

Branching ratios and photoelectron angular distributions through the Hopfield bands in N₂ between 650 and 730 Å

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Abstract. Vibrationally and angularly resolved photoelectron spectra have been recorded in the wavelength range 650–730 Å for N₂, in the region of the autoionising resonances leading to the B ²Σ_u⁺ state of the N₂⁺ ion. The influence of these resonances on both the partial cross sections to the A ²Π_u state and the X ²Σ_g⁺ state (the branching ratios) and the angular distribution of the photoemitted electrons is clearly demonstrated.

1. Introduction

The photoabsorption spectrum of N₂ between 1000 and 730 Å (12–17 eV) is dominated by Rydberg series converging to the ground (X ²Σ_g⁺) and first excited (A ²Π_u) states of N₂⁺. Predissociation occurs below the first ionisation limit of 796 Å (15.58 eV) and above it autoionisation is much in evidence (see, for example, Gürtler *et al* 1977). However, the enormously complex spectrum in this region gives way to an apparently simple absorption spectrum in the 730–660 Å region, where the Hopfield (1930a, b) series are to be seen. The excited Rydberg states involved, which are thought to be due to transitions of the 2σ_u electron to *n*dσ_g and *n*dπ_g orbitals, approach the B ²Σ_u⁺ state of N₂⁺ at a limit of 661 Å (18.75 eV). They may therefore autoionise into the X or A states with a certain branching ratio, or may conceivably dissociate. The two main series of resonances are of quite different character; one appears to have conventional Lorentzian profiles, the other ‘window’ profiles (*q* ~ 0; Fano 1961). The latter series, which became known as an ‘apparent emission’ series, see Huffman *et al* (1963), has a weak absorption series shadowing it on the long-wavelength side. Several assignments have been made to the structure in this region but none is unequivocally established, see also Lefebvre-Brion and Moser (1965), Lindholm (1969), Betts and McKoy (1971).

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Analysing the absorption spectrum provides important, but limited information. To proceed further in the understanding of the complex configuration interaction occurring in this spectral range, one must analyse the products of the absorption process by photoelectron spectroscopy (PES), mass spectrometry or fluorescence spectroscopy. In the experiment reported here, we study this region around 700 Å using the PES technique. More specifically, we combine a normal incidence monochromator with good spectral resolution with a rotatable hemispherical electron energy analyser of appropriate resolution to study the variations in vibrational intensities in the A and X states, and their branching ratios, on passing through the Hopfield series. In an earlier publication (Codling *et al* 1981), similar measurements were made on O₂ but values of the branching ratios were not specifically obtained. The individual partial cross sections for the X state of O₂⁺ were derived by normalisation to data obtained with emission line sources. Here, knowing the absolute photoionisation cross section for N₂ (Samson *et al* 1977), measurement of the A:X branching ratio allows assessment of the individual partial cross sections. (In the spectral range studied here, photoabsorption and photoionisation cross sections are not quite the same.)

In an earlier experiment Woodruff and Marr (1977) coupled PES with a source of monochromatised synchrotron radiation and measured relative partial photoionisation cross sections for the individual vibrational components of the X and A states but their spectral resolution appeared to be insufficient to determine unambiguously their behaviour in the region of the weaker window resonances. Indeed, their reconstructed total cross section showed almost no sign of window resonances. Plummer *et al* (1977) also used synchrotron radiation to measure partial cross sections over a more extended photon energy range but which included the region of the Hopfield series. They noted that the windows in the photoabsorption cross section are almost exclusively a result of windows in the A ²Π_u partial cross section rather than in the X ²Σ_g⁺ cross section. Data on branching ratios have been obtained with conventional emission line sources (e.g. Samson *et al* 1977) but such work clearly cannot map out in detail the behaviour in the region of autoionising resonances. In the present experiment the spectral band pass and wavelength increments were sufficiently small to allow a fairly detailed study of the partial cross sections.

Equally important, the asymmetry parameter, β , for the various vibrational components of the X and A states have been determined for the first time throughout the same spectral region. Earlier measurements of β using emission line sources (e.g. Grimm *et al* 1980) suffer from the same deficiencies mentioned above. Carlson *et al* (1980) have recently made β measurements in N₂ at shorter wavelengths than those reported here, also using synchrotron radiation. Their general conclusions on the effects of autoionisation on β for the various vibrational components of the ground state seem not to be entirely confirmed by the present data.

2. Experimental

A high-aperture two-metre normal-incidence monochromator (Ederer *et al* 1980) was attached to the National Bureau of Standards (SURF-II) storage ring and provided a flux of approximately 10¹¹ photons s⁻¹ Å⁻¹ at 600 Å. This flux was channelled through a 200 mm long capillary to the interaction region. The capillary created such a large impedance that a pressure of 10⁻⁸ Torr could be maintained in the monochromator whilst the experimental chamber was held at an ambient pressure of 10⁻⁴ Torr. The

photoelectron spectrometer was a 50 mm mean-radius hemispherical analyser set to give an energy resolution of somewhat better than 100 meV (Parr *et al* 1980b). The analyser could rotate in a plane at right angles to the photon beam with an angular resolution of $\pm 2^\circ$. The analyser was operated at a constant pass energy of 3 or 5 V and the relative efficiency of the pre-retarding (pre-accelerating) lens system was determined by setting the analyser at the 'pseudo-magic' angle (see below) and using Ar gas, whose absolute photoionisation cross sections is well known.

In the dipole approximation, the angular distribution of photoelectrons from randomly oriented atoms (or molecules) by plane-polarised light has the form (Cooper and Zare 1969):

$$\frac{d\sigma_i}{d\Omega} = \frac{\sigma_i}{4\pi} [1 + \frac{1}{2}\beta(3 \cos^2 \theta - 1)] \quad (2.1)$$

where σ_i is the partial cross section associated with channel i , θ is the angle between the E vector of the radiation and the outgoing electron and β is the asymmetry parameter. In the present experiment the light leaving the monochromator exit slit was elliptically polarised but this can be considered as the sum of two independent linearly polarised components at 90° to one another (Samson and Starace 1975). Equation (2.1) can then be written in the following form:

$$I(\theta) = k[1 + \frac{1}{4}\beta(3p \cos 2\theta + 1)] \quad (2.2)$$

where $I(\theta)$ is the electron intensity at angle θ to the major polarisation axis and k incorporates unknowns such as the partial cross section σ_i , the molecule number density and the electron analyser collection efficiency; $p (= (I_{\parallel} - I_{\perp}) / (I_{\parallel} + I_{\perp}))$ is the polarisation of the light which was measured at each wavelength with a three-mirror polarisation analyser (Parr *et al* 1980).

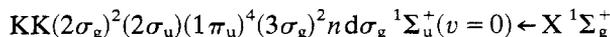
Before equation (2.2) could be used to determine β , any possible asymmetry in the interaction region was investigated using the inert gases, whose β values are known in this photon energy range. Any departure from the expected β value was assumed to be due to a non-cylindrical interaction region. Now, at each photon energy, electron spectra encompassing the vibrational components of both the X and A states of N₂⁺ were taken at three angles: 0, 45 and 90°. After correction for analyser efficiency, the vibrational peaks were fitted, using a least-squares procedure, to Gaussian profiles assuming the vibrational constants of the X and A states. From any two of these three measurements a value of β for each vibrational component could be obtained and checked against the third. In addition, once the β values had been obtained, these same data were re-used to determine the following branching ratios. Firstly, the vibrational branching ratio (defined here as the ratio of intensity of a particular vibrational level to the sum over the whole vibrational band) was determined for the X state (figure 2) and A state (figure 3) at each photon energy. Secondly, the electronic branching ratio, the conventional ratio of partial cross sections ($\sum_v A : \sum_v X$) was obtained (figure 4).

In a totally different set of runs, the electron energy analyser was set at the 'pseudo-magic' angle, that angle at which the term $3p \cos 2\theta + 1$ of equation (2.2) was zero. Measurements could then be made of relative partial cross sections at a particular photon energy in a single scan of electron energy. Figures 2, 3 and 4 include data taken in this and the previously described mode of operation and since the wavelength resolution used was the same, no distinction is made on these figures.

3. Results and discussion

The potential energy curves of N_2 and N_2^+ relevant to the present investigation are shown in figure 1 (Gilmore 1965). The neutral excited Rydberg states (not shown) approach the $B^2\Sigma_u^+$ state in the limit. Presumably their shape and location (equilibrium internuclear distance) are similar to that of the B state, particularly for higher series members. These quasi-stable states can autoionise into either the X or A states of N_2^+ . (They might dissociate or dissociatively ionise with a much smaller probability.)

The Rydberg series of strong absorption lines are unambiguously associated with transitions (Mulliken 1934):



where $n = 3, 4, \dots$. Tuckwell (1970) and others suggest a designation $(2\sigma_u)^{-1}nd\pi_g$ ($n = 3, 4, \dots$) for the window series; the weak absorption series on the long-wavelength side of the window resonances are assigned by Ogawa and Tanaka (1962) to $n\sigma_g$ ($n = 4, 5, \dots$). These various assignments have not been unequivocally established although this is clearly a prerequisite for analysing the data presented below.

3.1. Branching ratios

In figure 2 is shown how the partial cross section for leaving the N_2^+ ion in the $X^2\Sigma_g^+$ state is distributed among the various vibrational components. The data in the range

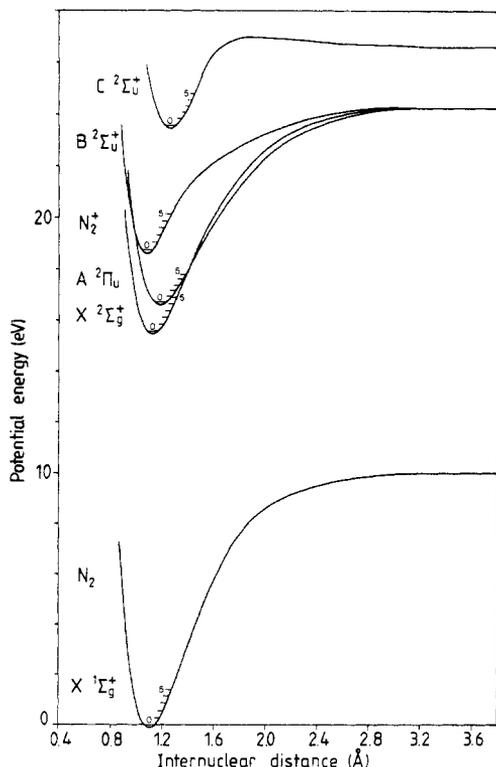


Figure 1. Potential energy curves for N_2 and N_2^+ from Gilmore (1965).

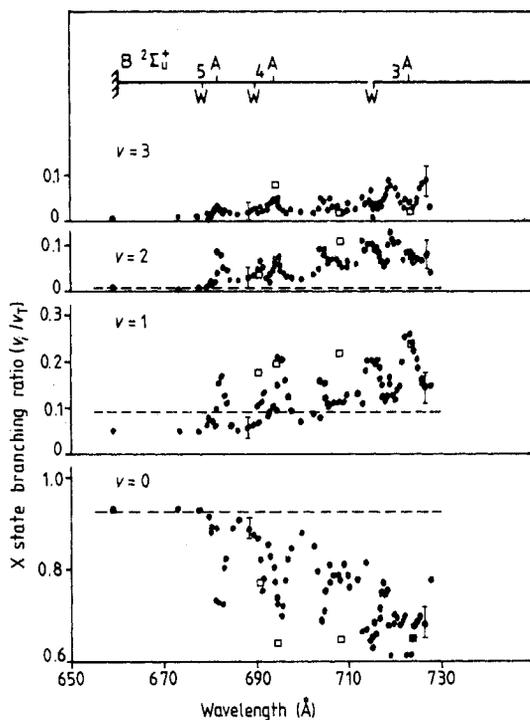


Figure 2. Vibrational branching ratios for the $X^2\Sigma^+$ state of N_2^+ . ●, present data; □, Woodruff and Marr (1976).

$710 \leq \lambda \leq 730 \text{ \AA}$ has been communicated previously (Parr *et al* 1981). Although the behaviour in the region around the $n = 3$ resonance is complex, it is quite evident that the much weaker $v = 1, 2$ and 3 components are enhanced at the expense of the $v = 0$ component on passing through the resonances; the major enhancement is directed to the $v = 1$ channel. Moreover, despite the great contrast between the window and absorption profiles in the photoionisation spectrum, the curves in figure 2 shows *similar* enhancement or depletion, depending on the channel. In other words, the line profile index, q , of the autoionising resonance does not appear to be of primary significance (see Smith 1970, Eland 1980). The $n = 3$ resonances unfortunately lie in the region of the high series members of the Worley (1953) series, whereas the $n = 4$ resonances do not suffer this additional complication and the interesting variation in the ratio in their vicinity may be more amenable to theoretical interpretation.

Because Woodruff and Marr (1977) did not present their data in tabular form it is difficult to make comparisons, but spot checks indicate the agreement is not perfect. They tabulate relative vibrational intensities at four wavelengths in an earlier publication (Marr and Woodruff 1976) and these points are shown in the figure. Although the agreement in the resonances is quite good, their values at 17.53 eV (707.2 Å) are significantly different from ours and would lead them to the conclusion that very little re-distribution of oscillator strength occurs in the resonance regions.

There is a strong feature in figure 2 around 704.5 Å which is not evident in the photoabsorption spectrum. Here, too, the $v = 1, 2$ and 3 components are enhanced relative to the $v = 0$ component. We were encouraged to note that Gardner and

Samson (1978) have coincidentally measured the vibrational intensities at this wavelength using an Ar II emission line at 704.52 Å and the agreement with the present data is excellent. (They have made ten other measurements in this wavelength range and the agreement is with the experimental error.) The feature at 704.5 Å therefore bears further consideration. It so happens that the $v = 4$ component of the $A^2\Pi_u$ state of N_2^+ lies at 17.60 eV (equivalent to a photon wavelength of 704.3 Å) and using photoelectron resonance spectroscopy, Peatman *et al* (1978) see strong signs of this component in their threshold spectra. The implication is that the process of rearrangement of oscillator strength within the $X^2\Sigma_g^+$ state at this wavelength involves the $v = 4$ component of the A state as an intermediary. If this is the case, we must look at the other components of this vibrational progression. The $v = 2$ component is at 17.16 eV (722.7 Å), which is again almost in coincidence with the $n = 3$ absorption line at 723 Å. The $v = 3$ component at 17.38 eV (713.3 Å) could account for part of the dip seen in figure 2 around that wavelength. (The $n = 3$ window line occurs at approximately 716 Å). The $v = 5$ component occurs at 17.82 eV (695.7 Å), quite close to the $n = 4$ absorption line at 694.0 Å. This accidental near-degeneracy should be borne in mind when attempting a theoretical interpretation of figure 2.

The theoretical FC factors for the direct $X^1\Sigma_g^+ \rightarrow X^2\Sigma_g^+$ transition are shown as broken horizontal lines on the figure (Albritton *et al* 1981). There should presumably be agreement with the experimental points beyond the Hopfield series limit but the $v = 1$ component shows considerable disagreement.

Figure 3 shows the variations in intensity within the vibrational components of the A state. The effect on passing through the resonances is not so dramatic, but a similar pattern emerges. That is, the oscillator strength in the higher vibrational components (particularly the $v = 3$ component) is enhanced at the expense of the lower components (particularly $v = 0$). Although little can be said about the behaviour in the region of the $n = 3$ resonances, this redistribution is much clearer in the $n = 4$ components of the Hopfield series. The values tabulated by Marr and Woodruff (1976) are shown on the figure. Once again, agreement with the data of Gardner and Samson (not shown) is probably within the combined experimental errors. In contrast to the $X \rightarrow X$ transition, the FC factors for the $X^1\Sigma_g^+ \rightarrow A^2\Pi_u$ transition show almost perfect agreement with the off-resonance values of figure 3.

Finally, in figure 4 is plotted the ratio of the partial cross sections (A : X) in the same spectral range. Shown for comparison are the data of Samson *et al* (1977); the agreement is satisfactory. One sees a general rise in the ratio from 730 to 660 Å and a complex behaviour in the region of the $n = 3$ resonances. Although the large error bar on the figure in the 720 Å region is indicative of the experimental problems caused by the low energy of the electrons associated with the A state, we are confident that the ratio goes through three oscillations in that region, with peaks located at approximately 721, 718 and 715 Å; thus the error bars indicate the possible error in the *absolute values* of the data. We note that the curve in figure 2 also shows three oscillations in the strongest ($v = 0$) component. One peak in the photoionisation spectrum of Dehmer and Chupka (1977) at 718.8 Å correlates reasonably well with the main interloper in figure 2. In the region of the $n = 4$ resonances, the ratio A : X drops initially but then changes by a factor of three in the space of 2 Å. That is, on passing through the absorption-type resonance, the oscillator strength is transferred from the X to the A state. A similar but less pronounced effect is observed in the $n = 4$ window resonance. The $n = 5$ resonances show similar overall behaviour, diluted by lack of spectral resolution.

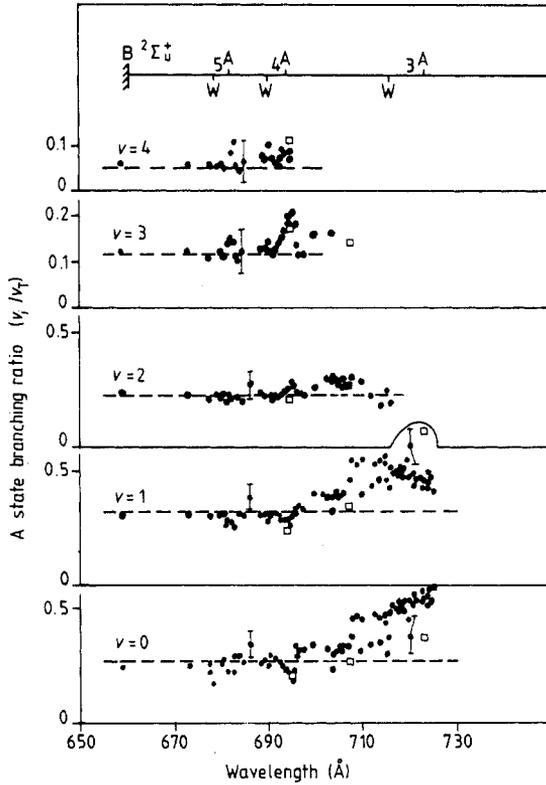


Figure 3. Vibrational branching ratios for the $A^2\Pi_u$ state of N_2^+ ; ●, present data; □, Woodruff and Marr (1976).

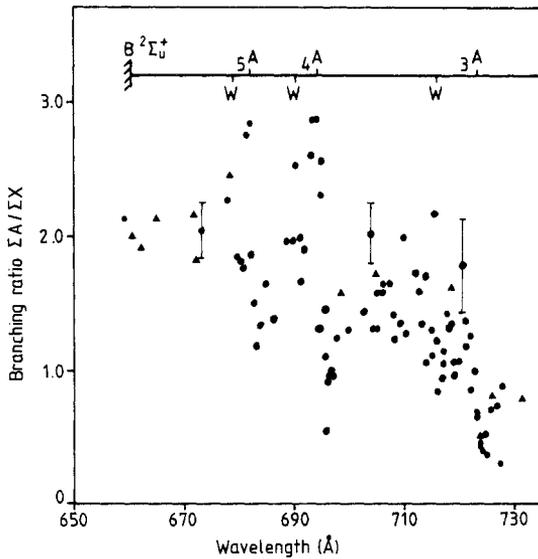


Figure 4. Electronic branching ratios. $A^2\Pi_u : X^2\Sigma_g^+$ for N_2^+ ; ●, present data; ▲, Samson *et al* (1977).

The explanation for the variation in branching ratios firstly within the vibrational components of a particular ionic state (figures 2 and 3) and secondly between the two ionic states involved (figure 4) must evidently be sought in terms of the additional complication introduced by the autoionising neutral states although, as pointed out in the context of figure 2, any coincidence between the photon energy and a higher vibrational state of the final ionic state can cause changes in the ratios. In addition, the ratio in the region of the $n = 3$ resonances may be complicated by vibrational autoionisation. In the absence of such complications, the theoretical FC factors and experimental vibrational intensities ought to agree quite well. Inspection of figure 1 tells us that the $v'' = 0$ to $v' = 0$ transition of the $N_2(X^1\Sigma_g^+) \rightarrow N_2^+(X^2\Sigma_g^+)$ manifold should be by far the strongest. Equally, the $v'' = 0$ to $v' = 1$ transition of the $N_2(X^1\Sigma_g^+) \rightarrow N_2^+(A^2\Pi_u)$ manifold should be the most intense, since the internuclear separation of the upper state has increased.

When the photon energy is such as to excite an intermediate quasi-discrete state, the vibrational overlap integrals from the ground to intermediate and intermediate to final states enter into the problem and it is not surprising that the relative intensities of the vibrational components of the X and A states are substantially modified. Moreover the configuration interaction (mixing) between the discrete state and the continua associated with the X and A states must be included in a theoretical approach (see for example Smith 1970).

3.2. Angular distributions

Angle-resolved PES is potentially an extremely powerful tool for the study of molecular orbital theory. The asymmetry parameter, β , depends upon the energy of the photoelectron which includes consideration of the total final state and the nature of the molecular orbital from which the photoelectron is ejected (Grimm *et al* 1981). Also contained in β is information on the relative phases of the alternative vibrational ionisation channels. Although great strides have been made on the theoretical front in atomic systems, see Dill (1973) and Johnson *et al* (1980), progress for molecules has for obvious reasons lagged behind. Even in the simple process of direct photoionisation, theory is inadequate, although some success has been achieved using the $X\alpha$ scattering method (Wallace *et al* 1979). Add to this the possibility of autoionisation, where electronic excitation energy can be converted to molecular vibration and rotation and the problem becomes even more difficult to handle theoretically. So far only H_2 has been studied in detail (Dill 1972, Raoult and Jungen 1981, Raoult *et al* 1981).

Whereas in H_2 no appreciable electronic autoionisation occurs, in N_2 it is dominant. It is therefore possible that N_2 will provide the prototype molecular system where the full rotational-vibrational-autoionisation process comes into play and that its analysis could form the basis of the detailed treatment of molecular autoionisation in general. In figure 5 are shown the variations in β with photon energy for the vibrational components of the X state of the N_2^+ ion. In the earlier publication of Parr *et al* (1981), β values were given for the region between 710 and 730 Å. There is seen to be considerable structure in the regions of the $n = 3$ and 4 resonances. The structure varies from one final vibrational level to another. For example, the β curve near the $n = 3$ window line exhibits a peak for $v = 0$ which evolves into a dip for $v = 3$. At the $n = 4$ resonances the $v = 0$ component shows a large variation in β , whereas the $v = 2$ and 3 show hardly any. The $v = 3$ component appears to give an isotropic emission.

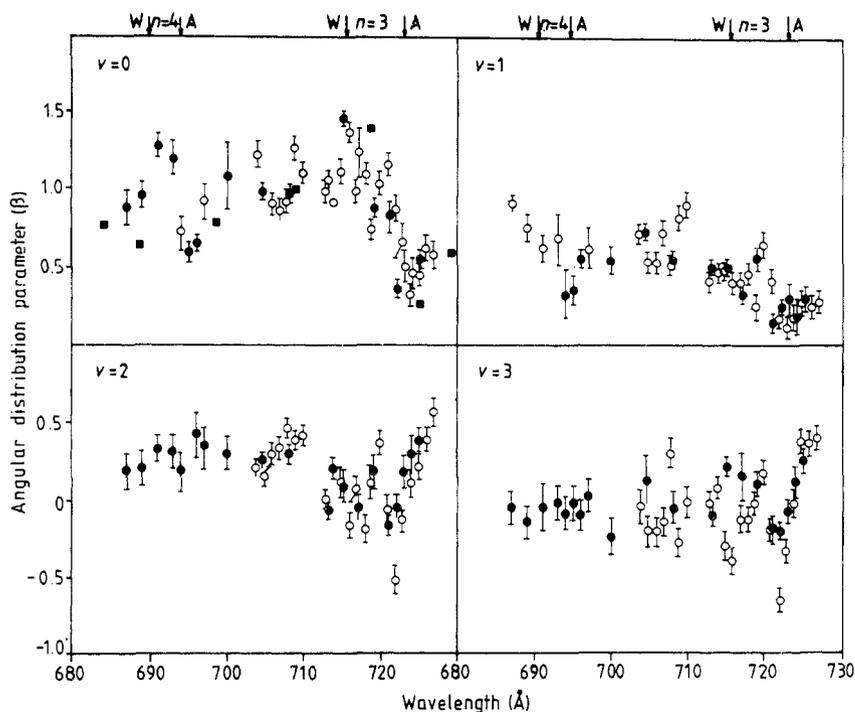


Figure 5. Angular distribution parameters for the vibrational members of the $X^2\Sigma^+$ state of N_2^+ . ●, present data taken with approximately 1.5 \AA spectral resolution; ○, present data taken with approximately 0.8 \AA spectral resolution. ■, Holmes (1980).

In figure 6 we show the behaviour of β of the vibrational components of the A state. One would hesitate to draw too many conclusions in the region of the $n = 3$ resonances, but it seems that there is considerable variation in the $v = 1$ and 2 components and almost none in the $v = 0$ component. The variation in β in the vicinity of the $n = 4$ resonances is virtually independent of the vibrational quantum number. If anything, the β values tend to be small and negative, with a small rise in β in the region of the absorption-type resonance. One might argue, therefore, on the basis of figures 5 and 6, that the Carlson *et al* (1980) suggestion that β will be close to zero in a region of autoionisation but generally somewhat higher away from such a region certainly does not hold in this particular case.

The only reasonably extensive data available with which we are able to compare the present results are those of Holmes (1980), and Holmes and Marr (1980), who used the Bonn synchrotron to determine β values for the X and A state of N_2^+ . Even though their spectral resolution was considerably worse, they saw a large change in β from 0.26 to 1.38 in the region of the $n = 3$ resonances for the $v = 0$ component. Their data are shown in figure 5; the agreement with the present data is quite satisfactory. They measured values of β for the $v = 1$ component at 718.7 \AA (-0.07 ± 0.14) and 688.8 \AA (0.2 ± 0.2) but our data would suggest that they have problems with the unresolved $v = 2$ (and higher) components. The only measurement they made on the A state of N_2^+ in this spectral range was at 688.8 \AA , where they obtained a value of -0.38 ± 0.03 . This is also in fair agreement with the present data.

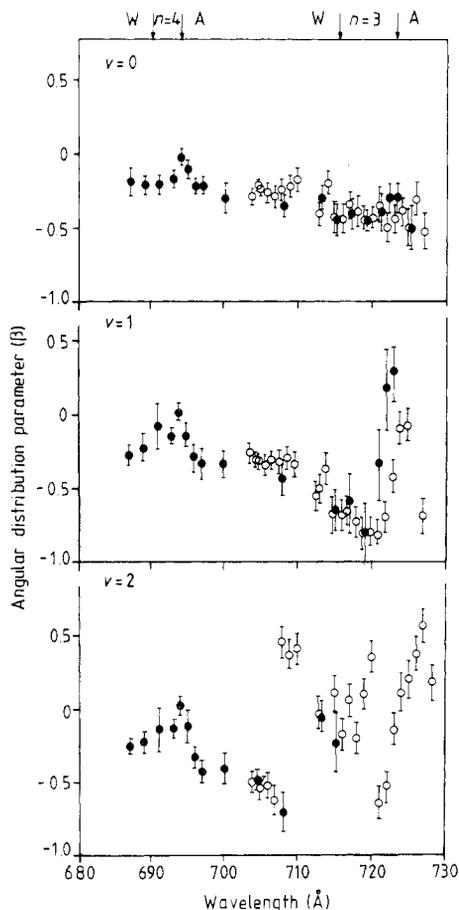


Figure 6. Angular distribution parameter for the vibrational members of the $A^2\Pi_u$ state of N_2^+ . ●, present data taken with approximately 1.5 \AA spectral resolution. ○, present data taken with approximately 0.8 \AA spectral resolution.

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