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Electron scattering on N_2O-from cross sections to diffusion coefficients

J. Mechlińska-Drewko[a,*], T. Wróblewski[b], Z. Lj. Petrović[c], V. Novaković[c], G.P. Karwasz[b]

[a] *Faculty of Applied Physics and Mathematics, Gdañsk University of Technology, Narutowicza 11/12, Gdańsk 80-952, Poland*
[b] *Institute of Physics, Pomeranian Pedagogical Academy, Arciszewskiego 22b, 76-200 Słupsk, Poland*
[c] *Institute of Physics, POB 57, Belgrade 11001, Yugoslavia*

Abstract

Results of measurements of the ratio of transverse (D_T/μ) and longitudinal (D_L/μ) diffusion coefficients to mobility and drift velocity (W) as function of reduced electrical field (E/N) for electrons in nitrous oxide are presented. The coefficients D_T/μ and D_L/μ have been determined by applying the Townsend–Huxley method. The drift velocities were obtained by using the Bradbury–Nielsen technique. Also the deduced set of total and partial cross sections has been used to calculate the D_T/μ and W.

Keywords: Electron transport coefficients; Nitrous oxide

1. Introduction

Electronegative gases such as nitrous oxide have numerous applications. N_2O are important for chemistry, medicine and technology. Electron interaction with N_2O is important for atmospheric chemistry, being a greenhouse gas with approximately 200 years of permanence in stratosphere (Crutzen, 1971; Graedel and Crutzen, 1993). In spite of this, few experiments were performed on electron scattering-mainly by beam techniques. We noted that between existing data are some discrepancies. However, the measurements of total CS (cross sections) of Zecca et al. (1974) are in agreement with measurements of CS for elastic scattering and vibrational excitation by Azria et al. (1975). These data agree also with semiempirical momentum transfer CS by Hayashi (private information). From other side, measurements of total CS by Brüche (1927) agree with those by Szmytkowski et al. (1984) and Kwan et al. (1984). The two data sets differ by almost a factor of 2 at the resonant maximum of total (momentum transfer) CS at about 2.5 eV. The sum of the most recent elastic and vibrational CS coming from two laboratories—Canberra and Tokyo (Kitajima et al., 2000) is once more 20% lower than total CS of Szmytkowski et al. (1984) and Kwan et al. (1984). Note, that integral cross sections of Kitajima et al. (2000) have been obtained by integration (and extrapolation into angles inaccessible experimentally—the procedure which can introduce some errors) of their differential cross sections. All data indicate rise of the CS below 1 eV, in agreement with momentum transfer CS measured in cyclotron- resonance experiment by Tice and Kivelson (1967).

Also swarm measurements in N_2O were only sporadic and solely at low reduced fields (presented here in units Townsend—Td, 1 Td = 10^{-21} Vm^2). The drift velocity and ratio of diffusion to mobility in N_2O was measured in the early part of the last century (Bailey and Rudd, 1932). Other swarm studies were concentrated on measurements of the electron attachment coefficient to concentration (η/N) (Phelps and Voshall, 1968) or

*Corresponding author.
E-mail address: iga@mifgate.pg.gda.pl (J. Mechlińska-Drewko).

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electron growth constant to concentration (λ/N) (Dutton et al., 1975). In this work, measurements of drift velocity and the ratio of transverse and longitudinal diffusion coefficients to the mobility (D/μ and D_L/μ) for electrons in N_2O are extended to intermediate reduced electrical field values—the range E/N from 15 to 200 Td. In this range the swarm data lose a part of their "competitiveness" with beam experiments compared to ultra-low energies. However, we show that the diffusion coefficients in this E/N range remain extremely sensitive to presence of inelastic processes.

2. Experimental

To determine the ratio of transverse (D_T/μ) and longitudinal (D_L/μ) diffusion coefficients to mobility the experimental Townsend–Huxley technique was applied. Details of the experimental set-up and of the numerical procedure used to analyse the data were described earlier (Roznerski et al., 1994). Briefly, electrons produced photoelectrically at the gold leaf cathode and emitted from a small source hole were moved in a homogeneous electric field. They diffused laterally (and axially) to produce a widening radial spread of the electron swarm and was collected by the anode. Length of the drift space was 9.88 cm. In this experiment the ratios of the current reaching the arbitrarily chosen parts of the anode, divided into five concentric rings were determined. The expression from the fraction of the electron current i and ion current I falling onto the coaxial part of the anode is determined by integrating the electron and ion current density over a ring-shaped area between the inner and outer radii. The formula for the fraction of the total current falling on the selected part of the anode has the form:

$$R = \frac{i_{bc} + I_{bc}}{i_{bd} + I_{bd}}$$

in which b, c and d are the inner radius, the outer radius of the internal ring and the outer radius of the anode, respectively.

The expression for R can be formally treated as a function of two variables: D_T/μ and D_L/μ. Assuming that all transport coefficients are independent of pressure, we can find the quantity of R for a range of pressures and consequently obtain a set of s equations of the form

$$R_s = F_s(D_T/\mu, D_L/\mu), \quad s = 1, 2, 3, \ldots,$$

where s denotes a set of all quantities determining the physical conditions of the measurement chosen to find value R at a fixed E/N. This equation is solved numerically to obtain both D_T/μ and D_L/μ. The estimated maximum uncertainty is 3% and 7%, respectively, for all the E/N values.

The double grid Bradbury–Nielsen system have been used to determine the drift velocity W. The apparatus for measuring drift velocities has been described in detail by Roznerski and Leja (1984). Some dependence of W on the gas density was observed; this is due to influence of diffusion effects. Values given are extrapolated to the infinite density limit. Overall uncertainty was 1.5% at the lowest E/N and 3% at the highest E/N.

3. Results and discussion

3.1. D_T/μ and D_L/μ

Present results for D_T/μ are shown in Fig. 1. Measurements of D_T/μ agree well with those of Bailey and Rudd (1932) up to 50×10^{-21} Vm^2. At 100×10^{-21} Vm^2 the results of Bailey and Rudd are higher than present, we hypothesise gas impurity problems in the experiment of Bailey and Rudd. Present D_T/μ values agree reasonably well with semiempirical values of Hayashi (1992) shown in Fig. 1. by "Hayashi II".

According to our knowledge, measurements of longitudinal diffusion coefficient to mobility in nitrous oxide are made the first time. Because other data of D_L/μ in N_2O no exist we made comparison with results obtained earlier in the same laboratory for carbon dioxide (Roznerski and Mechlińska-Drewko, 1994). Both gases have a linear configuration but N_2O is asymmetric—for this reason N_2O has a slight (0.28 D) dipole moment Fig. 2. Total cross section for CO_2 (Szmytkowski et al., 1987) exhibits a resonant structure around 3.8 eV and another, wide maximum at 25 eV; for N_2O TCS is similar: two resonance for about 2.3 and 20 eV (Szmytkowski et al., 1984). Results for longitudinal

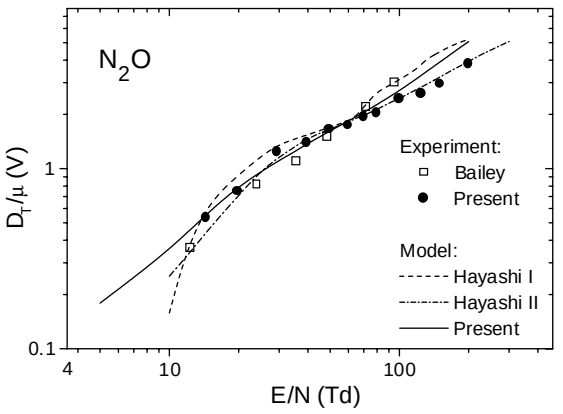

Fig. 1. Comparison between present and Hayashi's semiempirical calculations (Hayashi, 1992), experimental present (about 3% error bar) and Bailey's data (Bailey and Rudd, 1932) of D_T/μ coefficient in N_2O.

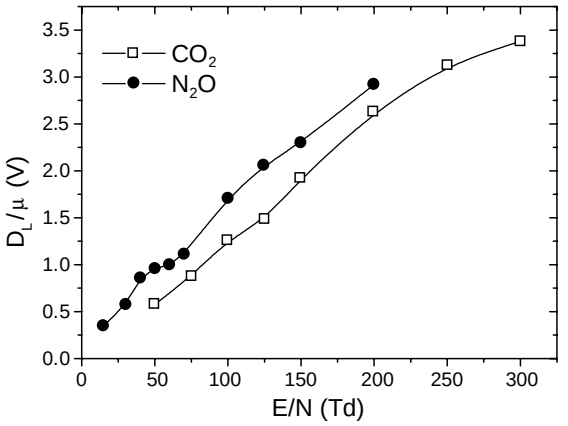

Fig. 2. D_L/μ coefficient in N_2O (7% combined error bar) compared to data in CO_2 (Roznerski and Mechlińska-Drewko, 1994).

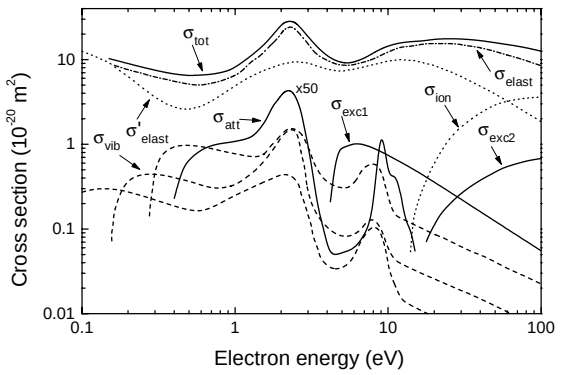

Fig. 3. A set of recommended integral cross sections and momentum transfer cross section of Hayashi (σ'_{elast}) for electron scattering in N_2O.

drift coefficient to mobility are shown in Fig. 3. In this case D_L/μ for CO_2 is lower by 10–30% for all values of E/N. Moreover, we note that in the contrast for CO_2 D_L/μ for N_2O increases slower in 40–70 Td range than for other values.

3.2. Model of cross sections

Comparison between swarm parameters and total and partial cross sections can be helpful to understanding of processes that occur during electron drift in gases. The derivation of cross sections from diffusion coefficients requires solving the Boltzmann equation and taking into account all possible inelastic processes. However, to the first approximation, the following simplified relations hold (see, for example, refer Crompton et al., 1991):

$$w = -\left(\frac{2}{m}\right)^{1/2}\frac{eF}{3N}\int_0^\infty \frac{E}{\sigma_m(E)}\frac{\mathrm{d}f_0(E)}{\mathrm{d}E}\,\mathrm{d}E,$$

$$D_T = \left(\frac{2}{m}\right)^{1/2}\frac{1}{3N}\int_0^\infty \frac{E}{\sigma_m(E)}f_0(E)\,\mathrm{d}E.$$

If attachment or ionisation occur, the spatial profile of the electron density can be described by an infinite dipole extension formula (Lowke and Parker, 1969):

$$n = \sum_{k=-\infty}^{+\infty} r_k^{-3}(z-2kh)(\beta r_k+1)\exp(\lambda_L z-\beta r_k),$$

where

$$r_k = \left[(z-2kh)^2+\left(D_L/D_T\right)\rho^2\right]^{1/2}$$

and

$$\beta = \lambda_L\left[1-\left(\frac{2\alpha}{\lambda_L}\right)\right]^{1/2}, \quad \lambda_L = \frac{W}{2D_L}.$$

The values α and W are the effective ionisation coefficient and the drift velocity. If we integrate the radial profile of the electron density we obtain the electron current to the corresponding segments between the inner and the outer radii (denoted by ρ_1 and ρ_2):

$$i = -2\pi D\sum_{k=-\infty}^{+\infty}[r_k^{-3}\exp(\lambda_L h-\beta r_k)[(\beta r_k+1)(2k-1)^2h^2 - (1-\lambda_L h(2k-1))r_k^2]]_{\rho_1}^{\rho_2}.$$

The assignment procedure of electron scattering cross sections from swarm values usually relies on a method of trial and error, i.e. the numerical solution of the Boltzmann equation for different sets of CS and selection this set for which calculated data have the best agreement with experimental.

In this paper, we tested recommended cross sections (Zecca et al., 2003) based on experimental data described in the introduction, see Fig. 3. Because experimental values of electronic excitation CS were measured sporadically and these data are rather incomplete we adopted semiempirical values of Hayashi (described by σ'_{exc} in Fig. 3). For calculation of D_T/μ from CS we used program BOLSIG. This program was designed to generate electron and transport data in pure gases or gas mixtures over a wide range of values of E/N by the numerical solution of the Boltzmann equation. The solution technique used in BOLSIG is based in part on the technique described by Pitchford et al. (1981).

Comparison between results of semiempirical calculations and experimental swarm data are shown in Fig. 1. Our semiempirical data obtained from recommended cross sections are in good agreement with experimental up to about 100 Td range of reduced electric field and only for 30 Td there can be noted a difference. For higher E/N agreement is quite reasonable-as the present model still does not contain higher electronic excitation states, for which we lack experimental data (see Ref. (Marinković et al., 1999). Improvement of the model is under way.

We have also done calculations using "shareware" cross sections of Hayashi (1992) ("Hayashi I" in Fig. 1). For clarity reasons, in Fig. 3 we show only momentum transfer cross sections from that set. Data deduced from semiempirical CS of Hayashi ("Hayashi I") and showed in Fig. 1 are in good agreement with experimental of Bailey in 50–100 Td but this curve tends quickly to the zero value below 15 Td. On the other hand for 30–70 Td it corresponds to our experimental results but for other values of E/N we can notice relatively higher differences. Agreement of Hayashi's model II (Hayashi, private information) in multiterm Bolztmann analysis with experimental values is better than of the model "Hayashi I", the model II falls in-between present and Bailey's values. Unfortunately, we do not know details of the cross sections used by Hayashi for that calculation.

3.3. Drift velocity

Good agreement of D_T/μ with Hayashi is not the case of the drift velocity, see Fig. 4. In the calculation of the drift velocity from semiempirical cross sections any differences in input data influences directly the evaluation of the W value. Present W values are conformable to data of Pack et al. (1962) and Nielsen and Bradbury (1937) but at intermediate reduced fields almost 50% lower than those calculated by Hayashi. This is a clear indication that the cross sections used by Hayashi should be verified. The present measurements indicates that the set of Kwan et al. (1984) and Szmytkowski et al. (1984) is more appropriate for modelling diffusion coefficients at intermediate E/N values. Further modelling of diffusion coefficients from different sets of cross sections is planned.

In Fig. 4 we show also the drift velocity values calculated in ELENDIF Bolztmann-equation code (Morgan and Penetrante, 2000). For test goals we have first done this calculation using Hayashi's set of cross sections available on internet and we reproduced well his "W" values (but in disagreement with the experiment). A trial to remove from his cross sections the electronic excitation with the 4.5 eV threshold, worsens utterly the agreement with the experiment. The work is in progress to explain this discrepancy.

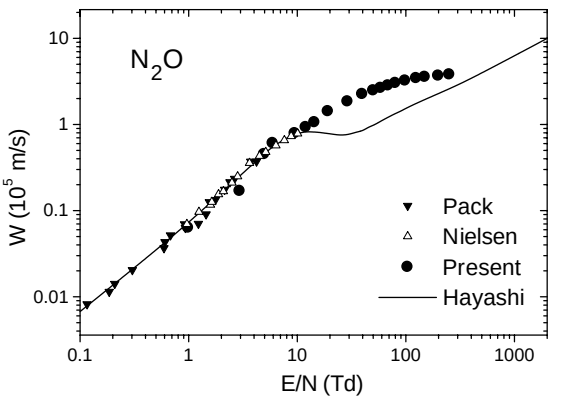

Fig. 4. Comparison between present and other (Pack et al., 1962; Nielsen and Brandbury, 1937) experimental values and semiempirical present and Hayashi's data (1992) for electron drift velocity in N_2O.

4. Conclusion

In this work, we present experimental results of the transverse diffusion coefficient to mobility (D_T/μ), the ratio of longitudinal diffusion coefficient to mobility (D_L/μ) and the drift velocities for electrons in nitrous oxide, in particular measurements of D_L/μ are shown the first time. Values of all presented electron transport parameters are generally in good agreement with data obtained by other authors. Moreover, we produce the model of integral cross sections for electron scattering in N_2O for different kind of excitations (momentum transfer, vibrational, attachment, ionisation and electronic excitation). This model is used to reproduce of the transverse diffusion coefficient to mobility ratio by numeric solution of Boltzmann equation. Results of calculations correspond to other models and experimental data.

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