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Drift Velocity and Longitudinal Diffusion Coefficient of Electrons in CO_2–Ar Mixtures and Electron Collision Cross Sections for CO_2 Molecules*

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Abstract

The drift velocity and longitudinal diffusion coefficient of electrons in 0·2503% and 1·97% CO_2–Ar mixtures were measured for $0{\cdot}03 \leq E/N \leq 20$ Td. The measured electron swarm parameters in the mixtures were used to derive a set of consistent vibrational excitation cross sections for the CO_2 molecule. Analysis of electron swarms in pure CO_2 using the present vibrational excitation cross sections was also carried out in order to determine a new momentum transfer cross section for the CO_2 molecule.

1. Introduction

The CO_2 molecule is one of the most thoroughly investigated molecules because it is common in our planetary atmosphere and it is also the principal constituent gas of the CO_2 laser. Many theoretical (e.g. Whitten and Lane 1982) and experimental (Boness and Schulz 1974; Kochem *et al.* 1985; Field *et al.* 1991) investigations on the CO_2 electron scattering cross section have been carried out using a variety of electron scattering processes. It is now well known that a virtual state produces a large elastic cross section for sub-excitation electrons and a large vibrational threshold cross sections for the symmetric stretch mode. It is also well known that the vibrational excitation cross sections for two infrared active modes have a strong shape resonance at about 3·8 eV. There have been extensive swarm studies (Hake and Phelps 1967; Bulos and Phelps 1976) and the derived cross section sets have been widely used to analyse discharge plasmas in CO_2 lasers (Lowke *et al.* 1973). Nevertheless, the absolute magnitudes of these vibrational excitation cross sections from different sources show an appreciable discrepancy.

We have succeeded so far in determining low-lying inelastic collision cross sections for several molecules from the two measured electron swarm parameters, the drift velocity and longitudinal diffusion coefficient, in dilute molecular gas and rare gas mixtures (Kurachi and Nakamura 1988). The mixing ratio of the molecular gas to rare gas was usually less than a few percent, and argon was used as a buffer gas in most cases. The behaviour of the electron swarm parameters in these mixtures strongly depends on the magnitude and energy dependence of

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the low-lying inelastic cross sections of the minority molecular gas and, at the same time, has almost no dependence on the elastic cross section of the minority molecules. Therefore, it is possible to determine molecular inelastic cross sections, and vibrational excitation cross sections in particular, by analysing electron swarm data measured in the mixture without interference from the usually unknown minority molecular elastic collision cross section. This is one of the advantages of studying electron swarm parameters in dilute molecular gas–rare gas mixtures. After the vibrational excitation cross sections are determined by reproducing the measured swarm parameters in the mixtures, the elastic momentum transfer cross section for the molecule can be determined uniquely if electron swarm parameters in the pure molecular gas are available.

This procedure was applied to CO_2 in the present study. The electron drift velocity and the longitudinal diffusion coefficient in CO_2–Ar mixtures are measured for $0{\cdot}03 \leq E/N \leq 20$ Td, where the contribution from the vibrational excitation cross sections of CO_2 to the swarm parameters in the mixtures is most appreciable. The swarm parameters in the mixtures are analysed by using a multi-term Boltzmann equation analysis (Robson and Ness 1986) and then a set of electron collision cross sections for the CO_2 molecule is determined. Electron swarm parameters in pure CO_2 (Elford and Haddad 1980 and Hasegawa 1994 for the electron drift velocity, Conti and Williams 1975 and Alger and Rees 1976 for the ionisation coefficient) are also analysed using the newly derived vibrational cross sections. Then the elastic momentum transfer cross section for the CO_2 molecule is derived up to a maximum energy of 30 eV. These cross sections are also compared with published cross sections from various sources.

2. Experimental

A double-shutter (four-gauze) electron drift tube (Kurachi and Nakamura 1988) was used to measure the drift velocity W and the product of the longitudinal diffusion coefficient and gas number density ND_L for electrons in 0·203% and 1·97% CO_2–Ar mixtures. The drift distance in the tube can be varied up to 10 cm and the swarm parameters then determined differentially from the arrival time spectra of electrons recorded at several drift distances for each E/N value. Details of the measurement were given elsewhere (Nakamura 1987). The mixtures were prepared by Takachiho Chemicals Co. Ltd and are composed of pure CO_2 (99·999%) and pure Ar (99·9999%). The mixing ratio was determined by a gas chromatography test. The measurements were carried out over the E/N range 0·035–20 Td (E and N are the electric field and gas number density respectively and $1\ \text{Td} = 1\times10^{-17}\ \text{V cm}^2$) and for N values over the range $1{\cdot}7\times10^{17}$–$3{\cdot}6\times10^{19}\ \text{cm}^{-3}$.

The measured drift velocity W and ND_L are shown in Fig. 1 for the 0·203% mixture and in Fig. 2 for the 1·97% mixture. Each plot represents data measured at more than three different pressures and no appreciable pressure dependence was observed throughout the measurements. The scattering of plots is larger for ND_L than for the drift velocity in both mixtures, mainly because the former depends more on the stability of the background current. The maximum estimated error limits are 2% for the drift velocity and about 6% for ND_L (Nakamura 1987). The E/N dependence of the measured swarm parameters are similar to that observed in our previous measurement on SiH_4–rare gas mixtures (Kurachi and

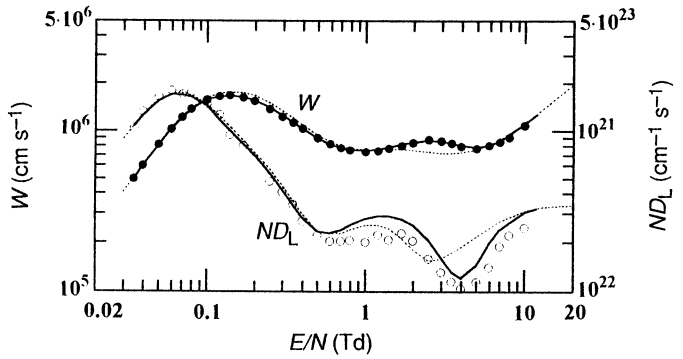

Fig. 1. Electron drift velocity W (solid circles) and the product of the longitudinal diffusion coefficient and gas number density ND_L (open circles) in the 0·203% CO_2–Ar mixture: solid curve, using the present cross sections; and dotted curve, using the cross sections of Phelps (1993).

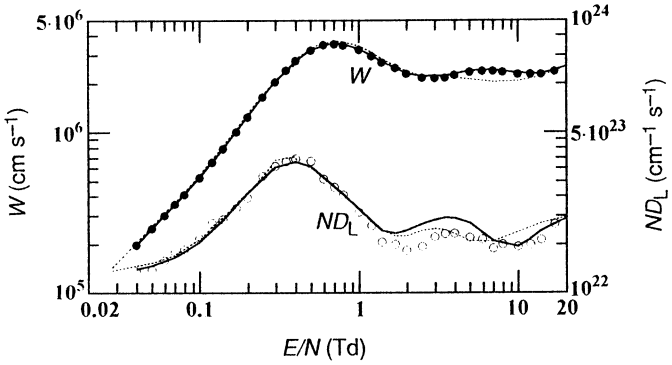

Fig. 2. Electron drift velocity W (solid circles) and the product of the longitudinal diffusion coefficient and gas number density ND_L (open circles) in the 1·97% CO_2–Ar mixture: solid curve, using the present cross sections; and dotted curve, using the cross sections of Phelps (1993).

Nakamura 1988), indicating the importance of threshold and shape resonance peaks in the vibrational excitation cross sections of CO_2

3. Electron Collision Cross Section Set for CO_2 from Swarm Data

The basic procedure used was that of the standard swarm study (Huxley and Crompton 1974, Chap. 13). The electron swarm parameters were investigated by a multi-term Boltzmann equation analysis (Robson and Ness 1986) and the results of the electron drift velocity were also confirmed by the FTI (flight time integral) analysis (Fukutoku and Ikuta 1990). In both analyses the scattering was assumed to be isotropic.

In the present study, the following swarm derived set of cross sections for argon atom was used throughout. It consists of the elastic momentum transfer cross section derived by Milloy *et al.* (0–2·5 eV, 1977) and Nakamura and Kurachi (over 2·5 eV, 1988), and the inelastic excitation cross sections including ionisation derived by Kurachi and Nakamura (1989).

The data compiled by Phelps (1993) were used as an initial set of electron collision cross sections for the CO_2 molecule. It included an elastic momentum transfer cross section, vibrational excitation cross sections for three fundamental modes and five higher modes ($n10$- and $n00$- series), an attachment cross section, two excitation cross sections (thresholds at 7 and 10·5 eV), and an ionisation cross section. The relative magnitude of the vibrational excitation cross sections at the shape resonance for the fundamental and the higher mode excitations were determined in accordance with the measurements (Boness and Schulz 1974; Register *et al.* 1980) Rotational excitations of the CO_2 molecule were included in the elastic scattering because of its small rotational constant.

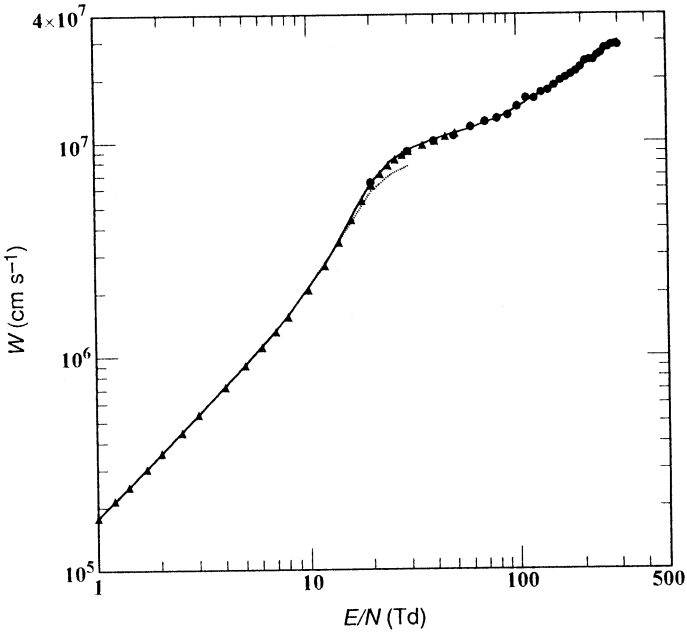

Fig. 3. Electron drift velocity in pure CO_2: solid curve, using the present cross sections; dotted curve, using the cross sections of Phelps (1993); triangles, Elford and Haddad (1980); and circles, Hasegawa (1994).

First, the vibrational excitation cross section for CO_2 was adjusted in a trial-and-error manner by repeating the Boltzmann equation analysis until the revised cross sections gave electron swarm parameters satisfactorily consistent with those measured in the mixtures. Second, electron swarm parameters in pure CO_2 were analysed using a cross section set which consists of an initial choice of elastic momentum transfer cross section, the set of vibrational cross sections determined from the analysis for the mixtures, and other inelastic cross sections. The calculated electron drift velocity and ionisation coefficient were

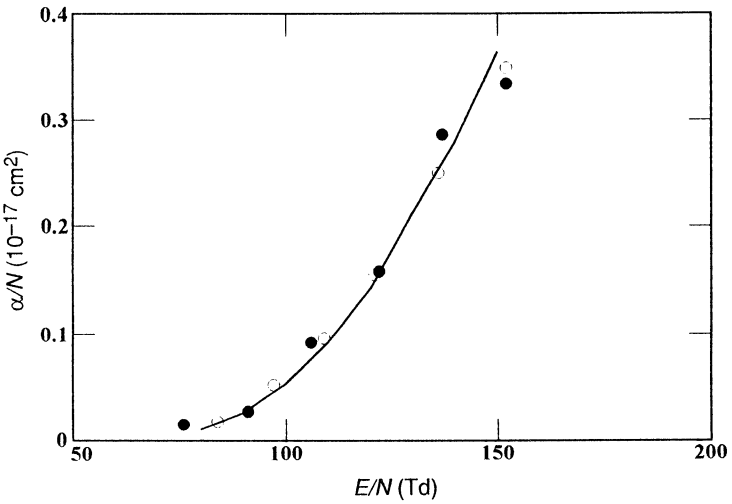

Fig. 4. Townsend's first ionisation coefficient in pure CO_2: solid curve, using the present cross sections; solid circles, Alger and Rees (1976); and open circles, Conti and Williams (1975).

compared with experiment and the elastic momentum transfer cross section and electronic excitation cross sections were amended after, as explained before, the vibrational excitation cross sections derived from the swarm data measured in mixtures were determined.

Electron swarm parameters calculated by using the latest set of cross sections for CO_2 are shown in Figs 1–4 by the solid curves. Also shown in Figs 1–3 by the dotted curves are the respective electron swarm parameters calculated using the initial cross section set of Phelps (1993). The vibrational excitation cross sections around the resonance peak and the elastic momentum transfer cross section at energies higher than 2 eV were the most effective in reducing deviations from the experimental swarm parameters in the mixtures and in pure CO_2 respectively. The most recent cross section set is shown by the solid curves in Fig. 5 and is compared with the cross sections of Phelps (dotted curves, 1993) and those from other sources. As can be seen the present set can reproduce the electron swarm parameters fairly well in both the mixtures and pure CO_2, except ND_L over the medium E/N range in the mixtures.

Details are now given on the cross sections determined in the present study.

(3a) Vibrational Excitation Cross Sections

The threshold behaviour described by Phelps of the vibrational excitation cross sections for three fundamental modes up to 1·5 eV was found to be fairly consistent with the present swarm parameters for low E/N. The beam-derived threshold behaviour, however, was not compatible with the present swarm parameters. In order to produce the structure in W in the medium E/N region, the magnitude of the vibrational cross sections around the shape resonance peak ($\epsilon > 1{\cdot}5$ eV) must be about twice as large as that measured by Boness and Schulz (1974).

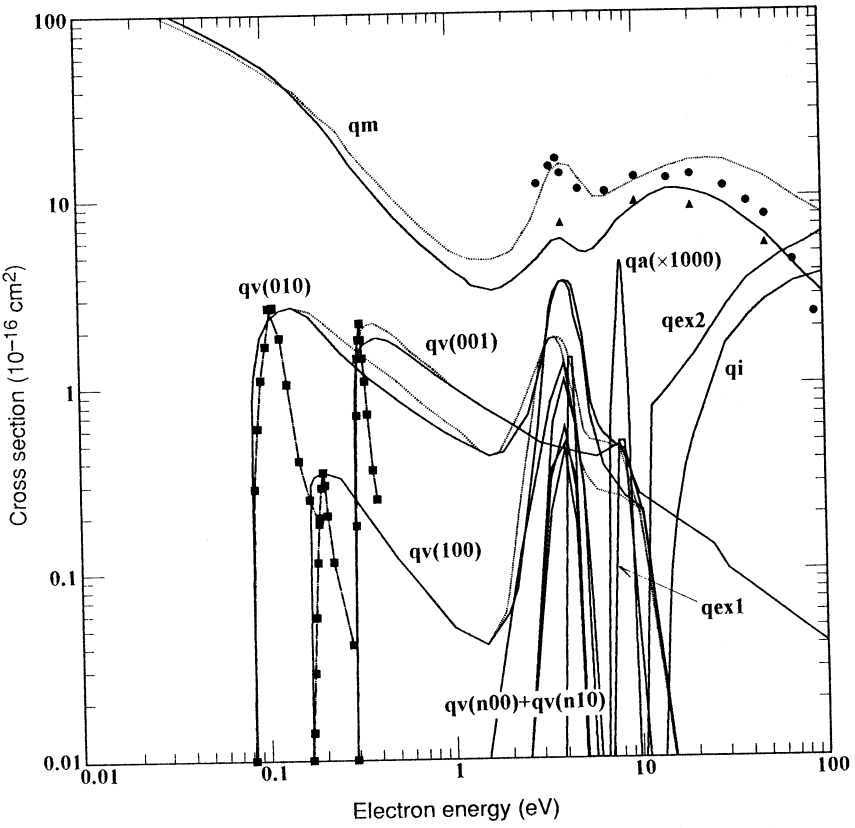

Fig. 5. Electron collision cross sections for the CO_2 molecule: solid curve, present cross sections; dotted curve Phelps (1993); triangles, Register *et al.* (1980); circles, Shyn *et al.* (1978); and curve with squares, Field *et al.* (1991). The vibrational cross sections of Field *et al.* are arbitrarily normalised to those of Phelps only for comparison.

(3b) Elastic Momentum Transfer and Electronic Excitation Cross Sections (1–30 eV)

The elastic momentum transfer cross section for the energy range below the vibrational threshold was determined from W and ND_L in the 1·97% CO_2–Ar mixture over the lowest part of the E/N range measured. The electron drift velocity measured in pure CO_2 (Hasegawa 1994) and the vibrational cross sections derived in the preceding section enabled us to determine elastic momentum transfer cross section over the energy range 1–30 eV. The resultant cross section is quite close to the measurement of Register *et al.* (1980) except near 4 eV. At the same time, the Townsend ionisation coefficient was compared with published measurements (Conti and Williams 1975; Alger and Rees 1976) and electronic excitation cross sections were determined. Electronic excitation cross sections for two thresholds at 7 and 10·5 eV were assumed (Hake and Phelps 1967). The magnitude of the 7 eV cross section was reduced to 6×10^{-17} cm^2 and that of the 10·5 eV cross section was increased by 10% in order to reproduce the measured ionisation coefficient.

4. Conclusions

The drift velocity and longitudinal diffusion coefficient of electrons in 0·203% and 1·97% CO_2–Ar mixtures were measured for $0{\cdot}03 \leq E/N \leq 20$ Td and a consistent set of vibrational excitation cross sections for the CO_2 molecule was determined. Beam-derived threshold cross sections are not compatible with the present swarm parameters measured in the mixtures at low E/N. The magnitude of the vibrational cross sections at the shape resonance peak ($\epsilon > 1{\cdot}5$ eV) should be about twice as large as that measured by Boness and Schulz (1974). The use of the vibrational excitation cross sections derived here and the published electron swarm data in pure CO_2 at high E/N also enabled us to determine a consistent momentum transfer cross section and an electronic excitation cross section.

An independent determination of the vibrational excitation cross sections and the elastic momentum transfer cross section of the CO_2 molecule was realised by analysing electron swarm parameters measured in dilute CO_2–Ar mixtures and in pure CO_2.

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