Excitation coefficients and cross-sections for electron swarms in methane

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Abstract. We have measured electron excitation coefficients for production of excited fragments H(n = 3), H(n = 4), CH(A²Σ–Δ) and CH(B²Σ–) from the ground-state methane molecules by an electron swarm in a drift tube type experiment (parallel plate Townsend discharge at very low currents). Hα and Hβ lines as well as CH(A²Σ–X²Π) and CH(B²Σ––X²Π) bands were used. Cross-sections from binary collision experiments were renormalized by fitting the measured data with the results of Boltzmann equation and Monte Carlo calculations for electron transport.

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1. Introduction

Methane is one of the key sources of energy both from the existing deposits and also through generation from biological waste, both man-made and natural [1]. On the other hand, methane is the second most important greenhouse gas with a global warming potential of 21 (relative to the effect of CO$_2$) [2]. It was even suggested that massive releases of methane in the past were the main cause of major extinctions of life on the planet through global warming [3]. Thus it is very important to study the kinetics of methane in the atmosphere, to follow basic biochemical processes that lead to its production, release and destruction, and to reduce its production by modifying some of the important biochemical processes [4]. Finally, in addition to its presence on planet Earth, methane is a major constituent of the atmospheres of some major planets or satellites such as Jupiter, Saturn, Uranus and Titan [5]. Some of the processes observed in the atmospheres of those planets and in the Earth’s atmosphere require significant improvement of the existing cross-section sets, in particular the cross-sections for electron-induced dissociation and dissociative excitation. In these efforts, and in the modelling of plasma applications in general, it is important to have benchmark cross-sections [6, 7]. These could be used as a basis for testing new theories since experiments, and in particular swarm experiments, cannot be performed for many gases and in particular free radicals.

In addition to being an important source of energy, pollutant to the atmosphere and a result of numerous biochemical processes, methane has been used in a number of technologies involving low temperature plasmas. Those include deposition of diamond-like thin films [8], plasma etching [9] and many more. In addition, it is frequently applied in high energy particle detectors [10]. At the same time, low temperature plasmas may be used to remove the methane from the air.

The bases for the modelling of such plasmas are the cross-section and transport coefficient sets. Measurements of swarm parameters, so far, have been focused at lower mean energies, where vibrational excitation is the dominant energy exchange process [11, 12]. The cross-sections obtained by using those data and the swarm-type analysis were confined to energies below the threshold of electronic excitation. As a result of extensive studies, methane is regarded as one of the test benchmarks for swarm studies at lower energies [13]. From the standpoint of swarm physics, methane is an extremely interesting case as it shows a number of kinetic phenomena and it should be regarded as one of the critical benchmarks. Those kinetic effects include enhanced mobility [14] and negative differential conductivity in both dc [15, 16] and rf [17, 18] fields and are mainly produced by a combination of the Ramsauer–Townsend minimum and large vibrational excitation losses in the same energy region.

However, for the conditions found in most plasma applications and particle detectors, higher mean energies are of interest and those have not been covered very well by the existing swarm studies [19]. Here we deal with mean energies higher than 2 eV. Under these conditions, it is often important to determine the channels for dissociation of methane into chemically active radicals. The cross-section for dissociation into ground state neutrals is the most difficult to measure and these data are often not available. Dissociation of methane also proceeds through excitation. In this case, the dissociative excitation cross-sections or even rate coefficients may be used to obtain knowledge of the efficiency of dissociation processes and their spatial distributions.

In this paper we perform a swarm type drift-tube experiment and the corresponding analysis of the excitation coefficients obtained in the limit of low currents (i.e. for extremely low charged-particle densities where the external field is not perturbed and standard swarm analysis is applicable). Excitation coefficients measured in drift tubes have been the best way.
to normalize the cross-sections for specific channels of excitation and thus to avoid the use of
the fictitious effective cross-section. In this paper we present the data for dissociative excitation
of methane and the corresponding cross-sections obtained by the swarm procedure. We study
processes:

\[
\text{CH}_4 + e \rightarrow \text{CH}_4^+ + e \rightarrow \text{CH}^+ + \text{products} + e,
\]

\[
\text{CH}_4 + e \rightarrow \text{CH}_4^+ + e \rightarrow \text{H}^+ + \text{products} + e,
\]

where emission from the excited fragments is detected. One should note that in all cases, under
swarm conditions, collisions between electrons and excited species or radicals are negligible and
thus only the excitations from the ground-state methane are detected.

The data may be of value for modelling of plasma-etching devices, diamond-like thin film
deposition and discharges in gas mixtures containing methane.

2. Experimental set-up

A standard parallel-plate drift tube is used in the measurements of excitation coefficients and the
setup has been described in our previous references [20]–[23]. The anode is made of graphite to
reduce the backscattering of electrons, and the cathode is made of highly polished stainless steel.
A closely fitting quartz tube is used to prevent the long path breakdown at low pressures to the left
of the Paschen minimum. The gap between the electrodes and the glass is however large enough
to allow efficient pumping. The system was evacuated to pressures of the order of \(< 10^{-6}\) Torr and
filled with gas that was replaced every 15–20 min. The spectrum was used to test the presence of
impurities, especially nitrogen. However, as methane is a molecular gas, the density of molecular
pollutants may be larger when compared with atomic gases without affecting the results of a
swarm experiment. Nevertheless, we have maintained the same procedure as used for rare gases
even though we have never observed lines or other effects due to pollution from air molecules.
The gap between electrodes was 1.8 cm and the diameter was approximately 8 cm, hence the
field in the system may be regarded as uniform since the maximum current was limited to
2 \(\mu\)A [24].

The optical emission was detected by a system consisting of a collimator, a set of lenses,
a spectrometer, a photomultiplier operating in a single-photon-counting regime and a pulse
counting and shaping electronics. The system was calibrated by using a standard tungsten
ribbon lamp and indirectly tested either by making repeated measurements of the excitation
coefficients for several lines of argon [23, 25] or by repeated relative measurements of emission
of a tungsten ribbon lamp. The monochromator and the optical system were mounted on a
movable platform controlled by a computer and thus the spatial profiles were scanned. The
spatial profiles of emission were recorded and extrapolated to the anode to obtain the absolute
excitation coefficients. In addition, one could obtain from the slope the ionization coefficient.

In Townsend discharges, where electron impact excitation dominates over other processes,
populating the upper level and where electrons are in equilibrium with the electric field, the
electron excitation coefficient \(\varepsilon_m/N\) of the level \(m\) is given by [20]–[22]

\[
\frac{\varepsilon_m}{N} = \frac{S_a}{f_e} \frac{e}{(\Omega/4\pi) Q(\lambda) N A_m} \left(1 + \frac{N}{A_m} k_q\right),
\]
where $S_a$ is the emission signal, $j_e$ the electron current density at the anode, $e$ the electron charge, $\Omega$ the effective solid angle of the detector, $Q(\lambda)$ the quantum efficiency of the detector and $k_q$ is the rate coefficient for collisional quenching of the upper state $m$.

3. Excitation and ionization coefficients

Few examples of spatial profiles for the emission of H$\alpha$ line are shown in figure 1. The exponential growth towards the anode was fitted and used to obtain both the ionization and the excitation coefficients at the anode (by using normalization to the electron current at the anode). The whole profile was then normalized to provide an emission profile absolutely calibrated and normalized to the excitation coefficient at the anode. The exponential growth from the cathode to the anode is replaced at higher $E/N$ by the double peak dependence indicating a very effective excitation by fast neutrals as discussed previously by Petrovi´c and Phelps [26]. Thus, we have limited our determination of electron ionization and excitation coefficients to 5 kTd ($1 \text{Td} = 10^{-21} \text{V m}^2$), as we have indication that up to 3 kTd there are no effects of heavy particles and at 5 kTd the effects are not large and the extrapolation to the anode may be performed.

The ionization coefficients obtained from the fits to the optical emission profiles are shown in figure 2, where they are compared with the available experimental data of Heylen [27] and Davis et al [28]. The agreement is quite good although optical emission data have a larger scatter due to the use of lines of different intensity. Since these measurements are quite simple, do not depend on absolute calibration and may be compared with very accurate ionization growth data, the comparison of ionization coefficients is a good test of the experiment.

The emission of bands of methane radicals CH($A^2\Delta$–$X^2\Pi$) and CH($B^2\Sigma^+–X^2\Pi$) was spectrally analysed and integrated to give the total excitation of the upper level of a particular...
Figure 2. Ionization coefficients from different experiments [27, 28] compared with calculations. Final in the legend denotes the calculation with the final set of cross-sections.

band. The results for dissociative excitation of H(n = 3) (from Hα line) and H(n = 4) (Hβ) levels from methane are shown in figure 3 and the results for CH(A^2 Δ) and CH(B^2 Σ−) states are shown in figure 4. In the analysis of the data, we have used the transition probabilities from [29] and quenching coefficients from [30]. To our knowledge there are no available experimental data to compare with, except for the preliminary results from our group and mainly higher E/N data of Petrović and Phelps [26] that have been normalized by using the calculated rate coefficients.

4. Swarm analysis and the cross-sections

We have used both a two-term code ELENDIF [31] and our Monte Carlo code [32, 33], for the calculation of transport coefficients and, in particular, excitation coefficients. Two-term calculations were limited to 1500 Td in order to assure that stable and converged solutions were reached. This, however, does not cover the issue of the adequacy of the two-term theory for electrons in methane in general [11]. Monte Carlo simulations could be used for all E/N covered here with accuracy limited mainly by the statistics and quality of the cross-sections. The basic set of cross-sections was adopted from Hayashi [34] as it is most detailed with inclusion of numerous excitation and dissociation processes required in plasma modelling. The set was tested by making comparisons with the available experimental transport data for drift velocities and characteristic energies. However, we have not pursued exact agreement with the high accuracy results at lower E/N [11]–[13], [35] as these do not overlap with our energy range. However, even in this case, the agreement with the experiment was within the expected accuracy. It is important for our purpose however that the ionization rate coefficients available in the literature [27, 28] and also those measured in the present experiment have been properly fitted.
Figure 3. Electron excitation coefficients for H\((n = 3)\) and H\((n = 4)\) levels, the lines that were used are also indicated. Two-term calculations were performed with the ‘initial’ cross-sections (solid triangles) and with the ‘final’, rescaled cross-sections (solid line). Lengthier Monte Carlo calculations were performed with final (rescaled) cross-sections only (solid squares). The same notation is maintained in other figures with comparisons.

Figure 4. Excitation coefficients for CH\((A^2\Delta)\) and CH\((B^2\Sigma^-)\) states. The notation is the same as in figure 3.
Figure 5. The cross-sections for dissociative excitation of molecular bands of CH fragments from the ground state methane molecules. The data for the A state is obtained by rescaling the experimental beam data and the data for the B state by using the cross-section for the A state and shifting it by the required threshold energy and rescaling it to obtain the fit of excitation coefficients.

For the purpose of obtaining the excitation cross-sections for the upper levels of the transitions measured in our experiment we have used the data of Tsurubuchi and co-workers [36] and de Heer and co-workers [37, 38] as initial guesses. The first set of cross-sections was extrapolated beyond 100 eV in accordance with the shape of the cross-sections obtained in [37]. Extrapolation to the threshold was also made.

The $E/N$ dependence of calculated excitation coefficients was shown to be in agreement with the experimental data and thus there was no need to change the energy dependence. However, as can be seen from the data for figure 3 for H$^+$ levels and from figure 4 for CH$^+$ states, the absolute magnitudes had to be modified. A very good fit of the experimental data may be obtained when the cross-section for the excitation of H$\alpha$ line is normalized by 0.7 and for the H$\beta$ line by 0.72. On the other hand, the cross-section for excitation of CH(A$^2\Delta$) state had to be multiplied by 1.98. For the CH(B$^2\Sigma^-$) state we have used the same shape as for the CH(A$^2\Delta$) state but we have shifted it according to the effective threshold. The resulting cross-sections are shown in figures 5 and 6.

The final sets, i.e. those with rescaled cross-section in general give us a reasonably good fit of the excitation coefficients at $E/N < 2$ kTd. For H($n=3$) level, there is a rather small discrepancy at the highest $E/N$ where experimental data are slightly larger than the predictions. We have not attempted to modify this since there is a probability of contribution of heavy particles of the same or smaller magnitude. The axial gap required for ions to cross, to gain enough energy to reach the excitation threshold, is relatively small and overlaps with the spatial resolution of
Motohashi et al. present cross-sections for dissociative excitation of methane into excited radicals $H(n = 3)$ (from the line $H\alpha$) and $H(n = 4)$ ($H\beta$). Final cross-sections are obtained by rescaling the available beam collision data.

The discrepancy at the highest $E/N$ for $H(n = 4)$ state is larger and in the same direction. However, the difference exceeds the possible contribution by heavy particle excitation and indicates that further modification of the cross-section may be required that may involve modification of the shape, for which we had insufficient data. The best overall results could be obtained with the original cross-section modified in the threshold region by a constant factor.

As for the molecular excited fragments, the agreement for $CH(A^2\Delta)$ state is very good after rescaling, but at the highest $E/N$, experimental data are actually below the predicted data. The opposite is true for $CH(B^2\Sigma^-)$ state but due to the low level of emission at highest $E/N$ the scatter is large and we have not attempted to modify the cross-section any further. However, for the purpose of modelling emission and dissociation kinetics from rf discharges, the accuracy of the cross-section set is sufficient as other uncertainties in plasma models exceed those of the swarm parameters. It is difficult to quantify the uncertainties in plasma models for two reasons:

- most errors of the plasma models are by omission (e.g. dc data for electron transport in a pure electric field are usually used to model rf plasmas in $E \times B$ fields);
- it is impossible for those who raise objections to test the accuracy due to omissions or due to other causes as there were no real, detailed studies of the uncertainties in complex plasma models.

Judging by the evident simplifications in the models and by the available benchmark calculations [39] we may estimate that one may expect discrepancies of one order of magnitude in which case a factor of two agreement may be regarded as satisfactory.

In general, we may say that, subject to some rescaling both the magnitudes and the shapes of the cross-sections for dissociative excitation of methane are consistent with measurements of excitation coefficients.
5. Conclusion

Absolute coefficients for dissociative excitation of methane in collisions with electron swarms have been obtained in a standard steady-state Townsend experiment. These appear to be the only available experimental excitation coefficients that were normalized absolutely. The earlier measurements of Petrović and Phelps [26] in a different drift tube and under different set of conditions were relative and normalized to calculated excitation coefficients based on the cross-sections that were available at that time. These experiments also revealed a very strong excitation by fast neutrals that was confirmed in this experiment. The coefficients are generally consistent with the available cross-sections provided that those have been renormalized. The scaling of $H_\alpha$ and $H_\beta$ lines of excitation cross-sections appears to be within the combined error bars. Since both of these are narrow lines, the issue of not integrating the entire profile does not apply. However, the scaling of A-X and B-X bands is consistent with either cascading effects in our measurements or an insufficient profile integration in the beam experiment. Whatever be the cause for the discrepancy, it exceeds the expected combined uncertainties. However, the obtained cross-section may be used in modelling the overall emission of those bands and dissociation through excitation.

We should clarify two points here. The first point is that the seemingly poor fit for some lines at the highest $E/N$ is due to several basic limitations and choices made in the procedure. Limitations are due to the weak signal of the lines from higher states and the need to subtract the contribution of fast neutrals. In addition, the non-hydrodynamic region close to the cathode becomes appreciable. The choice was not to try to fit the data for weaker lines when stronger lines supported the energy dependence of the experimental data for binary-collision, since insufficient information was available to modify the cross-sections at the highest energies.

The second point is that two-term analysis was found to be particularly inadequate for electrons in methane [11, 35, 40] and many other gases. This is due to large vibrational cross-sections in the Ramsauer–Townsend region and it is true mainly for the $E/N$ range lower than that covered in this paper and we have not analysed this point further. At moderate $E/N$ one expects a two-term approximation to perform better with the exception of excitation coefficients close to the onset of excitation [41]. There were no systematic studies of the adequacy of the two-term approximation at very high $E/N$. However, under those conditions, and mainly due to the extended region of non-hydrodynamic conditions we have chosen Monte Carlo simulations. In addition, our version of the two-term codes had numerical limitations that did not allow its convergence and accurate representation of all energy loss processes beyond 1500 Td.

The present data for the cross-sections for the formation of excited radicals CH$^*$ and H$^*$ could be of use for normalization of fast neutral excitation cross-sections [26] and for modelling the kinetics of dc and rf collisional plasmas that are used in plasma technologies [42, 43] and in particular for modelling diamond-like thin film deposition [44] and growth of nanotubes in non-equilibrium discharges [45]. The present results will be of interest for numerous particle detectors including drift chambers [46]–[48] and proportional counters [49]. In addition, dissociative excitation of methane may be a good benchmark cross-section for testing theories that would be required to calculate data for the dissociation of other gases and free radicals [6], though more work both from the swarm and beam experiments would be required in that respect. Understanding the dissociation kinetics of methane is a prerequisite to understand its kinetics in atmospheric chemistry and for controlling the global warming. It is also a key component of the complete sets of cross-sections for plasma models of all discharges involving methane [50].
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