were for all our purposes identical. We also assumed that vibrationally excited molecules may be excited to higher vibrational states with a cross-section identical to that for excitation from the ground state. The cross-section for excitation from the $v=1$ to the $v=2$ state may, however, be significantly higher than that for the $v=0$ to $v=1$ transition [17], and this effect may produce a significant influence on the EEDF and, consequently, on all the rate coefficients.

We chose 2000 K as a reasonably easily achievable value of the non-equilibrium vibrational temperature, but we did not develop the model of vibrational kinetics to establish under which conditions this would occur. This was because we were interested in r.f. discharges, where such a model cannot be developed easily in a self-consistent manner, and using the effective field d.c. approximation, which works well for d.c. discharges, would yield questionable results. Also, experimental measurements of the non-equilibrium temperatures of vibrational levels are available which indicate values of several hundred or more than one thousand kelvin. The higher relaxation rate for methane compared with silane [18] means that the currents at which such vibrational temperatures would be achieved are higher than for silane, but still within realistic current densities [11].

The selection of the value of $T_{vib}=2000$ K is within the range of the gas kinetic and rotational temperatures found by Chu et al. [19] in hollow cathode d.c. discharges used for diamond film deposition. Vibrational temperatures in r.f. discharges used for similar purposes in methane were determined by Terazono et al. [12] to be up to 6000 K, while the rotational and gas kinetic temperatures were of the order of 600 K.

In Fig. 1, we show the influence of increased vibrational temperature on the dissociation (see Fig. 1(a)) and ionization (see Fig. 1(b)) rates in pure methane as a function of E/N. The superelastic collisions with vibrationally excited methane molecules increase the rate coefficients in the region below 100 Td. The increase in the ionization rate coefficient may affect the operating point of the discharge, and it is the relatively low energy electrons, which in r.f. discharges may be found in the bulk and in the negative glow-like region across the powered electrode, whose properties will be influenced the most and may contribute more to the ionization.

Our calculations give rough boundaries of the $E/N<100$ Td values that are likely to be affected by the superelastic collisions. In Fig. 2, we show the EEDF for $T_{vib}=300$ K and $T_{vib}=2000$ K at $E/N=25$ Td. Differences in the EEDF induced by superelastic collisions become very small above 100 Td.

As mentioned above, further effects on the rate coefficients may also be produced by the different cross-sections for the vibrational excitation from $v=j$ to $v=j+1$ states ($j>0$). Vibrationally excited molecules may also have a larger momentum transfer cross- section and the threshold for ionization will be lower, but we do not expect any of these processes to be appreciable at the accuracy level required to model the discharges.

3. The influence of superelastic collisions on the drift velocity in methane

The drift velocity of electrons in methane shows the effect of the NDC both for d.c. [20–23] and a.c. [24]

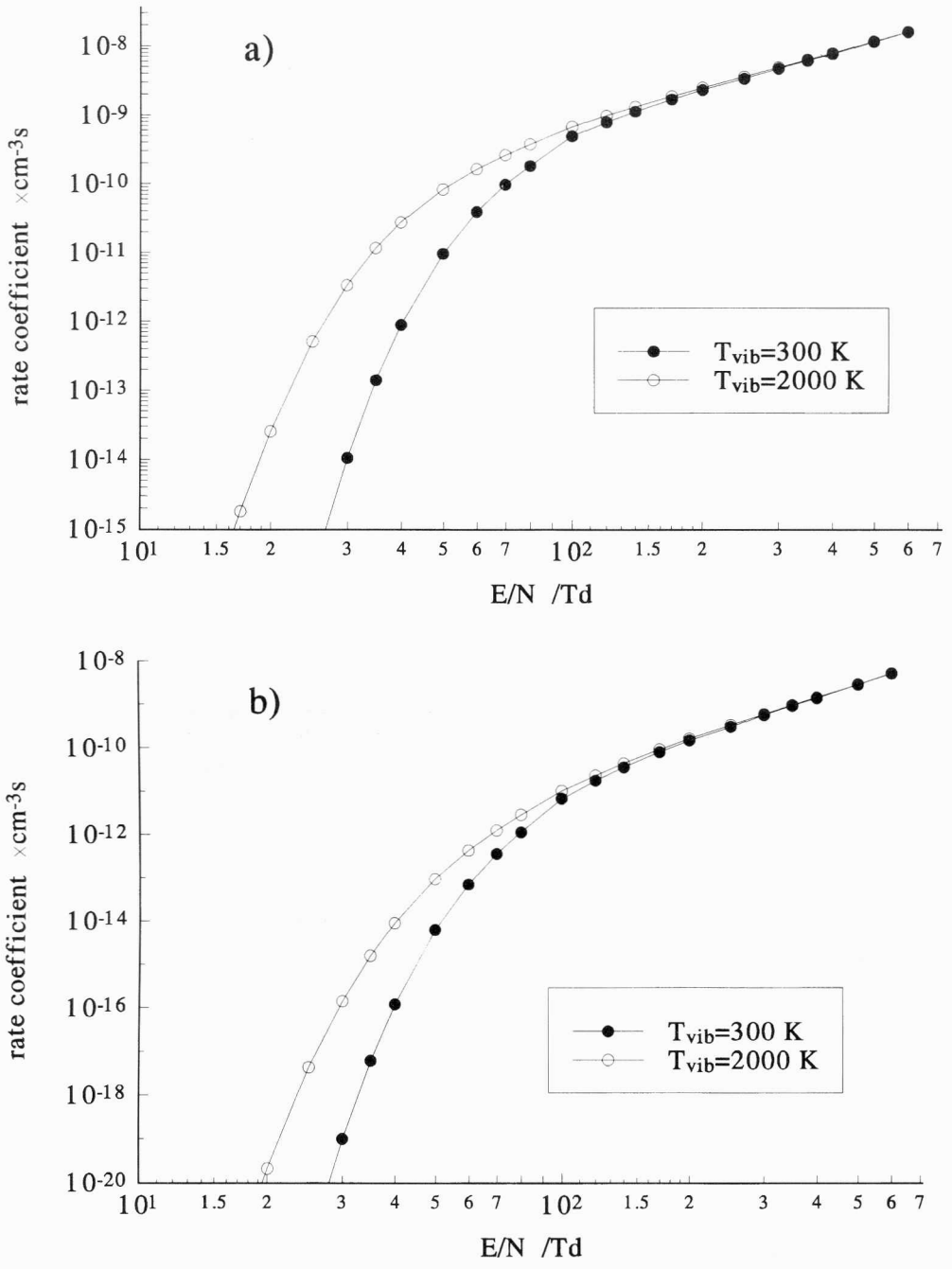

Fig. 1. Rate coefficients for dissociation (a) and ionization (b) in methane with superelastic collisions corresponding to vibrational temperatures of 300 K and 2000 K.

electric fields. For the purpose of this paper, we may define the NDC as the decrease in the drift velocity with an increase in the electric field. The phenomenon of NDC has been explained previously [25–28]. Petrović et al. [27] have discussed the influence of superelastic collisions on the NDC on the basis of model calculations for nitrogen at low E/N. They concluded that the NDC would be observed in most gases at low E/N due to the effect of rotational excitation, but is not observed due to the influence of superelastic collisions. The NDC occurs when inelastic processes reduce the mean energy of electrons in conjunction with increasing elastic scattering or decreasing inelastic scattering. Superelastic processes increase the energy of electrons and thereby reduce the E/N region of the NDC and its depth [11].

We have used the momentum transfer theory (MTT) developed by Vrhovac and Petrović [29], which is an extension of the MTT originally developed by Robson [28]. The momentum transfer approximation consists of developing number, momentum and energy balance

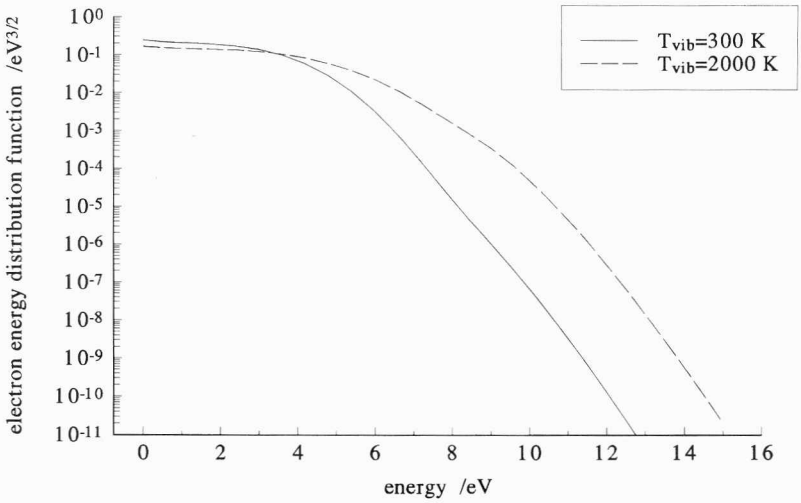

Fig. 2. Electron energy distribution function for electrons in methane at $E/N = 25$ Td for two different vibrational temperatures.

equations on the basis of the Boltzmann equation with an appropriate collision operator in the hydrodynamic limit [30]. The procedure is then applied to calculate the collisional frequencies for the effective mean energy with an appropriate weighting for the processes with thresholds higher than the mean energy [28]. This procedure is known to give good results, within 20% of the accurately calculated data, on the basis of numerical solutions of the Boltzmann equation. This level of accuracy is satisfactory for most discharge modelling and is also sufficient to check effects such as the NDC. The MTT also provides analytical solutions of the relation between certain variables and thereby yields physical insight and understanding.

Vrhovac and Petrović [29] have extended the theory of Robson [28] and developed the criterion for the NDC in the following form

$$\frac{d}{d\varepsilon}(\varepsilon S_e^{(*)}) + \frac{d\Omega_e^{(*)}}{d\varepsilon}\varepsilon < 0 \tag{1}$$

where

$$S_e^{(*)} = 1 + \frac{\nu^{(I)}(\varepsilon) + (2/3)\varepsilon[d\nu^{(A)}(\varepsilon)/d\varepsilon]}{\nu_e(\varepsilon)} \tag{2}$$

and

$$\Omega_e^{(*)} = \frac{\Lambda(\varepsilon)}{\nu_e(\varepsilon)}, \qquad \nu_e(\varepsilon) = 2\frac{m}{m_0}\nu_0^{(m)}(\varepsilon) \tag{3}$$

In Eq. (3), $\nu_0^{(m)}$ denotes the momentum transfer collision frequency for elastic and inelastic collisions. Likewise, $\nu^{(I)}(\varepsilon)$ and $\nu^{(A)}(\varepsilon)$ are the ionization and attachment collision frequencies respectively. It is difficult to asign a clear physical meaning to quantities $\Omega_e^{(*)}$ and $S_e^{(*)}$ without more detailed discussion than justified by the objective of the present paper. Thus these two quantities may be viewed as a convenient grouping of the relevant physical quantities. The quantity $\Lambda(\varepsilon)$ is

$$\Lambda(\varepsilon) = \sum_i \nu_i(\varepsilon)\Delta E^i + \nu^{(I)}(\varepsilon)\varepsilon^{(I)} + \sum_s \nu_s^{(I)}\Delta\varepsilon_s^{(I)} \tag{4}$$

Here the collision frequency for inelastic process i is $\nu_i(\varepsilon)$. The thresholds for these inelastic collisions and ionization are denoted by ΔE^i and $\varepsilon^{(I)}$. In Eq. (4), the index s denotes all possible ionization channels with excitation energy $\Delta\varepsilon_s^{(I)}$, and $\nu_s^{(I)}(\varepsilon)$ denotes the corresponding collision frequency.

For the purpose of this paper, the criterion of Vrhovac and Petrović [29] is identical to that of Robson [28] and, in both cases, it is obvious that the superelastic processes reduce the effect of inelastic processes in the condition of Eq. (1). Further discussion of the general implications of superelastic processes on the NDC is given by Vrhovac and Petrović [29]. Here, we concentrate on how it affects the transport coefficients in pure methane. The collisional frequencies, drift velocities and mean energies were calculated from the general MTT equations following the procedure developed by Robson [28]. Although the equations have the same approximations and are the basis for developing the NDC criterion, the results of the calculations provide an independent confirmation of NDC. In Fig. 3, we show both the calculated drift velocity (see Fig. 3(a)) and the calculated left-hand side of the criterion of Eq. (1) (see Fig. 3(b)). There is very good agreement between the criterion of Eq. (1) and the E/N region where NDC occurs in the drift velocity. The agreement is still very good when a numerical solution of the Boltzmann equation is applied to obtain the drift velocity. Most importantly, when superelastic collisions are introduced corresponding to the vibrational temperature of 2000 K, the NDC region and its depth are reduced as expected from the criterion of Eq. (1). A further decrease in the NDC is obvious for calculations at $T_{vib} = 6000$ K.

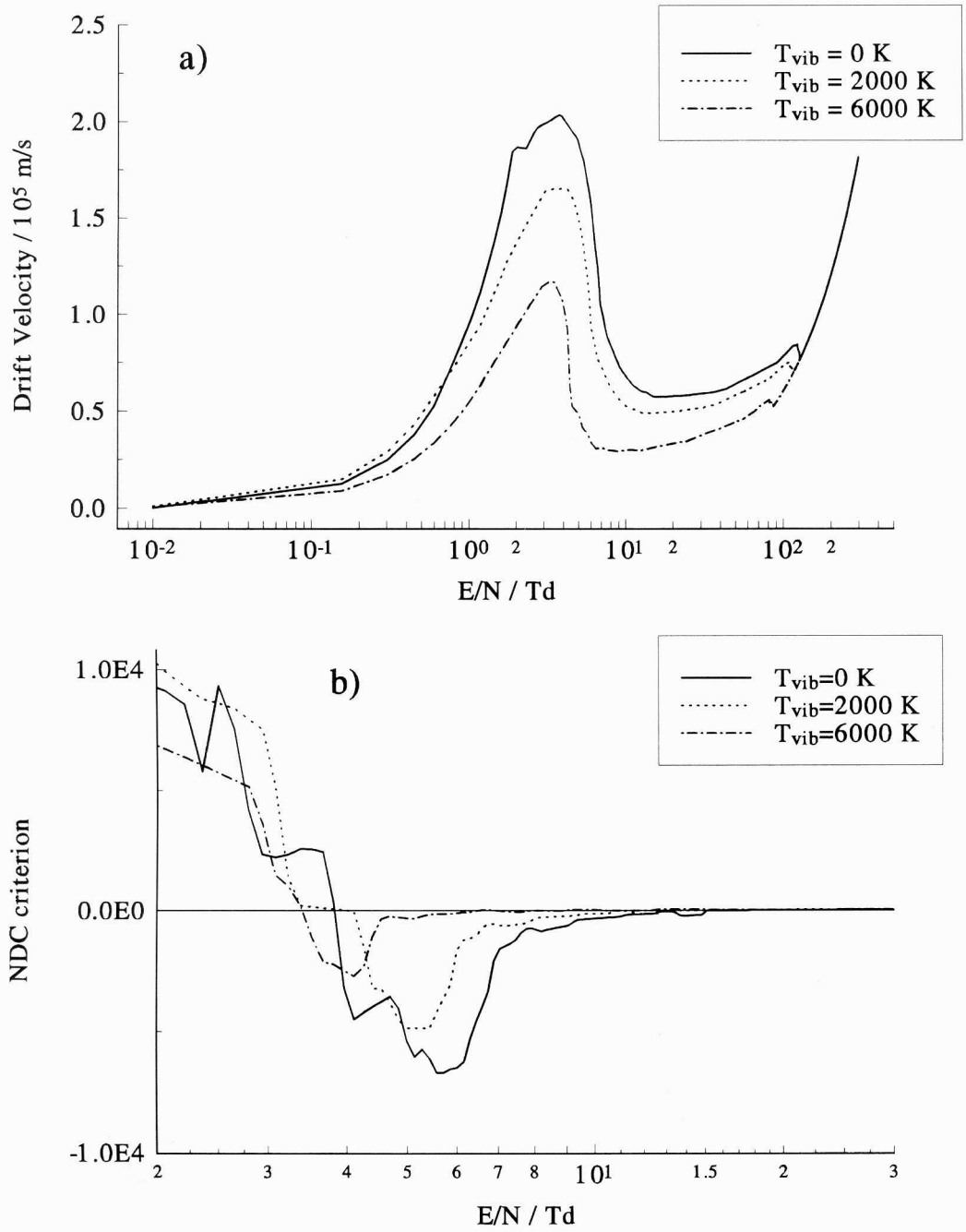

Fig. 3. Dependence of the drift velocity (a) and NDC criterion (b) in methane as a function of E/N obtained with MTT.

4. Calculation of the rate coefficients and transport parameters in a.c. discharge in methane

In this section, we discuss the calculation of the rate coefficients for a.c. electric fields. NDC plays an important role in a.c. fields as shown by Makabe and Goto [24]. We show how NDC modifies the temporal development of the a.c. drift velocity, which may lead to complex effective electrical parameters and a time dependence of the power deposition.

A Monte Carlo code for calculating the electron transport properties in a.c. fields has been developed by Bzenić and Petrović [31]. A Monte Carlo simulation for time-dependent discharges with space charge development has been used as part of the more complex discharge simulation schemes, but not for a.c. swarms. There are several presentations in the literature of the calculations based on the solution of two-term [13] and multi-term [24,32] forms of the Boltzmann equation. Swarm experiments in a.c. fields have recently been developed to provide data of sufficient accuracy that warrant establishing the accuracy of the calculated

transport coefficients by comparing the numerical solutions with Monte Carlo predictions. Details of the Monte Carlo technique, basic tests and comparisons will be presented elsewhere; here, we limit ourselves to specific calculations for methane discharges.

In Fig. 4, we present the results of the calculations of the temporal development of the mean energy and dissociation (including dissociative excitation) rates in pure methane at $E/N = 100Mr2\sin(\omega t)$ Td for different values of ω and a pressure of 1 Torr. The degree of modulation and the efficiency of coupling with the electric field are visible in the figure. The dependence of the dissociation rates on E/N for $\omega/N = 1.91 \times 10^{-21}$ MHz m^3 is shown in Fig. 5.

Finally, in Fig. 6, we show the time dependence of the drift velocity (v_{dr}) under conditions in which NDC develops. The complex behaviour of v_{dr} with time represents very well the behaviour that can be projected from the E/N dependence of v_{dr} as shown in Fig. 3. The increase and decrease in the drift velocity, followed by another increase towards the middle of the half period, can thus be easily explained. The delay of the drift velocity and the different time decay correspond well to the shape of the momentum transfer and inelastic cross-sections.

The results of the Monte Carlo simulations agree very well with the previously obtained results of Makabe and Goto [24].

5. The influence of excited states in methane–argon mixtures

In this section, we analyse the kinetics of ionization and dissociation in methane–argon mixtures, which are often used for diamond-like and diamond thin film deposition.

The calculations are performed with the same Boltzmann equation codes as for pure methane. The cross-section sets for methane are the same. For argon, we used the cross-section set developed by Hayashi [33] and a simplified set put together by Morgan [34]. These sets give a very good representation of the rate coefficients and transport coefficients in pure argon and therefore give a good EEDF.

The basic cross-section set for argon has been augmented by the cross-sections for the excited states of argon, namely for the 4s metastables. Excitation from 4s metastables to the resonant levels has been taken into account by using the cross- sections of Baranov et al. [35] and Clark et al. [36]. The excitation from 4s to 4p levels and to the higher states has been taken on the basis of the theory of Hyman [37] and Behnke et al. [38] and, finally, the ionization from 4s metastables has been calculated on the basis of the cross-section proposed by Vriens [39]. (For a comparison and evaluation of these cross-sections and a general source of data for argon, see Ref. [10].)

In Fig. 7, we show the rates of dissociation (see Fig. 7(a)) and ionization (see Fig. 7(b)) for a 3% mixture of methane in argon as a function of E/N with and without a significant metastable population. The density of metastables was taken to be 10^{-4} of the ground state argon atoms, which corresponds well with the measured excited state densities [4].

Similar studies in pure argon have been performed by several workers [7,10,40]. Here, we include the effect of the metastable atoms on the overall rates of

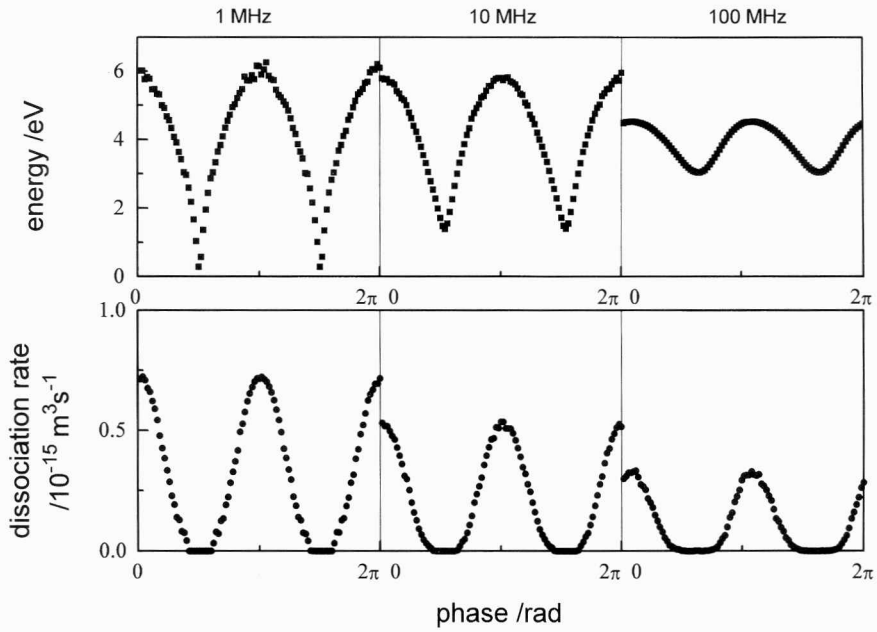

Fig. 4. Phase dependence of the dissociation rate and mean energy in methane for different values of ω and a pressure of 1 Torr.

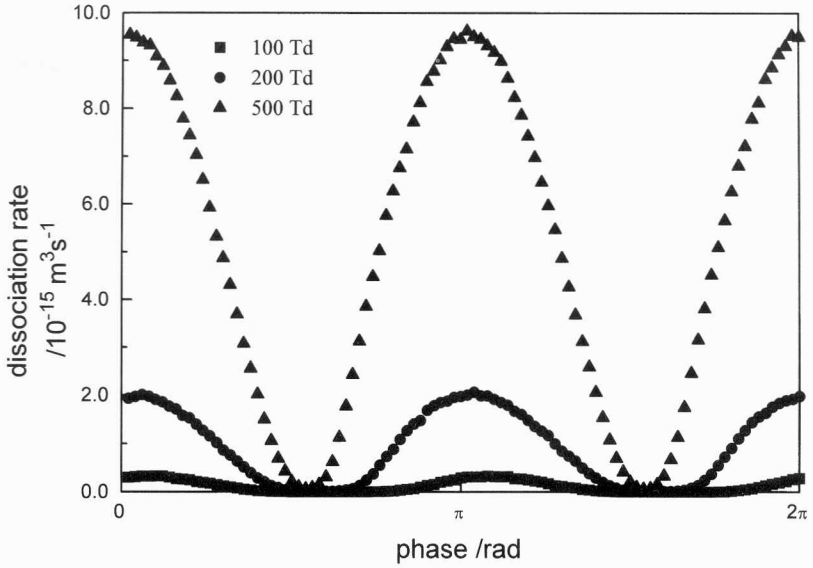

Fig. 5. Dissociation rates in methane as a function of E/N for $\omega/N = 1.91 \times 10^{-21}$ MHz m^3.

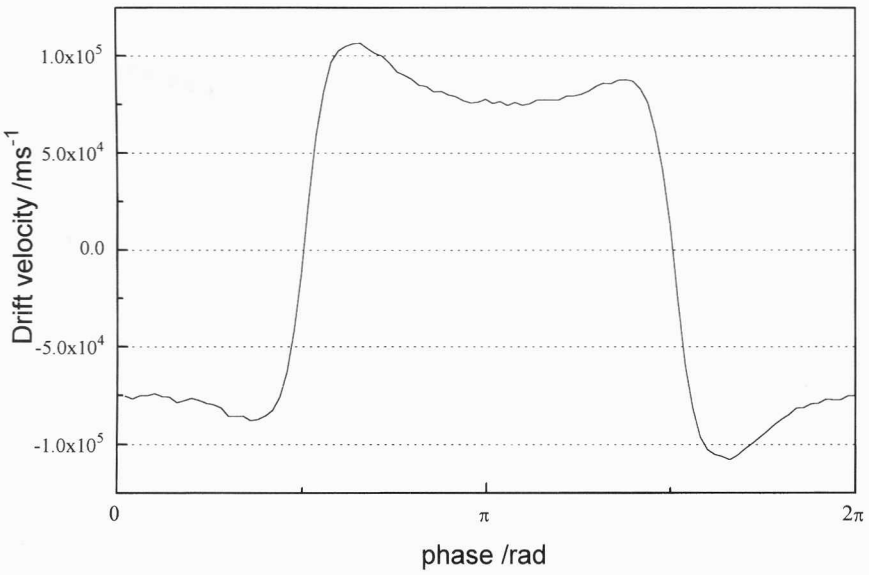

Fig. 6. Drift velocity of electrons in methane r.f. discharge as a function of phase for NDC conditions, $E/N = 20 \sin(\omega t)$ Td and $\omega/N = 6.28 \times 10^{-23}$ MHz m^3.

the process and on the EEDF through superelastic collisions; the influence of low threshold collisions with excited states on the EEDF is much smaller in the mixture due to the presence of low threshold vibrational excitation. In addition to direct ionization, stepwise processes may affect the kinetics significantly [4]; we have calculated the rates for different methane abundances, but they are not presented here as they will be of interest for specific situations depending on the metastable atom density and abundance. Metastable atoms at higher electron densities may be quenched in electron-induced transitions and superelastic processes.

In Fig. 8, we show the rate coefficients for electron-induced quenching of argon metastables as a function of E/N and also of the methane abundance. The data for pure argon and the basic rate cross-sections are taken from Jovanović et al. [10]. The electron-induced transitions from metastables to resonant levels contribute significantly to the quenching of metastables and reduce their density, while superelastic collisions make a small contribution to the overall metastable quenching rates. Nevertheless, the populations of the metastables are sufficient to affect significantly the overall ionization/excitation/dissociation kinetics in argon-containing mixtures.

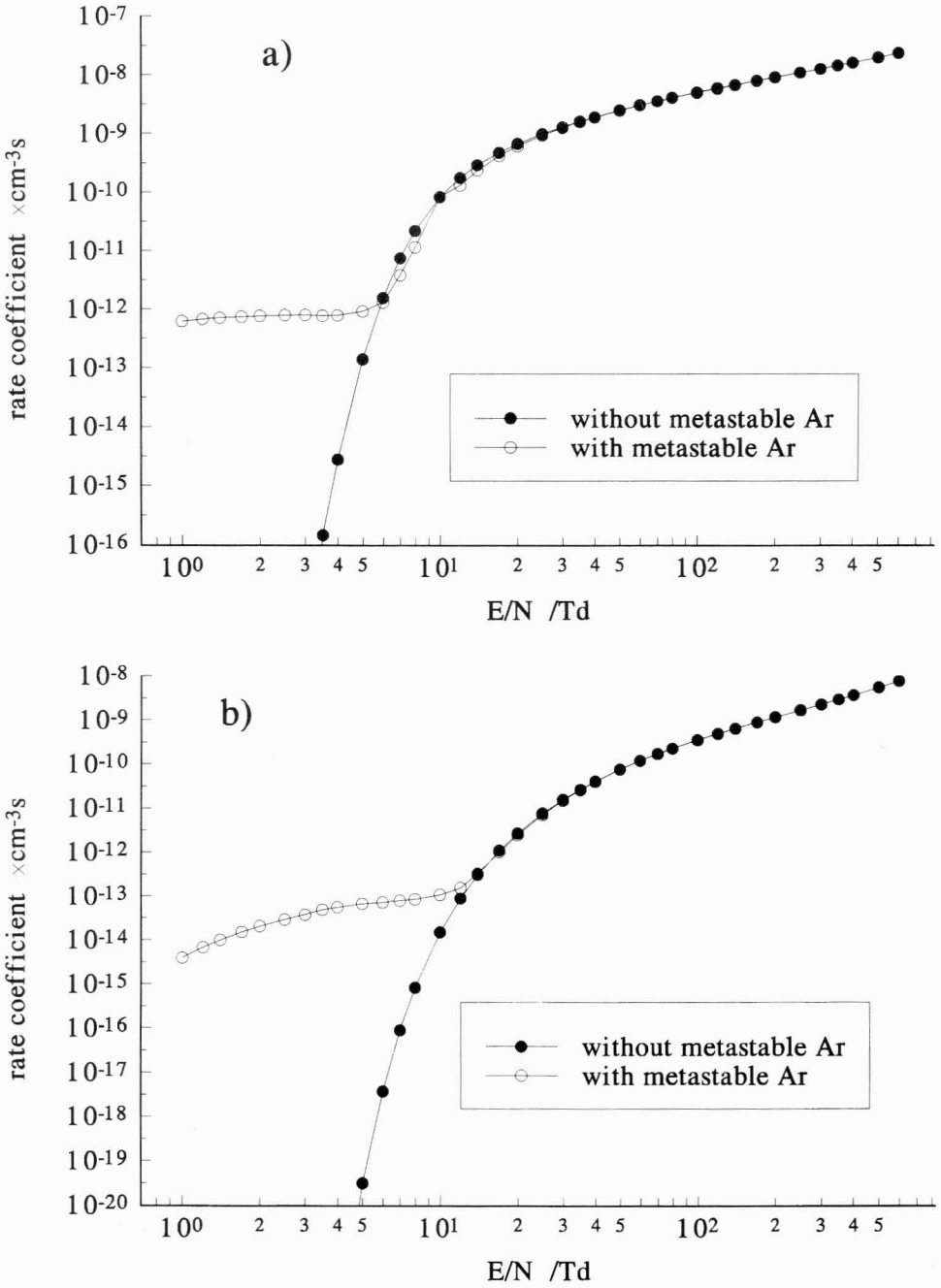

Fig. 7. Rate coefficients for dissociation (a) and ionization (b) for 3% CH_4–Ar mixture with and without 10^{-4} population of metastable argon atoms.

6. Conclusions

Excited states make a significant contribution to the electron excitation and ionization kinetics in methane and methane- containing mixtures which are often used for diamond-like or diamond film deposition. The non-equilibrium vibrational temperature of methane leads to a high population of vibrational states of methane which, through superelastic collisions, affect the EEDF, but only at relatively low E/N and high current densities. Similarly, the superelastic collisions affect the EEDF in mixtures of methane and argon. The effect on dissociation and ionization appears to be small above 100 Td for pure methane and 20 Td for 3% methane in an argon mixture.

The influence of superelastic processes on the behaviour of the drift velocity as a function of E/N is to reduce the region and depth of the NDC. This was shown by applying the recently developed MTT based equations of electron transport and the analytical NDC criterion

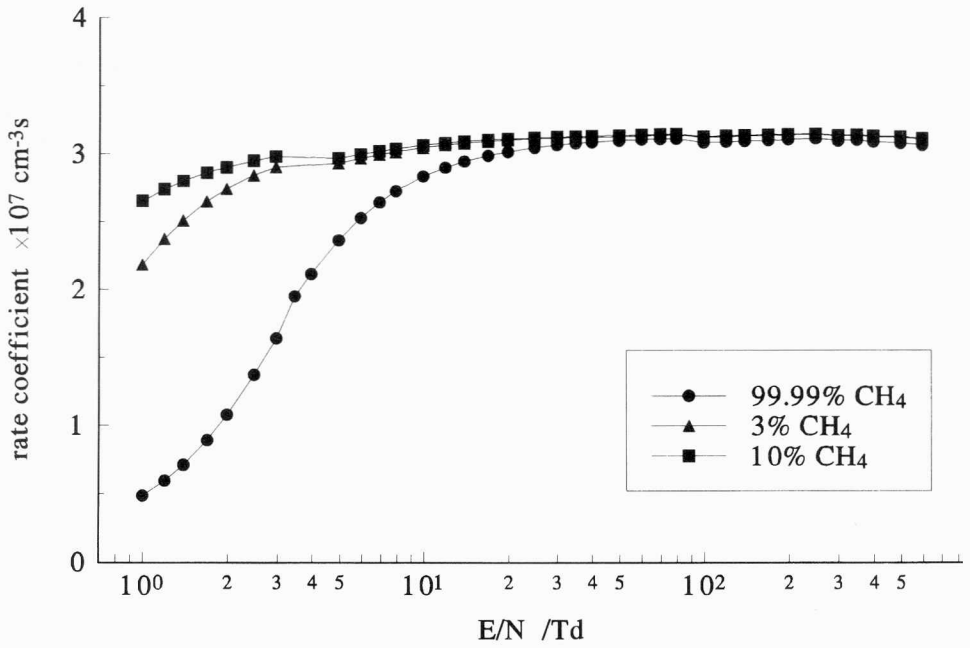

Fig. 8. Rate coefficients for electron-induced quenching of argon metastables for different methane abundances.

[27–29]. The predictions of the theory are in excellent agreement with the calculations for electrons in pure methane.

Since the NDC leads to a complex behaviour of the drift velocity for a.c. electric fields, we have applied our technique for calculating the rate and transport coefficients of electrons in a.c. fields based on the Monte Carlo simulation. The predictions of the theory are presented and are in good agreement with the predictions based on the time-dependent Boltzmann equation theories [32]. In particular, we have shown that the time dependence of the drift velocity can be explained by the effect of the NDC and that, for high excited state densities, this effect will be reduced.

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During the review of this paper, one of the authors (Z.Lj.P.) received information from Professor R.E. Robson of James Cook University about unpublished results obtained independently of this work in which a similar NDC behaviour of the electron drift velocity for r.f. fields was observed using time-dependent MTT and cross-sections for a simple NDC model [27]. We acknowledge very useful discussions with Professor Robson on both the r.f. Monte Carlo and MTT results.

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