# ASSOCIATIVE IONIZATION OF N(²D) AND O

M. R. TORR* and D. G. TORR*

Space Physics Research Laboratory, The University of Michigan, Ann Arbor, MI 48109 U.S.A.

Abstract—Recent laboratory measurements have shown that N(²P) atoms, and thus probably hot N(²D) atoms, will recombine with atomic oxygen via an associative ionization process at the gas kinetic rate. While the reaction is endothermic, it has been suggested that this has interesting implications for the upper atmosphere in that N(²D) atoms in the tail of the velocity distribution could provide an additional source of NO⁺ through the reverse of the dissociative recombination reaction

$$NO^+ + e \leftrightarrows N(^2D) + O.$$
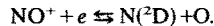
It has also been suggested that this process might account for the difference between a laboratory determination of the rate coefficient and that determined from the Atmospheric Explorer Satellite data. In this paper we investigate further the likelihood of the associative ionization of N(²D) and O playing a significant role in the normal ionosphere, in the light of several recent relevant studies. We conclude that the associative ionization process is not an important factor and that a more probable cause for disagreements in the various determinations of the recombination coefficient, is the difference in excited states of the ions in the various experiments.
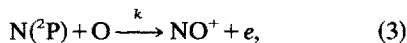
INTRODUCTION

At mid-latitudes, at night and at altitudes where photochemical equilibrium prevails, the major source of NO⁺ is

$$O^+ + N_2 \xrightarrow{k_1} NO^+ + N \tag{1}$$
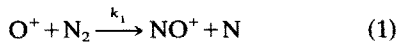
and loss of NO⁺ is via dissociative recombination

$$NO^+ + e \xrightarrow{\alpha} N + O. \tag{2}$$
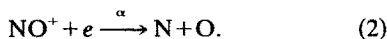
Laboratory studies have shown (Zipf, 1978) that metastable N(²P) atoms will undergo the associative ionization reaction

$$N(^2P) + O \xrightarrow{k} NO^+ + e, \tag{3}$$

at the gas kinetic rate.

If N(²D) atoms with sufficient kinetic energy are present, it is likely that they also will react with atomic oxygen to form NO⁺ by associative ionization. Zipf (1978) has suggested that this source of NO⁺ might be large enough in the midlatitude nocturnal ionosphere to account for the difference between the laboratory measurement of α by Huang *et al.* (1975) and the determination of α

from the AE satellite data (Torr *et al.*, 1976; Torr *et al.*, 1977).

Because it is the major loss mechanism for ions, the dissociative recombination process is of fundamental importance to studies of the photochemistry of the ionosphere and thermosphere. Recently several relevant new studies have been reported, and we relate these in this paper. The recent studies include a new determination of the dissociative recombination rate coefficient from the AE data and its implications for the associative ionization reaction (Torr and Torr, 1979), a laboratory measurement of the cross-section for the associative ionization process (Ringer and Gentry, 1978), a calculation of the reaction rate coefficient from the Ringer and Gentry cross-section by Dalgarno and Black (1978), and a new laboratory measurement of the dissociative recombination process by Mul and McGowan (1979). When considered together, useful conclusions can be drawn from the various investigations.

RESULTS

In Fig. 1 we show a comparison of four current determinations of the dissociative recombination rate coefficient (reaction 2). These are the microwave afterglow/mass spectrometer measurements by Huang *et al.* (1975), which can be represented by the expression

$$\alpha_H = (4.3 \pm 0.3) \times 10^{-7} (T_e/300)^{-(0.37 \pm 0.03)} \text{ cm}^3\text{s}^{-1}, \tag{4}$$

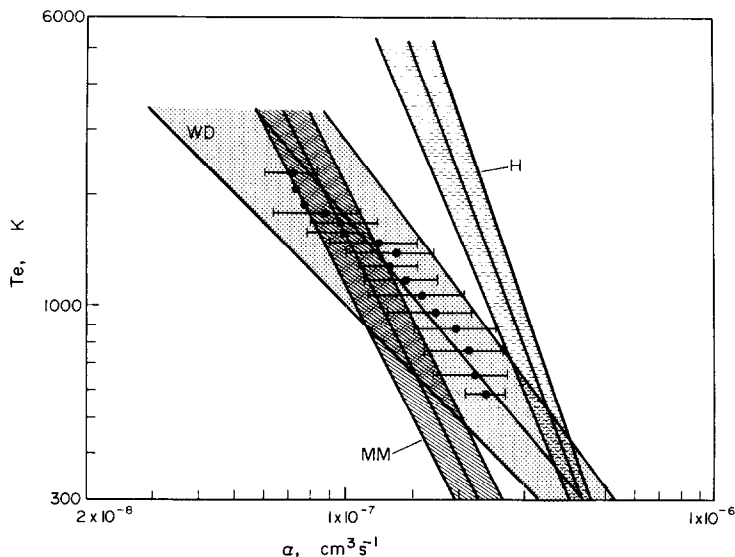* Also at National Institute for Telecommunications Research, C.S.I.R., P.O. Box 3718, Johannesburg, South Africa.

FIG. 1. COMPARISON OF DETERMINATIONS OF α BY HUANG et al. (1975), WALLS AND DUNN (1975),
TORR et al. (1977) AND MUL AND MCGOWAN (1979).
The shaded areas indicate the magnitude of the uncertainty in the laboratory determinations.

the trapped ion measurements of Walls and Dunn (1975) given by

$$\alpha_{WD} = (4.3 \pm 1) + 10^{-7}(T_e/300)^{-(0.83-0.08)^{+0.16}} \text{ cm}^3\text{s}^{-1},$$ (5)

the satellite data determination by Torr et al. (1977) which can also be represented by equation (5), and a recent laboratory measurement by Mul and McGowan (1979) using a merged electron–ion beam technique, which is reproduced by the expression

$$\alpha_{MM} = 2.3 \times 10^{-7}(T_e/300)^{-0.5}(\pm 15\%) \text{ cm}^3\text{s}^{-1}.$$ (6)

In Fig. 1, we have shown as shaded regions, the range of uncertainty in each determination. The bars on the AE results represent the standard deviation on the average of a large number of determinations at each temperature, and are not measurement error bars. The satellite data study is based on the simple nocturnal NO^+ chemistry, from which we can write

$$\alpha_{AE}(T_e) = \frac{k_1[O^+][N_2]}{[NO^+][N_e]}.$$ (7)

All of the parameters on the RHS of (7), except k_1, are measured directly by the satellite instrumentation. The N_2 and N_e concentrations are accurate to within 10%, and the O^+ and NO^+ concentrations

are accurate to within 20% for the data shown in Fig. 1. This is confirmed by the fact that each of these parameters is measured by two instruments using different techniques. We believe that the combined measurement error is of the order of 30%. For the bulk of the AE data shown in Fig. 1, $T_i \sim 750°$ where k_1 is not strongly dependent on ion temperature. Some adjustment might still be possible for the absolute magnitude of k_1. We have used k_1 as determined from the AE data (Torr et al., 1977), which is in good agreement with the laboratory results of Albritton et al. (1977). There is thus nothing complex about the AE determination of α, as it depends on four directly and straightforwardly measured parameters. In addition, the NO^+ ions are known to be in the ground vibrational state.

From the results shown in Fig. 1, it would appear that the latter point may be important. The two determinations which yield the larger temperature dependence (Walls and Dunn, 1975; Torr et al., 1977) both involve NO^+ ions in the ground vibrational state. It should perhaps be pointed out that over a significant part of the T_e range covered by the measurements of Mul and McGowan (1979) and Walls and Dunn (1974), >3000 K, the results agree. However, over the range of T_e used in the AE determination, the Walls and Dunn (1974) results show a slope change which brings them into agreement with the AE data.

The two experiments yielding a smaller value for

the temperature dependence involve NO^+ ions in excited states. In the Huang *et al.* (1975) experiment, the NO^+ ions are believed to be mainly in the $v = 1$ and 2 states of the $X^1\Sigma^+$ ground electronic state, while in the Mul and McGowan (1979) measurement, the ions are produced in a variety of vibrationally and perhaps electronically excited states.

The discrepancy between the Huang *et al.* (1975) results on the one hand, and those of Walls and Dunn (1975) and Torr *et al.* (1976, 1977) on the other hand, is large, and could be simulated by a large source of NO^+ with a pronounced T_e dependence. This fact led Zipf (1978) to suggest that such a source might be the associative ionization reaction

$$N(^2D) + O \xrightarrow{k_2} NO^+ + e. \qquad (8)$$
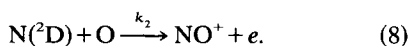
The results of Mul and McGowan (1979), however, while agreeing much better in overall magnitude with the AE determination, would require an additional sink for NO^+ for $Te < 1000$ K, rather than a source. The Mul and McGowan (1979) result does not therefore support the associative ionization process. The major discrepancy in this case is in the slope of the T_e dependence. As was mentioned above, the merged electron–ion beam

technique produces NO^+ ions in a variety of excited states, and the effect of the spiralling energy is uncertain.

In a recent study, Torr and Torr (1979) used measurements made by the AE-C satellite in the midlatitude ionization trough, in which the electron temperature covered a large range ($\sim$600–3300 K) over a fairly small data sample. The results showed that the AE data determination is very sensitive to the T_e slope parameter. Torr and Torr (1979) using $\alpha = \alpha_0 (T_e/300)^{-y}$, wrote

$$\log \frac{\alpha_0 [N_2][NO^+]}{k_1 [O^+][N_2]} = y \log (T_e/300) \qquad (9)$$

and solved for y, the inverse slope of the T_e dependence. The results are reproduced here in Fig. 2, and again support a T_e dependence of ~ -1. The slope parameter was determined both using the measured N_2 concentrations and those given by the MSIS model (Hedin *et al.*, 1977). In both cases the value obtained for y was essentially the same. However, an offset in the intercept of the ordinate might be indicative of a somewhat smaller value for α_0 than the 4.3×10^{-7} used. We are not able to distinguish between this, and a requirement for a larger value for k_1 or a calibration error in N_2. (The latter is considered only in view of the fact that these AE measurements were made in 1976,
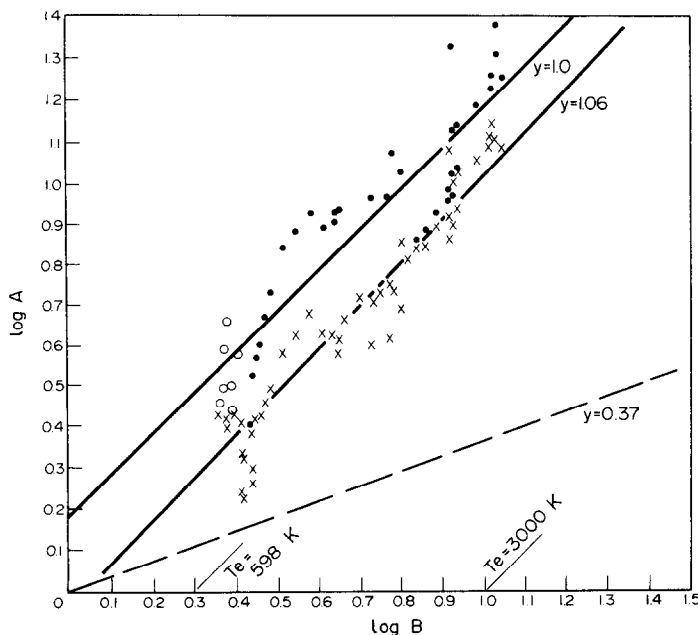

FIG. 2. DETERMINATION OF THE MAGNITUDE OF THE INVERSE TEMPERATURE DEPENDENCE, y, OF α (i.e.
$\alpha = \alpha_0 (T_e/300)^{-y}$).
A slope of $y = 0.37$ is shown for comparison (from Torr and Torr, 1979).

almost two years later than those shown in Fig. 1.)

Torr and Torr (1979) considered the magnitude of k_2 required to bring the AE data into agreement with the laboratory results of Huang et al. (1975). The associative ionization reaction is endothermic, requiring 0.37 eV of energy in order to proceed. The $N(^2D)$ atoms are produced under typical nocturnal conditions by reaction (2), namely dissociative recombination of NO^+ with electrons. As discussed by Torr and Torr (1979), the energy available to the products of (2) is 0.37 eV plus the energy of the electrons. Thus for a T_e range of 600–3000 K, each $N(^2D)$ will on the average have between 0.22 and 0.37 eV. Only a small fraction of the $N(^2D)$ population in the tail of the energy distribution will therefore be capable of undergoing the reaction, and thus one would expect the thermal associative ionization coefficient to be small.

This is borne out by the laboratory measurements of the associative ionization cross-section by Ringer and Gentry (1978). Dalgarno and Black (1978) have calculated the associative ionization reaction rate coefficient from the cross-section measurements, and find that k_2 is 5×10^{-14} cm^{3}s^{-1} at an effective gas temperature of 2000 K.

Torr and Torr (1979) found that k_2 could be expressed by

$$k_2 = k_3 \left(\frac{\alpha_H}{\alpha_{AE}} - 1 \right), \qquad (10)$$

where k_3 is the rate coefficient for quenching of $N(^2D)$ by O. From this k_2 would require a T_e dependence of 0.63. Using an AE determination of k_3 (Frederick and Rusch, 1977), namely 4×10^{-13} cm^3 s^{-1}, k_2 would have to be $\sim 1 \times 10^{-12}$ cm^3 s^{-1} at an electron temperature of 2000 K. This would disagree by more than two orders of magnitude with the rate coefficient determined by Dalgarno and Black (1978) from the associative ionization cross-section measurement by Ringer and Gentry (1978). A laboratory measurement of k_3 by Davenport et al. (1976) yielded $k_3 \geqslant 2 \times 10^{-12}$ cm^{3}s^{-1} at F-region temperatures, or 5 times larger than the Frederick and Rusch result. Such a coefficient would produce an even larger discrepancy between the value required for k_2 and the Ringer and Gentry (1978) measurement.

CONCLUSION

In this paper we assess the implications of several recent studies for the dissociative ionization of NO^+ with electrons, and also the potential for associative ionization to play a significant role in the normal ionosphere. We conclude that the recombination

rate coefficient has a T_e dependence of -1 in agreement with our earlier work and with the laboratory measurements of Walls and Dunn (1975), and can be represented by

$$\alpha(T_e) = (4.3^{+0.3}_{-1.3}) \times 10^{-7}(T_e/300)^{-(1.0^{+0.1}_{-0.2})} \text{ cm}^3 \text{ s}^{-1}. \qquad (11)$$

A suggestion that associative ionization of $N(^2D)$ and O explains the AE determination of α and that yielded by the Huang et al. (1975) measurement, does not appear to be supported by other data. A more recent measurement by Mul and McGowan (1979) would require an additional sink for NO^+ for $T_e < 1000$ K, rather than a source, in order to be compatible with the AE data. In addition, the rate coefficient required for the associative ionization process would have to be more than two orders of magnitude larger than that determined from the Ringer and Gentry (1978) cross-section measurement. On the basis of the latter, Dalgarno and Black (1978) have found that reaction (8) produces a source of $NO^+ \leqslant 10^{-4}$ of reaction (1). We therefore conclude that the associative ionization process does not play a significant role in the normal ionosphere and thermosphere.

Furthermore, as the determinations of α in which $v = 0$ agree, while those with a smaller value for the T_e dependence parameter involve NO^+ ions in various excited states, we conclude that the explanation of the disagreements in α is due to the NO^+ excited states.

REFERENCES

Albritton, D. L., Dotan, I., Lindinger, W., McFarland, M., Tellinghuiser, J. and Fehsenfeld, F. C., (1977). Effects of ion speed distribution in flow drift tube studies on ion–neutral reactions. J. chem. Phys. 66, 410.

Dalgarno, A. and Black, J. H. (1978). Comments on an associative ionization process. Paper presented at the Atmosphere Explorer Symposium, Bryce Mountain, 2–6 October.

Davenport, J. E., Slanger, T. G. and Black, G. (1976). The quenching of $N(^2D)$ by $O(^3P)$. J. geophys. Res. 81, 12.

Frederick, J. E. and Rusch, D. W. (1977). On the chemistry of metastable atomic nitrogen in the F-region deduced from simultaneous satellite measurements on the 5200 Å airglow and atmospheric composition. J. geophys. Res. 82, 3509.

Hedin, A. E., Salah, J. E., Evans, J. V., Reber, C. A., Newton, G. P., Spencer, N. W., Kayser, D. C., Alcayde,

D., Bauer, P., Cogger, L. and McClure, J. P. (1977). A global thermospheric model based on mass spectrometer and incoherent scatter data, MSIS1, N_2 density and temperature. *J. geophys. Res.* **82,** 2139.

Huang, C. M., Biondi, M. A. and Johnsen, R. (1975). Variation of electron NO^+ + ion recombination coefficient with electron temperature. *Phys. Rev. A.* **11,** 901.

Mul, P. M. and McGowan, J. W. (1979). Temperature dependence of dissociative recombination for atmospheric ions NO^+, O_2^+, N_2^+. *J. Phys. B.* To be published.

Ringer, G. (1978). Ph.D. Thesis, School of Chemistry, University of Minnesota.

Torr, D. G., Torr, M. R., Walker, J. C. G., Brace, L. H., Brinton, H. C., Hanson, W. B., Hoffman, J. H., Nier, A. O. and Oppenheimer, M. (1976). Recombination of NO^+ in the ionosphere. *Geophys. Res. Lett.* **3,** 209.

Torr, M. R., St. Maurice, J. P. and Torr, D. G. (1977). The rate coefficient for the $O^+ + N_2$ reaction in the ionosphere. *J. geophys. Res.* **22,** 3287.

Torr, M. R. and Torr, D. G. (1979). Recombination of NO^+ in the mid-latitude trough and the polar ionization hole. *J. geophys. Res.* To be published.

Walls, F. L. and Dunn, G. H. (1974). Measurement of total cross-sections for electron recombinations with NO^+ and O_2^+ using storage techniques. *J. geophys. Res.* **79,** 1911.

Zipf, E. (1978). N(^{2}P) and N(^{2}D) atoms: their production by e-impact, dissociation of N_2 and destruction by associative ionization. *EOS* **59,** 336.