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Two- and Three-body Ion–Electron Recombination Rate Coefficients in Neon*

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Abstract

The rates of recombination of electrons with Ne_2^+ ions over a wide range of pressure (100–1000 Torr) and at temperatures of 133, 233 and 295 K were measured. Two- and three-body recombination processes were resolved. The observed two-body rate coefficient is lower than earlier reports. The three-body rate measured agrees well with predictions from Flannery's modified theory by Bates for termolecular ion–electron recombination in a monatomic gas.

1. Introduction

In recent studies we have reported the existence of two- and three-body recombination mechanisms for ion–electron recombination in gaseous helium (van Sonsbeek *et al.* 1992) and argon (Cooper *et al.* 1993). Earlier reports were restricted to measurements at low pressures in plasmas created using microwave breakdown. This places an upper limit of gas pressure of about 10 Torr (1 Torr $\equiv$ 133 Pa) which may be used, as it is essential to create an evenly distributed plasma in the system. The low pressure range studied by all previous workers has failed to show any three-body effect for the same reasons as in the helium and argon systems. No pressure dependence for α has been reported. Table 1 lists the previous determinations made of the total ion–electron recombination rate constant in neon.

Recently, pulse radiolysis techniques have been successfully employed by Sennhauser *et al.* (1980) to observe and resolve two- and three-body recombination processes in monatomic and simple molecular gases for pressures up to several atmospheres. Temperature dependent studies of ion–electron recombination in helium and argon have been reported by us.

Previous Measurements

Biondi and Brown (1949) first used the technique of microwave probing which has come to dominate measurements of α in neon. A large microwave field was used to produce an electrodeless discharge which ionised the gas samples. The decay of electrons was monitored by measurement of the resonant frequency of the microwave cavity as a function of time. A value of $(2{\cdot}07\pm0{\cdot}05)\times10^{-7}$ cm^3 s^{-1}

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Table 1. Previous measurements of the ion–electron recombination rate constant in neon

At the low pressures of all of these studies, the rate constant α is effectively the two-body rate constant, with little or no contribution from three-body recombination

Worker(s)	α (10^{-7} cm^3 s^{-1})	Analysis Technique	Pressure range (Torr)	Comments
Biondi & Brown (1949)	2·07±0·05	Microwave probing	15–30	Independent of gas temp. between 195 and 410 K
Holt *et al.* (1950)	1·1	Microwave probing Optical spectroscopy	10–30	Emitting light intensity ∝ square of electron density
Oskam (1958)	2·4±0·2	Microwave probing	18·1–19·8	
Oskam & Mittelstadt (1963)	2·2±0·2	Microwave probing Optical spectroscopy	17–35	Studied influence of plasma excitation
Biondi (1963	2·2±0·1	Microwave probing Optical spectroscopy	9·5–23·5	Adjusted value based on Gray and Kerr (1962) analysis
Frommhold *et al.* (1968)	1·7±0·1	Microwave probing	20	Electron temp. dependence of $T_e^{-0\cdot43}$ observed
Kasner (1968)	1·8±0·2	Mass spectrometry Microwave probing	8–30	Gas temp. dependence of $T_{gas}^{-0\cdot42\pm0\cdot04}$ observed from 295–503 K
Philbrick *et al.* (1969)	14·75±0·2	Microwave probing Mass spectrometry	6	Electron temp. dependence of $T_e^{-0\cdot49}$ observed
Lukac *et al.* (1977)	0·2	Microwave probing		Value quoted for Ne_2^+, Ne/He gas mixtures used
Chen (1969)	∼2·5	Mass spectrometry Microwave probing		Value found to be essentially independent of gas temp.

was measured, which was invariant over the pressure range 15 to 30 Torr. Further, over the temperature range $T = 300$ to 410 K, α showed no systematic change larger than 5%. It was concluded that there was no temperature effect on α. Other measurements by these workers were made at 195 and 77 K. At 195 K there was still no pressure dependence for α which was found to be equal to the 300 K result. At 77 K, however, α was found to increase with pressure over the range 15 to 30 Torr. At low pressures, α approached the value observed at the higher temperatures.

This result is in agreement with the trend predicted by all theories of three-body recombination, i.e. the three-body rate constant will be greater at lower temperatures. Hence, any third-body effect is most likely to be observed at low temperatures. The residual α value measured at and above 195 K is clearly the two-body rate constant α_2. However, Biondi and Brown observed an unexplained exponential dependence of α on pressure. Holt *et al.* (1950) conducted one of the few optical emission studies of recombination in neon ever attempted. They simultaneously used the microwave resonant frequency shift method to determine electron density, and also measured the light intensity from recombination fluorescence. Holt *et al.* (1950) produced plasmas in 10–30 Torr of spectroscopically pure neon by a pulsed microwave electrodeless discharge. The fact that the emitted light intensity was found to be proportional to the square of the electron density indicated no change in the mechanism of recombination during the period of the afterglow studied. The value for α determined by Holt *et al.* (1950) of $1{\cdot}1\times10^{-7}$ cm^3 s^{-1} is the lowest recorded value by all previous workers.

Oskam and Mittelstadt (1963) reported α values for all the rare gases except radon, but did not report any evidence of pressure dependence. Their value (Table 1) for room temperature is in agreement with earlier reports. However, their study of the influence of the duration of the plasma excitation pulse on α is of interest, since it clearly showed that the plasma was very inhomogeneous at high powers leading to incorrect values of α.

Biondi's (1963) further studies used discharges initiated in the gas samples by 10 μs to 1 ms pulses from a pulsed magnetron. He confirmed in his optical studies that the afterglow radiation originated in the volume of ionised gas, and not at the cell walls. A value for α of $(2{\cdot}2\pm0{\cdot}1)\times10^{-7}$ cm^3 s^{-1} was measured; no pressure effect was found.

Frommhold *et al.* (1968) studied the effect of varying electron temperature; a dependence of $T_e^{-0{\cdot}43}$ observed suggested that the initial capture step is rate limiting in the dissociative recombination mechanism in neon. An α value of $(1{\cdot}7\pm0{\cdot}1)\times10^{-7}$ cm^3 s^{-1} was reported at $T_e = 300$ K.

Kasner (1968) used mass spectrometry, as well as conventional microwave techniques, to study recombination in neon over the pressure range 8 to 30 Torr. These experimental techniques showed similar decay rates for the Ne_2^+ as well as electron species. The measured recombination coefficient was $(1{\cdot}8\pm0{\cdot}2)\times10^{-7}$ cm^3 s^{-1} at 295 K, with a temperature dependence of $T_{gas}^{-0{\cdot}42\pm0{\cdot}04}$ over the range 295 to 503 K. At all temperatures, Kasner (1968) reported no systematic variation of α with neon pressure, indicating that the recombination process is a two-body reaction. Similar studies by Philbrick *et al.* (1969) in 6 Torr of pure neon gave $\alpha = (1{\cdot}75\pm0{\cdot}2)\times10^{-7}$ cm^3 s^{-1} at $T_e = 300$ K. The value of α

was found to decrease with increasing electron temperature as $T_e^{-0\cdot49}$, in good agreement with previous measurements.

Chen (1969) found that the absolute value of α_2 at a given electron temperature, and the extent of the electron temperature *dependence* of α_2, were both affected by the atom or gas temperature in helium and argon. In neon, however, an α value of $3\cdot5\times10^{-7}$ cm^3 s^{-1} was observed at $T_e = 300$ K, a value virtually independent of the gas temperature. This unexpected result supports the observations made twenty years earlier in 1949 by Biondi and Brown, who showed that α in neon was temperature independent between 195 and 410 K.

In the present studies, electron beam pulse radiolysis has been employed in order to resolve the two- and three-body components of the total rate coefficients and the first systematic study of the dependence of both these rate constants on bulk gas temperature has been made.

2. Experimental

The pulsed e-beam facility used for the current study in neon is similar to that described by van Sonsbeek *et al.* (1992). A Febetron 706 electron pulser, generating 3 ns (FWHM) pulses of 0·2–0·6 MeV electrons, was used to create weakly ionised neon plasmas. Initial electron and ion densities were of the order of 10^{11} cm^{-3}.

Materials

Neon and helium both CIG-UHP grade were used in this study. The gas was further purified immediately prior to use by passage through a liquid nitrogen cooled molecular sieve (5 Å) trap. This procedure ensured the removal of trace amounts of impurities such as O_2, H_2O etc. Pressure measurements were made using an MKS 'Baratron' type 170M gauge.

Detection System

A microwave absorption technique was used to monitor electron concentrations within the irradiation cell. This technique relates the change in power of microwaves on passing through a region of ionised gas to the conductivity of the gas. In this system, microwaves are generated at 9 GHz by a Gunn diode oscillator; maximum output power is 10 mW. The microwaves are directed using standard waveguide fittings into an evacuable cell containing the gas under study. The cell is directly attached to an all metal vacuum line. The microwaves pass through the irradiated gas and the change in power is monitored by a fast response Schottky barrier diode. The output of the diode is recorded using a fast analog oscilloscope. Details of this microwave absorption technique are fully described by Infelta *et al.* (1977).

Data Treatment

The technique of microwave absorption can be used to determine changes in conductivity in the medium which is given by

$$\Delta\sigma = eN_e\,\mu_e\,. \tag{1}$$

Use of this equation to determine the electron concentration N_e requires a knowledge of the mobility of electrons in the plasma at various pressures. This is calculated from the relationship between the observed microwave conductivity and both the momentum-transfer collision frequency $\nu_m(u)$ in a gas and the radian microwave frequency ω (assuming a Maxwellian electron energy distribution):

$$\Delta\sigma(\omega) = \frac{4}{3\sqrt{\pi}} \frac{e^2 N_e}{m\omega} \int_0^\infty \frac{\nu_m(u)/\omega}{1+[\nu_m(u)/\omega]^2} (u/u_k)^{3/2} e^{-u/u_k} \, du/u_k \,, \qquad (2)$$

where u_k is the characteristic energy of an electron energy distribution, and m the electron mass. This calculation is performed to determine N_e for each sample at the various pressures and temperatures used. The values of $\nu(u)$ (the energy dependent momentum transfer collision frequency) are obtained from the momentum transfer cross sections of O'Malley (1980).

3. Results

The initial radiolysis product of neon is Ne^+, which is dimerised to Ne_2^+ by a three-body process with rate constant $4{\cdot}4\times10^{-32}$ cm^6 s^{-1}. The dimerisation half-life is $1{\cdot}57$ μs for the lowest pressure of neon used in this study, and 35 ns at 1 atmosphere (1 atm $\equiv$ 101·325 KPa), whereas a typical recombination time scale is of the order of 100 μs.

The ion–electron recombination mechanism is mainly divided into two- and three-body processes irrespective of the nature of the recombining positive ion. In a typical case the two-body reaction may be written as

$$(A_2)^+ + e^- \rightarrow A + A + h\nu \,,$$

with a rate constant of α_2. The three-body process may be written as

$$(A_2)^+ + e^- + M \rightarrow A + A + M + h\nu \,,$$

with the rate constant α_3. The total recombination rate constant is the sum of these two processes, i.e.

$$\alpha_{\text{total}} = \alpha_2 + \alpha_3[M] \,.$$

It can be seen that for any contribution due to a three-body recombination mechanism, the total recombination rate will increase with increasing bulk gas pressure.

The initial experiments with pure neon revealed an anomalous pressure dependence of α similar to that observed by us earlier in argon. A nonlinear *decrease* in α with pressure is observed which is exactly the reverse to that anticipated. This is due to the overlapping of thermalisation and ion–electron recombination time scales (see below). The low pressure values of α were thus in error, since the loss of conductivity in the plasma (from which α is determined) was not solely due to recombination, but due also to a change in the mobility of the electrons as they thermalise.

The change in conductivity of the medium is given by

$$\Delta\sigma = en_e \mu_e . \tag{3}$$

Use of this equation to determine the ion concentration n_e indicates that the mobility of electrons in the plasma is constant. The evolution of a thermally relaxed spectrum of positive ions and electrons is not instantaneous. The time required for this process is conventionally known as the thermalisation time and varies dramatically with the nature of the gaseous system. In 1 atmosphere of pure neon, the time required to reduce the electron energy to thermal level is several microseconds, which is considerably longer than in helium (55 ns) (Scales 1987). It is a prerequisite that thermalisation is complete before substantial ion–electron recombination rates can occur.

Experiments were thus conducted to determine the amount of pure helium required to thermalise the electrons sufficiently rapidly, but not to interfere with the slower recombination process. It was not until the amount of helium added reached ~22 Torr that the α values measured between 200 and 600 Torr neon pressure showed a constant increase with pressure. It was thus decided that a constant amount of 25 Torr helium would be added to each neon sample in order to eliminate the overlapping of the thermalisation and recombination timescales. Though not affecting the gradient of the α versus pressure plots, the intercepts of such plots may include a contribution from the third-body effect of 25 Torr of helium. From our earlier data in helium, the effect of this added helium, will be to increase the intercept value by $1{\cdot}86\times10^{-9}$ cm^3 s^{-1}. This represents a contribution to the intercept of a plot such as Fig. 2 of approximately 20%. It should be noted that there will be no significant contribution from helium ion–electron recombination itself, since only a minute quantity of He^+ will be created upon irradiation (we estimate less than 1% at the lowest neon pressure used; even less at higher pressures). Further, these helium ions will rapidly transfer their charge to form further Ne^+.

Typical experimental data for the decay of conductivity with time and the transformed second order plots are shown in Fig. 1. The linearity of the reciprocal conductivity plots typified in Fig. 1 demonstrate clean second order kinetics over at least two half-lives. The experimentally determined total recombination coefficient for various pressures of neon are shown plotted in Fig. 2. There is an increasing linear dependence of the experimentally determined recombination coefficient with pressure. This clearly shows that both two- and three-body processes are present. Table 2 lists the values of α_2 and α_3 for neon obtained from the analysis of this and other pressure profiles at the three temperatures studied.

4. Discussion

The results clearly show that both two- and three-body processes are operative in this system. The effect does require the recombination rates to be studied at pressures above 200 Torr before the effect is conclusively established. This means that earlier studies in discharges limited to pressures up to only a few tens of Torr would not detect this effect.

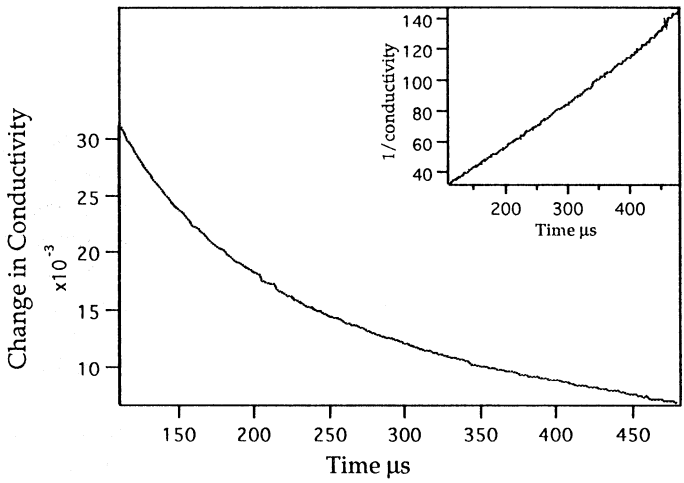

Fig. 1. Variation of conductivity and (inset) reciprocal conductivity with time for 500 Torr at room temperature. The linearity of the inset plot indicates pure second order kinetics.

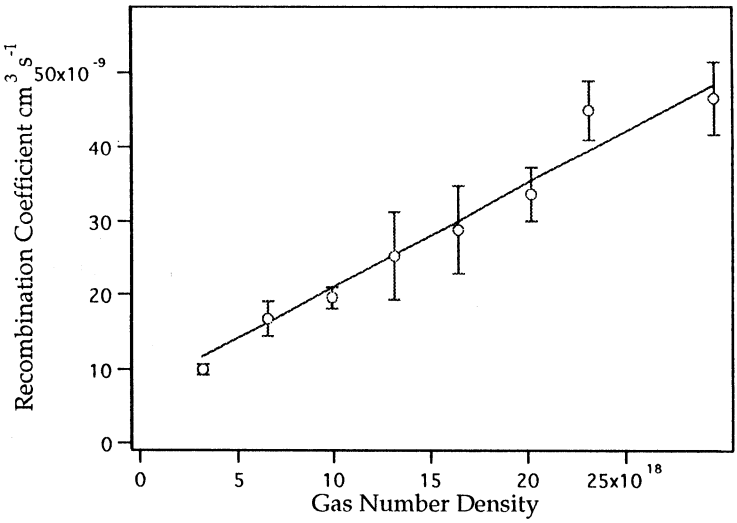

Fig. 2. Variation of the ion–electron recombination rate coefficient with pressure at 295 K. Bulk gas pressures are expressed as gas number density.

Table 2. Neon recombination coefficients

Temperature (K)	α_2 (10^{-9} cm^3 s^{-1})	α_3 (10^{-27} cm^6 s^{-1})
295	7·01	1·393±0·12
233	7·88	1·75±0·12
133	7·90	1·07±0·17

The two-body rate constant α_2 shows no significant variation with temperature. In fact, the α_2 values measured from the intercepts of the pressure plots for data from 295 to 133 K are equal within the limits of uncertainty. The value of α_2 measured in this work at 295 K of $\sim 0{\cdot}8\times10^{-8}$ cm^3 s^{-1} is substantially lower than the earlier reports of 2×10^{-7} cm^3 s^{-1}, except for the value of Lukac *et al.* (1977) who recorded $\alpha_2 = 2\times10^{-8}$ cm^3 s^{-1}. The reason for our unique low value, we believe, lies in the sample purity used in those experiments. The low cross section for electron–Ne collisions means that impurities will have a dramatic effect on electron diffusion and loss rates. In our experiments the gas samples are purified and used within minutes of preparation. At high pressures there is little chance of impurities diffusing into the irradiation zone from outgassing of the walls produced by electron beam impact. All impurity effects would lead to a more rapid decay of conductivity and hence lead to a 'high' value for α_2. From our previous studies (Cooper *et al.* 1982), the gas preparation technique showed N_2 concentrations in 1 atm helium and neon to be significantly less than $\sim$2 mTorr (i.e. $\sim$2 ppm maximum impurity level). At this maximum concentration, electrons reacting at collisional rates would have half-lives of the order 100 μs. This is much longer than the timescales of the current experiments. Further, our earlier reported data for argon (Cooper *et al.* 1993) agree well with all earlier studies. These arguments lead us to believe that our technique is sound and the result for neon is valid.

The electron density (10^{10}–10^{11} cm^{-3}) in these experiments is not high enough to produce electron assisted recombination. The effective two-body recombination coefficient calculated from Flannery (1994),

$$\alpha_{ee} = 3{\cdot}8 \times 10^{-8} T_e^{-4{\cdot}5} n_e , \qquad (4)$$

gives, at 300 K and an n_e of 10^{11} cm^{-3}, a value for α of $2{\cdot}7\times10^{-9}$ cm^{-3} s^{-1}, which is slightly less than our observed value of 8×10^{-9}. Thus electron assisted recombination (which would increase our result) is not a significant factor.

The three-body rate constant α_3, at 295 K, is $(1{\cdot}39\pm0{\cdot}12)\times10^{-27}$ cm^6 s^{-1} and represents the first measurement of this parameter. The value of this constant at other temperatures is shown in Table 2. There is no clear temperature dependence observed over this temperature range.

Comparison with Theory

Recently, Flannery (1994) has reviewed the current status of the theory of ionic recombination. He states that neon dimer cations, along with the other rare gas ions except helium, should be members of the 'super' class of two-body dissociative recombination with recombination coefficients of $\sim10^{-6}$ cm^3 s^{-1}. Our present result of $(0{\cdot}8\pm0{\cdot}1)\times10^{-8}$ cm^3 s^{-1} is supported by the work of Lukac *et al.* who obtained a value of 2×10^{-8} cm^3 s^{-1}. Our earlier result for argon of $1{\cdot}1\times10^{-6}$ cm^3 s^{-1} does agree with Flannery's classification in the super category. In the present studies with measurements being performed in a high purity, high pressure system, the invariance of the two-body rate coefficient with temperature leads us to conclude that these data are valid. Further, the total rate coefficient observed in these studies even at the highest pressures is always much less than the values observed by other workers, i.e. $\sim2\times10^{-7}$ cm^3 s^{-1}.

The values of the three-body coefficients are unique and cannot be compared with other experimental values. Flannery's (1991) modification of an earlier theory for termolecular ion–electron recombination in a monatomic gas enables an estimate to be made from

$$\alpha_3 = \alpha_M(T) \approx \frac{10^{-26}(300/T)^{2\cdot5}}{M} \text{ cm}^6\,\text{s}^{-1}, \tag{5}$$

where M is the atomic mass of the bulk gas.

Table 3. Comparison of experimental and theoretical value of termolecular recombination coeffieicnts

Gas	α_3 (10^{-27} cm^6 s^{-1})	
	Theory	Experiment
Neon	0·52	1·39
Helium	2·6	2·2

A comparison of the experimental results determined here and the earlier results published for helium calculated from Flannery's equation are shown in Table 3. Theory predicts a value of $0\cdot52\times10^{-27}$ cm^3 s^{-1}, with neon acting as a third body, which compares reasonably with the experimental value of $1\cdot39\times10^{-27}$ cm^6 s^{-1}. Table 3 shows even closer agreement between theory and experiment in the helium system. This supports the validity of the current α_3 data.

Flannery's contention that neon is in the *super* class of two-body recombination coefficients is not supported by the current study. If α_2 is indeed as high as 1×10^{-6} cm^3 s^{-1} then this imposes the following condition on the experimental results; in order to detect a three-body effect then $\alpha_3\times$[Ne] must be of similar magnitude to α_2. Assuming a value of 1×10^{-27} cm^3 s^{-1} for α_3, then

$$\alpha_2 = \alpha_3 \times p \times 3\cdot3 \times 10^{16}, \tag{6}$$

where p is the pressure (Torr) on neon required. This calculation gives $p = 30\,354$ Torr i.e. ~40 atm. This is too far away from experimental reality—the effect is seen at and above 100 Torr—to be attributable to experimental error. The reasonably close agreement between experiment and theory for α_3 would indicate that the inclusion of neon in the super class of two-body α_2 recombination coefficients is incorrect.

Other theoretical predictions for α_3 in different gases have been made by several investigators (Warman *et al.* 1979). According to the Thomson (1924) model, recombination occurs if an electron loses energy equal to or more than $\frac{3}{2}kT$, while within a distance r_T from a positive ion. Massey and Burhop (1952) suggested that, by replacing $2m/M$ by the mean fractional energy loss per collision λ, and also by replacing the mean electron velocity V and the average cross section for electron atom collisions σ by a unit density collision frequency ν/N, then α_3 is

$$\alpha_3 = \frac{4\pi}{3} r_T^3\, \lambda\nu/N. \tag{7}$$

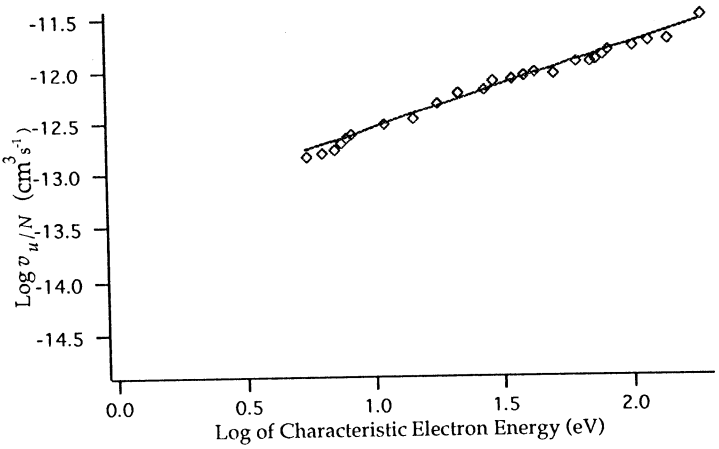

Fig. 3. Dependence of the energy exchange rate coefficient on characteristic electron energy.

All these models consider elastic collisions as the only mode to lose excess electron energy. These models were extended by taking account of energy losses due to excitation of internal modes of the molecules. Sennhauser *et al.* (1980) in their study of recombination in diatomic gases replaced the term $\lambda\nu/N$ in equation (7) by the experimentally measurable parameter ν_u/N and used this to calculate α_3 for NH_3, H_2O and CO_2 gases,

$$\alpha_3 = Kr_T^3\nu_u/N\,, \tag{8}$$

where K is a constant representing all the numerical factors appearing in equation (7). The term ν_u/N is the energy exchange rate coefficient and is defined by

$$\nu_u/N = e(\mu N)(E/N)^2/(eD/\mu - kT)\,, \tag{9}$$

where μ is the mobility and D the electron diffusion coefficient. Using the data from electron swarm experiments for the drift velocity and the diffusion coefficient as a function of field strength E, we have calculated ν_u/N for neon using electron drift velocity data from Robertson (1972) and diffusion data from Huxley and Crompton (1974), and this is plotted as a function of the characteristic energy in Fig. 3. As can be seen from the plot ν_u/N increases with an increase in mean electron energy above thermal. Use of the ν_u/N value at thermal energies obtained by extrapolation is used with (8) to calculate α_3. The calculated value of $0{\cdot}7\times10^{-29}$ $cm^6\,s^{-1}$ compares poorly with the observed value of $1{\cdot}39\times10^{-27}$ $cm^6\,s^{-1}$, implying that the use of ν_u/N at thermal energy is invalid. A similar discrepancy between observed and calculated α_3 values for CO_2 was observed by Sennhauser *et al.* (1980). Their suggestion for this discrepancy was that the value of ν_u/N corresponding to the mean electron energy increases significantly from 195 to 300 K. This behaviour is not seen in the case of neon suggesting that the use of an energy exchange coefficient is not a useful alternative to calculate an α_3 value. In order to get reasonable agreement by this method, an electron characteristic energy some 200 times thermal would be needed.

We have been unable to find any significant effect of bulk gas temperature on either the two- or three-body rate coefficients in the neon system.

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References

Bates, D. R., and Khare, S. P. (1965). *Proc. Phys. Soc. Lond.* **85**, 213.
Biondi, M. A. (1963). *Phys. Rev.* **129**, 1181.
Biondi, M. A., and Brown, S. C. (1949). *Phys. Rev.* **75**, 1700.
Chen, C. L. (1969). *Phys. Rev.* **177**, 245.
Cooper, R., Denison, L., and Sauer, M. C., Jr. (1982). *J. Phys. Chem.* **86**, 5093.
Cooper, R., van Sonsbeek, R. J., and Bhave, R. N. (1993). *J. Chem. Phys.* **98**, 383.
Flannery, M. R. (1991). *J. Chem. Phys.* **95**, 8205.
Flannery, M. R. (1994). *Adv. Atom. Mol. Opt. Phys.* **32**, 117.
Frommhold, L., Biondi, M. A., and Mehr, F. J. (1968). *Phys. Rev.* **165**, 44.
Gray, E. P., and Kerr, D. E. (1962). *Ann. Phys. (NY)* **17**, 276.
Holt, R. B., Richardson, J. M., Howland, B., and McClure, B. T. (1950). *Phys. Rev.* **77**, 239.
Huxley, L. G. H., and Crompton, R. W. (1974). 'The Drift and Diffusion of Electrons in Gases' (Wiley: New York).
Infelta, P. P., de Haas, M. P., and Warman, J. M. (1977). *Radiat. Phys. Chem.* **10**, 353.
Kasner, W. H. (1968). *Phys. Rev.* **167**, 148.
Lukac, P., Trnovec, J., and Mikus, O. (1977). *Acta Fac. Retum Nat. Univ. Comenianae Phys. (Czechoslovakia)* **18**, 51.
Massey, H. S. W., and Burhop, E. H. S. (1952). 'Electronic and Ionic Impact Phenomena', p. 635 (Oxford Univ. Press: London).
O'Malley, T. F., and Crompton, R. W. (1980). *J. Phys.* B **13**, 3451.
Oskam, H. J. (1958). *Philips Res. Rep.* **13**, 401.
Oskam, H. J., and Mittelstadt, V. R. (1963). *Phys. Rev.* **132**, 1445.
Philbrick, J., Mehr, F. J., and Biondi, M. A. (1969). *Phys. Rev.* **181**, 271.
Pitaevskii, L. P. (1962). *Sov. Phys. JETP* **15**, 5.
Robertson, A. G. (1972). *J. Phys.* B **5**, 648.
Scales, M. J., Cooper, R., Warman, J. M., and de Maas, M. P. (1987). *Radiat. Phys. Chem.* **29**, 365.
Sennhauser, E. S., Armstrong, D. A., and Warman, J. M. (1980). *Radiat. Phys. Chem.* **15**, 479.
Thomson, J. J. (1924). *Philos. Mag.* **47**, 337.
van Sonsbeek, R. J., Cooper, R., and Bhave, R. N. (1992). *J. Chem. Phys.* **97**, 1800.
Warman, J. M., Sennhauser, E. S., and Armstrong, D. A. (1979). *J. Chem. Phys.* **70**, 995.

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