J. Phys. B: At. Mol. Phys. 19 (1986) 3327-3332. Printed in Great Britain

Electron impact excitation of the N_2^+ Meinel band

Lawrence G Piper†, B David Green†, William A M Blumberg‡ and Stanley J Wolnik‡

† Physical Sciences Inc, Dascomb Research Park, PO Box 3100, Andover, MA 01810, USA
‡ LSI, Air Force Geophysics Laboratory, Hanscom Air Force Base, MA 01731, USA

Received 25 September 1985, in final form 25 February 1986

Abstract. We have measured rates for the excitation of vibrational levels 2-7 of the $A\,^2\Pi_u$ state of N_2^+ by electron impact on N_2 relative to each other and to $N_2^+(B\,^2\Sigma_u^+, v'=0)$. These rates are consistent with Franck-Condon factors for ionisation, previous laboratory measurements and high-altitude auroral observations. The total cross section for production of the $N_2^+(A\,^2\Pi_u)$ state by the impact of electrons between 2.5 and 6.0 kV on N_2 is 4.1 ± 0.7 times as large as the production rate for the B state. Given the invariance with energy in the ratio of the electron impact cross sections for A-state production to those for B-state production at energies greater than 50 eV, our result implies a total cross section for A-state production at 100 eV of $(1.15 \pm 0.23) \times 10^{-16}$ cm^2.

1. Introduction

The $N_2^+(A\,^2\Pi_u)$ state plays an important role in the aurora or disturbed upper atmosphere. Because $N_2^+(A\,^2\Pi_u)$ is efficiently produced in the ionisation of N_2 (Vallance Jones and Gattinger 1978, Gattinger and Vallance Jones 1981) the $N_2^+(A\,^2\Pi_u - X\,^2\Sigma_g^+)$ Meinel bands are bright features in the auroral spectrum. Radiative and collisional loss of the N_2^+(A) state leads to vibrationally excited N_2^+. Thus the distribution of vibrational excitation of $N_2^+(X\,^2\Sigma_g^+)$ in the aurora depends, in part, on the excitation and relaxation of the $A\,^2\Pi_u$ state. The relative electron impact excitation rates of the lower vibrational levels of the $A\,^2\Pi_u$ state are reasonably well established (Gattinger and Vallance Jones 1981, Mandelbaum and Feldman 1976, Shemansky and Broadfoot 1971a, Skubenich and Zapesochnyy 1981). However, reported values for the absolute electron impact excitation cross section differ by an order of magnitude (Shemansky and Broadfoot 1971a, Skubenich and Zapesochnyy 1981, Holland and Maier 1972, 1973, Simpson and McConkey 1969, Stanton and St John 1969, Srivastava and Mizra 1968, Pendelton and Weaver 1973).

The discrepancies in absolute cross sections result, in part, from past difficulties in determining the effects of quenching of the $A\,^2\Pi_u$ state. We have reported recently the quenching rate coefficients for the ionic A state by air, N_2 and O_2 (Piper *et al* 1985). In this study we have measured relative rates for electron impact excitation of vibrational levels 2-7 of the $N_2^+(A\,^2\Pi_u)$ state by determining the relative intensities of Meinel-band emission from vibrational levels 2-7 at pressures for which quenching is negligible. By combining the relative intensities of the Meinel bands with an extrapolation to zero pressure of the ratio intensities of the N_2^+ first negative band to the Meinel bands, we have determined the ratio of the cross sections for electron impact ionisation into the A $^2\Pi_u$ state to that into the B $^2\Sigma_u^+$ state. From this ratio, and the known cross section for electron impact ionisation of N_2 into the B $^2\Sigma_u^+$ state (Borst and Zipf 1970), we can infer the total cross section for producing the $N_2^+(A\,^2\Pi_u)$ state by the impact of 3–6 keV electrons on N_2.

2. Experimental

These measurements were made using the Air Force Geophysics Laboratory's LABCEDE facility as described in Piper *et al* (1985). This apparatus consists of a cylindrical vacuum chamber measuring 1 m in diameter and 3.4 m in length in which beams of 3–6 keV electrons with currents up to 20 mA irradiate atmospheric species. The gas samples flow under plug flow conditions along the axis of the chamber sufficiently rapidly to eliminate the effects of quenching by electron-beam-created species. Fluorescence was observed both perpendicular to the electron beam and at an acute angle of 19° to the electron beam, both viewing geometries giving identical results. A 0.3 m (McPherson 218) monochromator operated with a 1200 groove/mm grating blazed at 500 nm resolved the fluorescence. A Corning 3-71 coloured glass filter eliminated second-order spectra to the red of 500 nm. The second-order rejection ratio was 10^{-6}, more than sufficient to prevent contamination of the Meinel-(2, 0)-band fluorescence at 782 nm by the second order of the first negative (0, 0) band at 391 nm. An HTV 955 photomultiplier tube, biased to provide a gain of 5×10^6, detected the signal. A picoammeter–recorder combination amplified and displayed the photomultiplier output.

The fluorescence was resolved spatially by collecting the fluorescence with a 5 cm diameter, 10 cm focal length Suprasil lens and focusing it onto the slits of the monochromator. The slit height was adjusted to limit the field of view of the monochromator to only the central region of the fluorescing volume excited by the electron beam. The spatial resolution permitted discrimination of the Meinel bands from the first-positive bands. Approximately 80% of the Meinel-band (and first-negative-band) excitation is due to primary electrons in the beam, whereas 90% of the nitrogen first-positive-band excitation is due to secondary electrons (Peterson *et al* 1973). The primary electrons in the beam are confined to a narrow and well defined central core of the electron beam as it traverses the chamber. On the other hand, the secondary electrons created in the ionisation processes scatter at preferred angles between 45 and 90° to the incident primaries (Opal *et al* 1972). In effect, therefore, the secondaries will appear to be distributed uniformly around the primary beam. Thus by limiting the field of view to the central core of the primary beam, Meinel emissions are observed preferentially. At the same time the field of view was kept sufficiently large to eliminate effects of diffusion of $N_2^+(A)$ out of the field of view. Of course, at the lowest pressures (less than about 1 mTorr) where the number of secondary electrons created is small and their range is very large compared with the size of the primary beam, the degree of first-positive-band excitation relative to Meinel-band excitation is only a few per cent at most. At higher pressures, however, the effects of excitation by secondary electrons grow much more rapidly than the effects of primary excitation. Thus spatial discrimination becomes imperative. The operating pressures always represented thin-target conditions, i.e. very little of the beam energy was deposited in the gas and little beam spread occurred.

3. Results and discussion

The relative excitation rates of the Meinel bands were measured by scanning the spectrum of the Meinel bands between 600 and 850 nm at pressures sufficiently low (roughly 0.70 mTorr) to minimise the effects of quenching and of secondary-electron excitation. Correcting the integrated intensities of the various emission features by the appropriate transition probabilities (Gattinger and Vallance Jones 1981, Wu and Shemansky 1976, Shemansky 1982) and the monochromator response function gives the relative populations in each of the observed emitting states. In most cases at least two different bands from the same upper levels, $v' = 2$–7, were observed in the spectral range. All such redundant observations agreed to better than 7%. Table 1 lists the present results normalised to the population in $v' = 2$. The relative populations of $v' = 0$ and 1 were estimated by taking the ratio of the relevant Franck-Condon factors (Lofthus and Krupenie 1977) for excitation of these levels to that of $v' = 2$.

Table 1. Relative Meinel-band excitation rates.

			Laboratory data			
Level	Present results	Auroral data†	Mandelbaum and Feldman (1976)	Shemansky and Broadfoot (1971a)	Skubenich and Zapesochnyy (1981)	Franck-Condon factors‡
0	(1.28)	1.4	1.42	1.07		1.28
1	(1.49)	1.59	1.44	1.46	1.41	1.49
2	1.0	1.0	1.0	1.0	1.0	1.0
3	0.51	0.61	0.52	0.53	0.52	0.52
4	0.26	0.23	0.24	0.25	0.25	0.23
5	0.105				0.110	0.092
6	0.047				0.051	0.035
7	0.036					0.013

† Gattinger and Vallance Jones (1981).
‡ Lofthus and Krupenie (1977).

The values for the relative electron impact excitation rates of vibrational levels $v = 2$–7 of the A $^2\Pi_u$ state reported here agree quite well with both the auroral observations of Gattinger and Vallance Jones (1981) and the laboratory measurements of Mandelbaum and Feldman (1976), Shemansky and Broadfoot (1971a) and Skubenich and Zapesochnyy (1981). The relative excitation rate measurements also agree with Franck-Condon factors for excitation of the A $^2\Pi_u$ state by ionisation of the ground state of the N_2 molecule. Katayama *et al* (1980) have shown that collisional coupling between the $N_2^+(X\,^2\Sigma_g)$ state and the $N_2^+(A\,^2\Pi_u)$ state is rapid even at fairly low pressures. The question arises, therefore, whether the relative electron impact excitation rates reported here are actually excitation rates into high vibrational levels of the X state with the A state being populated only by collisions. This collisional coupling is not important in these studies, however. At the electron energies used in this investigation, electron impact ionisation is a Franck-Condon process, and produces a vibrational distribution proportional to the appropriate Franck-Condon factors. The measured A-state vibrational level distribution agrees well with the relative Franck-Condon factors. The Franck–Condon factors for X-state production of vibrational levels with energies comparable with the A-state energies observed here (i.e. $v''=6$–12) are six to seven orders of magnitude smaller than those for producing the A-state levels (Lofthus and Krupenie 1977). Additionally no change in the relative distribution was observed as the pressure was slowly increased. Our quenching studies have already defined the range of pressures below which collisional effects are minimal (Piper *et al* 1985). Cross sections for exciting higher-lying states of N_2^+ which could then produce $N_2^+(A\,^2\Pi_u)$ via radiative cascade are too small to affect the present results. For example, no $D\,^2\Pi_g$–$A\,^2\Pi_u$ (Janin–d'Incan system) emission was observed between 200 and 300 nm.

The Stern–Volmer analysis used in the quenching measurements (Piper *et al* 1985) showed that the ratio of the first-negative-band emission intensity I_B to the Meinel-band emission intensity I_A is given by

$$\frac{I_B}{I_A}=\frac{1}{\alpha}+\frac{k_Q[Q]}{\alpha k_r} \qquad (1)$$

where α is the ratio of the Meinel-band excitation rate to the first-negative-band excitation rate, k_Q is the rate coefficient for quenching by species Q, $[Q]$ is the number density of Q and k_r is the total radiative rate for the given vibrational level of the A state.

When corrected for monochromator response and the appropriate factors to convert the peak height measurements used in the quenching runs to band areas, the intercepts of the quenching plots give the cross section ratios $\sigma_{B,v'=0\to X,v''=0}/\sigma_{A,v'\to X,v''}$ of 1.7, 2.5 and 8.0 for the 2, 0, the 3, 1 and the 4, 1 bands respectively. The uncertainty in each of these ratios is $\pm10\%$. These ratios were invariant for electron beam energies between 2.5 and 6 kV and beam currents between 6 and 21 mA. If we correct these values for the fraction of total $N_2^+(B)$ production appearing in the 0, 0 transition (Stanton and St John 1969, Broadfoot 1967, Lee and Judge 1973, Shemansky and Broadfoot 1971b, Lofthus and Krupenie 1977, Shaw and Campos 1983) and the branching fraction of total $N_2^+(A)$ emission from a given upper level to that from the observed bands (Wu and Shemansky 1976, Gattinger and Vallance Jones 1981), and then use the relative Meinel excitation rates determined here to correct further for total $N_2^+(A)$ production, we find that the ratio of the cross section for total A-state production to that for B-state production is 4.1 ± 0.7. This ratio concurs moderately with the ratio of 5.7 ± 2.0 determined by Gattinger and Vallance Jones (1974, 1981) from auroral observations. Their measurement is subject to substantial uncertainty because it involves estimates of absolute auroral intensities made in different wavelength regions at different times. In theory our laboratory observations and the auroral observations ought to agree on the ratio of A-state to B-state excitation because both systems involve excitation by electrons primarily in the keV range where the excitation cross section ratio is invariant with energy (Peterson *et al* 1973, Pendleton and Weaver 1973). Meinel quenching in aurorae is generally negligible, although some quenching occasionally appears in deeply penetrating aurorae (Vallance Jones and Gattinger 1978).

Given that the ratio of the A-state to B-state cross sections is invariant with electron energy down to below 100 eV, an absolute A-state excitation cross section can be determined using Borst and Zipf's (1970) measurement of the 391.4 nm excitation cross section at 100 eV, $(1.74\pm0.17)\times10^{-17}\,cm^2$, the peak of the excitation function curve. This results in excitation cross sections of (10.1 ± 1.4), (7.0 ± 1.0) and $(2.2\pm0.3)\times10^{-18}\,cm^2$ for excitation of the 2, 0, the 3, 1 and the 4, 1 Meinel bands respectively. From the total cross section ratio given above, we infer a total electron impact excitation cross section for $N_2^+(A)$ production of $(1.15\pm0.23)\times10^{-16}\,cm^2$. Table 2 compares the

Table 2. Absolute Meinel-band electron impact excitation cross sections (10^{-18} cm^2) at 100 eV.

Group	Band 2, 0	3, 1	4, 1	3, 0
Simpson and McConkey (1969)	2.1 ± 0.6		0.60 ± 0.17	0.65 ± 0.19
Stanton and St John (1969)	4.5 ± 0.2	2.9 ± 0.2	1.0 ± 0.1	
Srivastava and Mizra (1968, 1969)	6.0 ± 1.2	2.4 ± 0.5	0.7 ± 0.1	
Holland and Maier (1972, 1973)	11.4 ± 4.0	7.3 ± 2.6	2.6 ± 0.9	
Shemansky and Broadfoot (1971a)	>11.0	>7.9	>2.5	
Pendleton and Weaver (1973)	7.5 ± 1.5	5.0 ± 1.0	2.4 ± 0.5	
Skubenich and Zapesochnyy (1981)	5.7 ± 0.9	3.8 ± 0.8	1.3 ± 0.3	1.4 ± 0.3
Present work	10.1 ± 1.4	7.0 ± 1.0	2.2 ± 0.3	

present measurements with other reported values. The great range in the values reported for the electron impact excitation cross section of the Meinel bands is somewhat disturbing. The present results agree with the molecular-beam measurements of Holland and Maier (1972, 1973), and with Pendleton and Weaver (1973) and Shemansky and Broadfoot (1971a). The agreement with this last group is fortuitous since their analysis depends upon lifetime measurements which are low by a factor of two. Pendleton and Weaver (1973) corrected their results for quenching and for first-positive emission contamination as in the case of the present measurements. The molecular-beam measurements of Holland and Maier (1972, 1973) require no such corrections. The other groups listed in table 2 do not appear to have applied such corrections. That probably accounts for their results being substantially below the present ones.

4. Summary

Relative electron impact excitation rates for vibrational levels 2–7 of the $A\,^2\Pi_u$ state of N_2^+ have been measured. The present results agree with auroral observations, other laboratory measurements and relative Franck–Condon factors for production by ionisation of the N_2 ground state. The absolute cross section for production of the $N_2^+(A\,^2\Pi_u)$ state by 100 eV electron impact on N_2 has also been inferred. The new value is among the larger values obtained for this cross section. We have been careful, however, to eliminate quenching effects. These measurements, together with the quenching rate coefficient measurements reported in Piper *et al* (1985), should permit a more detailed understanding of the role the $N_2^+(A\,^2\Pi_u)$ plays in the dynamics of the aurora and the disturbed atmosphere.

Acknowledgments

This work was supported partially by the US Air Force Office of Scientific Research under Projects 2310G413 and 2310G417 and partially by the Defense Nuclear Agency. Helpful comments from G E Caledonia (PSI) and F R Gilmore (RDA) were welcome, as was H C Murphy's experimental expertise.

References

Borst W L and Zipf E C 1970 *Phys. Rev.* A **1** 834
Broadfoot A L 1967 *Planet. Space Sci.* **15** 1801
Gattinger R L and Vallance Jones A 1974 *Can. J. Phys.* **52** 2343
—— 1981 *Can. J. Phys.* **59** 480
Holland R F and Maier W B II 1972 *J. Chem. Phys.* **56** 5229
—— 1973 *J. Chem. Phys.* **58** 2672
Katayama D H, Miller T A and Bondybey V E 1980 *J. Chem. Phys.* **72** 5469
Lee L C and Judge D L 1973 *J. Phys. B: At. Mol. Phys.* **6** L121
Lofthus A and Krupenie P H 1977 *J. Phys. Chem. Ref. Data* **6** 113
Mandelbaum D and Feldman P D 1976 *J. Chem. Phys.* **65** 672
Opal C B, Beaty E C and Peterson W K 1972 *At. Data* **4** 209
Pendleton W R and Weaver L D 1973 *ARPA Report No 1691*
Peterson L R, Sawada T, Bass J N and Green A E S 1973 *Comput. Phys. Commun.* **5** 239
Piper L G, Green B D, Blumberg W A M and Wolnik S J 1985 *J. Chem. Phys.* **82** 3139
Shemansky D E 1982 Private communication
Shemansky D E and Broadfoot A L 1971a *J. Quant. Spectrosc. Radiat. Transfer* **11** 1401
—— 1971b *J. Quant. Spectrosc. Radiat. Transfer* **11** 1385
Shaw M and Campos J 1983 *J. Quant. Spectrosc. Radiat. Transfer* **30** 73
Simpson F R and McConkey J W 1969 *Planet. Space Sci.* **17** 1941
Skubenich V V and Zapesochnyy I P 1981 *Geomag. Aeronomy* **21** 355
Srivastava B N and Mizra I M 1968 *Phys. Rev.* **168** 86
—— 1969 *Can. J. Phys.* **47** 475
Stanton P N and St John R M 1969 *J. Opt. Soc. Am.* **59** 252
Vallance Jones A and Gattinger R L 1978 *J. Geophys. Res.* **83** 3255
Wu H H and Shemansky D E 1976 *J. Chem. Phys.* **64** 1134