The Determination of the Diffusion Coefficient for Thermal Electrons in Water Vapour by the Use of a Modified Blanc's Law Procedure

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Abstract

The Cavalleri electron density technique has been used to measure the diffusion coefficient for thermal electrons in water vapour. When analysed by a straightforward application of Blanc's law to determine the diffusion coefficient for water vapour, the normalized coefficient ND showed an anomalous pressure dependence. The application of a modified procedure, in which these data were corrected using a calculated correction factor, removed the anomalous dependence and gave data which are in agreement with previously published data.

1. Introduction

The only available values of ND for thermal electrons in water vapour are those that can be inferred from electron mobility data using the Nernst–Townsend (Einstein) relation (see Table 2 in Section 3). The aim of the work presented in this paper was to obtain an accurate value by a more direct technique, that is, one based on measurements of diffusion coefficients rather than mobilities.

The measurements were made using Cavalleri's electron density sampling technique (Cavalleri 1969; Huxley and Crompton 1974). The apparatus and its operation have been described elsewhere (Gibson *et al.* 1973; Rhymes *et al.* 1975; Rhymes and Crompton 1975; Rhymes 1976; Hegerberg and Crompton 1980).

The time constant τ for the decay of electron density in the diffusion cell is related to the diffusion coefficient and the attachment collision frequency ν_{att} by

$$\tau^{-1} = D/\Lambda^2 + \nu_{\mathrm{att}}, \tag{1}$$

where Λ is the characteristic dimension of the cell. The initial electron concentration is very small ($<10^4$ particles per cm^3) so that Coulomb interactions between charged particles are negligible.

The very large momentum transfer cross section for thermal electrons in H_2O results in a very small diffusion coefficient and time constants that are too large to be measured in our apparatus as presently configured. In principle, the pressure could be reduced in order to reduce the time constant to a value that is within the measurement range, but this would lead to unacceptable statistical errors due to

inadequate initial ionization and insufficient avalanche development by the sampling pulses. The problem was overcome by using N_2 (with its very much smaller cross section) as a buffer gas in mixtures chosen to have suitable characteristics on the basis of the calculations for the $H_2O–N_2$ mixtures as described in Section 4b of Petrović (1986; present issue p. 237).

2. Experimental Procedure

Matheson 'Research Grade' nitrogen was used for the mixtures. Twice-distilled and deionized water was further purified by freezing and removing permanent gases by evacuating a reservoir containing the water. This procedure was repeated a number of times in order to release the frozen impurities and to monitor any dependence of the results on residual impurities. Final results were taken only after successive purification produced no further change. Pressures were measured by a calibrated Texas Instruments quartz spiral manometer.

The apparatus was baked at 210°C for three days prior to the measurements.

Mixtures of 5, 10 and 20% H_2O in N_2 were prepared in the following way. The system was first pumped down to $<10^{-4}$ Pa. Water vapour was then introduced to a slightly higher pressure than desired and left for a short time to saturate the walls. The pressure drop due to adsorption was noted and the pressure finally adjusted to the desired value before nitrogen was slowly introduced. Mixing was monitored by measuring the time constants for electron density decay. Usually 12 to 48 hours mixing time was allowed before the final measurements were made.

The results were shown to be free from measurable error due to space charge, non-thermalization of the electrons, and the presence of higher order diffusion modes. For each mixture composition the final results were an average of those taken with gas mixtures made from two different samples of water and at several pressures.

3. Results and Discussion

Measurements with 10% and 20% mixtures of H_2O in N_2 were performed at pressures of 0·5, 1 and 2 kPa, and those with 5% at 2 kPa. The results, which showed no systematic dependence on pressure, were averaged and are presented in Table 1.

Blanc's (1908) law was first applied directly to obtain values of $ND_{BL}^{H_2O}$. These results, which are shown in Table 1 and Fig. 1, clearly show a systematic dependence on the mixture composition, revealing the breakdown of the law predicted for these gas mixtures by Petrović (1986). It is therefore necessary to correct the data using equation (10) and the data for $\delta_{BL}^{H_2O}$ shown in Fig. 2 of that paper (p. 243). After correction the data, which are also shown in Table 1 and Fig. 1, show no systematic dependence on the mixture composition. The final result for ND^{H_2O} is $(5·98\pm0·20)\times10^{19}$ cm^{-1} s^{-1} (using the measured value for ND^{N_2} of $9·65\times10^{21}$ cm^{-1} s^{-1}). This value is the average of the results for different abundances (and pressures).

The uncertainty of the measured values of ND^M in this experiment is 2–3% (Gibson et al. 1973; Rhymes 1976) but to this one should add 0·5–1% to account for the uncertainty in the mixture composition due to long term adsorption and desorption effects.

Table 1. Experimental values of ND in the mixture together with the values of ND for water vapour obtained by an application of Blanc's law, before and after correction

Abundance (%)	ND^{M}* (10^{20} cm^{-1} s^{-1})	Correction factor f	$ND_{BL}^{H_2O}$ (10^{19} cm^{-1} s^{-1})	$ND_{corr}^{H_2O}$ (10^{19} cm^{-1} s^{-1})
20	2·83 (2·86)	1·035	5·80	6·00
10	5·36 (5·36)	1·073	5·64	6·05
5	9·40 (9·64)	1·14	5·18	5·90
				Average value 5·98 ± 0·20

* Values in parentheses were calculated using the available cross sections (Petrović 1986).
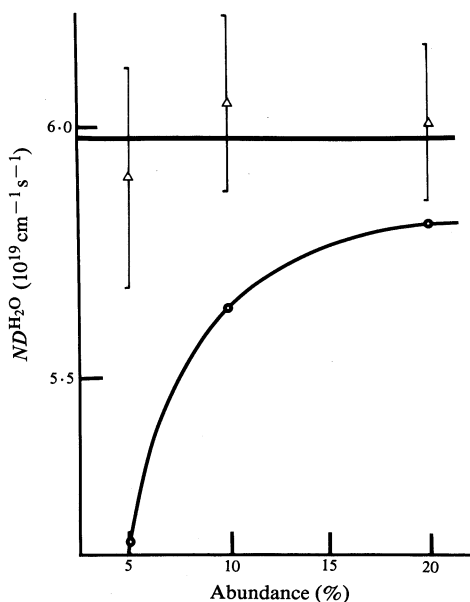

Fig. 1. Experimental results for ND^{H_2O} obtained using Blanc's law. Uncorrected data (i.e. $ND_{BL}^{H_2O}$ are given by circles and corrected data by triangles. The average value is represented by the horizontal straight line.

Table 2. Values of ND for water vapour calculated from thermal mobility data, given in the references cited, and the present experimental value

Reference[A]	ND^{H_2O} (10^{19} cm^{-1} s^{-1})
Pack *et al.* (1962)	6·05 (300 K)
Christophorou and Pittman (1970)	5·93
Lowke and Rees (1963)	5·93 (293 K)
This work	5·98 (293 K)

[A] See also Wilson *et al.* (1975) and Giraud and Krebs (1982).

Our result for ND^{H_2O} is consistent with the values obtained by the application of the Nernst–Townsend relation to the experimental thermal mobility data (see Table 2) and therefore with the cross sections derived from these data. However, the importance of making the correction to the 'raw' values of ND^{H_2O} is now apparent. If, for example, the result obtained from the mixture containing 5% of H_2O had not been corrected the inference would have been that the normalization factor in the published cross sections (Pack *et al.* 1962; Christophorou and Pittman 1970) required adjustment by about 15% in order to bring the values of ND^{H_2O} calculated from these cross sections into agreement with the experimental value. Note, however, that such an adjustment, even if required, would have little effect on the correction factor which, as shown by Petrović (1986), remains sufficiently accurate despite an uncertainty of this order.

4. Conclusions

There are two conclusions from the work presented in this paper. First, the prediction by Petrović (1986) that significant errors can arise when Blanc's law is applied to analyse the data from measurements in mixtures has been confirmed experimentally and the method for correcting these errors shown to be successful. Second, the final value of the diffusion coefficient for thermal electrons in water vapour confirms previous values obtained from electron mobility measurements and therefore the normalization of the cross sections inferred from these data.

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