

A High Resolution Angle Resolved Photoelectron Spectroscopy Study of N_2

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J. B. West and M. A. Hayes

Daresbury Laboratory, Warrington, U.K.

A. C. Parr, J. E. Hardis, S. H. Southworth and T. A. Ferrett

National Institute for Standards and Technology, Gaithersburg, MD 20899, U.S.A.

J. L. Dehmer

Argonne National Laboratory, Illinois 60439, U.S.A.

and

X.-M. Hu and G. V. Marr

Physics Department, Aberdeen University, U.K.

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Abstract

This is a preliminary report on a series of measurements, using high optical resolution, on the photoionisation of the nitrogen molecule in the wavelength region 740–780 Å where there are at least five Rydberg series converging onto the 1st excited state of N_2^+ $^2\Pi_u$. An advanced electron spectrometer system is used which provides measurements for the angular distribution parameter β for three members of the ground state of the ion, on a wavelength mesh sufficient to show variation in β over the width of the autoionising lines. This study was undertaken to assist in the identification of these series, and to encourage further theoretical work on interaction between electronic and vibrational motion in the region of autoionising resonances.

1. Introduction

The photoabsorption spectrum of N_2 in the wavelength region leading up to the second ionisation potential is rich with autoionising structure. Several series with vibrational progressions have been identified, but not all of these have been assigned, and for those that have there is some doubt over the details. This applies particularly to Worley's third series [1] and the Ogawa-Tanaka series [2], which converge onto the $^2\Pi_{u,1/2,3/2}$ states of N_2^+ and are labelled I and II. In addition Ogawa [3] identified four further vibrational progressions, which he labelled P(1) to P(4), and the first members of these form some of the strongest features in this spectral region.

In an earlier photoelectron experiment, Holland and West [4] measured the vibrational branching ratios in this same region and showed that there was a tendency for the higher members to be enhanced over the resonances, though no systematic pattern emerged. They also found that the most intense structures in the photoionisation spectrum appeared to cause the least deviation from Franck-Condon behaviour. Lefebvre-Brion and Yoshino [5] have pointed out that those measurements give some support to the reassignment of series I and II, originally thought to have the electron configurations $(\pi_u 2p)^3 (\sigma_g 2p)^2 n s \sigma_g$ ($n = 3, 4, \dots$) $^1\Pi_u$ for series I and $^3\Pi_u$ for series II, to $nd\delta_g$ for the running electron. Based on quantum defect arguments Kosman and Wallace [6]

suggest $nd\delta_g$ and $nd\sigma_g$ respectively for these two series, and for purposes of clarity in our diagrams we have used their assignments.

This experiment was undertaken to provide further information on this issue; since they are the first continuous measurements of the β -parameter with such high photon resolution, they will hopefully stimulate theoretical analysis of the photoionisation dynamics of the nitrogen spectrum in this region.

2. Experimental procedure

The electron spectrometer system used for these measurements was designed and constructed at the National Institute for Standards and Technology and Argonne National Laboratory. It was fitted to the 5-metre McPherson normal incidence monochromator on the Atomic and Molecular Science beam-line at the Daresbury Synchrotron radiation source, providing a flux of approximately 5×10^{10} photons/s within 0.2 Å bandpass in the interaction region. The system comprises two hemispherical analysers, one fixed and aligned along the E -vector of the incident radiation, the other rotatable about the incident light beam axis. The layout of the system is described in greater detail by Parr *et al.* [7]; since then a few changes have been made, primarily the introduction of multichannel detectors at the exit planes of both hemispheres. These were manufactured by Surface Science Inc. and have two-dimensional capability, enabling them to be used to focus the system and check for alignment errors, as well as providing a much enhanced count rate. The calibration of the system for efficiency and angular errors was achieved by making measurements on the rare gases, and has been fully described by Hardis *et al.* [8]. The polarisation of the incoming radiation was measured with a three mirror reflection analyser rotatable about the light beam axis as described by Parr *et al.* [9]; to check for consistency a polarisation measurement was made using helium, necessarily at a higher energy outside the range of the present measurements,

and no discrepancy was found. However, the polarisation was found to be very sensitive to the beam position in the storage ring and had to be checked frequently; there was no variation in polarisation with wavelength for the measurements shown here.

A comprehensive suite of computer programs enabled the analyser calibration and polarisation values to be used immediately to generate β -values, which enabled a rapid assessment of the data quality while the experiment was in progress and helped identify any anomalies. The β -parameter was calculated from the expression for the differential cross section

$$d\sigma/d\Omega = \sigma_v/4\pi\{1 + \beta/4[3P \cos(2\theta) + 1]\},$$

where σ_v is the partial cross section for photoionisation into the state with vibrational quantum number v , P is the polarisation of the incoming light and θ is the angle between the detection direction of the rotatable spectrometer and the major polarisation axis. To determine the direction of the major component of polarisation, the rotatable analyser was used to find the maximum signal position by rotating it about the approximate $\theta = 0^\circ$ position, using argon at a wavelength where β was approximately 1. In this way the exact position for $\theta = 0^\circ$ could be determined, accounting for any small rotation of the plane of polarisation due to preceding optics. The two analysers were then set at 0° and 90° (fixed and rotatable respectively), and both β and the vibrational ratios were calculated from measurements at these two angles.

The spectra themselves were analysed by summing the counts under the vibrational peaks after accounting for a sloping background, estimated in regions of the electron spectrum well above and below the peaks and generally small except at low (< 200 meV) electron energies. Measurements were taken at photon energy increments of 2 meV with a monochromator resolution of 0.2 \AA corresponding to an energy resolution of approximately 4 meV. The error bars shown are derived from statistical errors and include an amount for the uncertainty in the polarisation; however, beam fills are probably responsible for the discontinuous jumps seen most prominently on the β -values for $v = 0$ around 16.11 and 16.67 eV, where the polarisation may have changed rapidly. This is expected to affect only a few points just above these features in energy, and the general structure of the curves remains valid.

3. Results

Figures 1 and 2 show our measurements of the angular distribution parameter in the region of Worley's third series and the Ogawa-Tanaka series; at the top of Fig. 1 our total electron yield spectrum is shown, with the major spectral features identified from previous work (see, for example, Dehmer *et al.* [10]). The assignments shown are those put forward by Kosman and Wallace [6], and we have used these features to calibrate our wavelength scale within 1 meV; (the "g" subscripts have been omitted to reduce clutter). Our branching ratio data agree very well with those of Holland and West [4] and are thus not shown. The features marked "?" are shown because they have a pronounced effect on β , although they are small and unidentified in the photoionisation spectrum. This behaviour is reminiscent of the earlier branching ratio measurements.

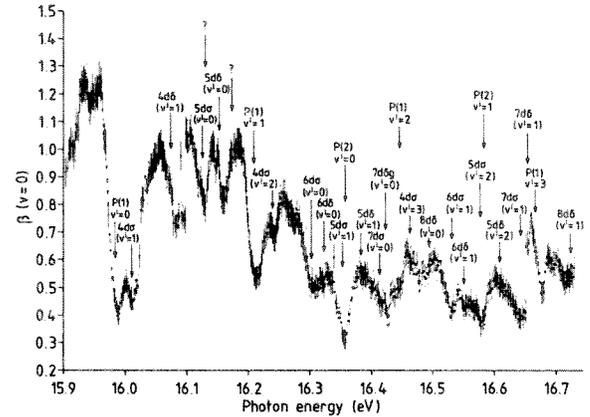
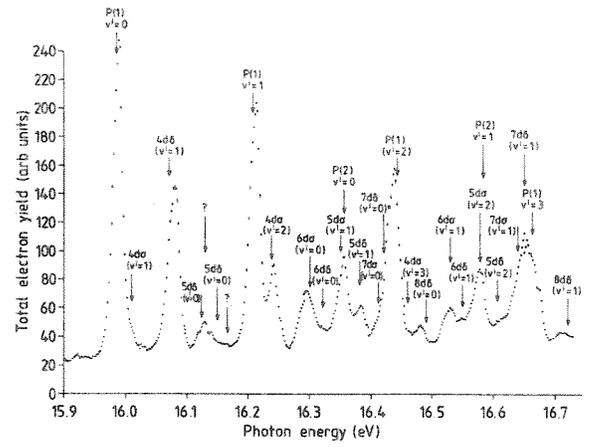


Fig. 1.

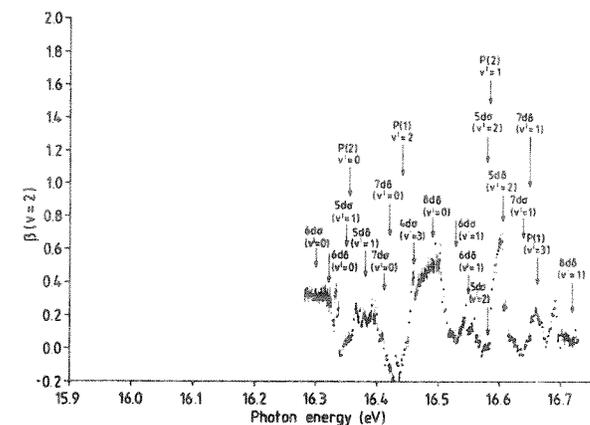
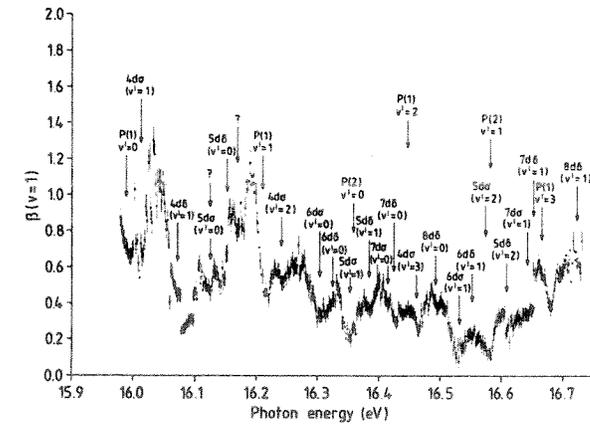


Fig. 2.

The most obvious feature of the graph of β -values for $v = 0$ of the ion is that in general β goes through a minimum in the region of a resonance. The $nd\delta$ series members tend to have higher β -values than the corresponding $nd\sigma$ member with the same vibrational quantum number; indeed, the $5d\delta_g$ ($v' = 1$), $6d\delta_g$ ($v' = 0$) and $7d\delta_g$ ($v' = 1$), coincide with maxima in β , but this may be spurious because of overlapping structure. Beyond the above it is difficult to perceive any pattern specific to a particular series; we note that the P(1) and P(2) progressions coincide with the deepest minima in the β -parameter, in distinct contrast to their effect on the branching ratio.

There are some differences in the behaviour of the individual vibrational members of the N_2^+ ion: β for $v = 1$ is generally lower than for $v = 0$, particularly in the region of the $4d\delta_g$ ($v' = 1$), $5d\sigma_g$ ($v' = 0$) and $5d\delta_g$ ($v' = 0$) resonances. There are now additional dips at 16.38 and 16.46 eV, corresponding to the $5d\delta_g$ ($v' = 1$) and $4d\sigma_g$ ($v' = 3$) transitions, and at 16.17 eV where there is an unidentified feature in the photoionisation spectrum. For $v = 2$ β is generally lower still, with a pronounced peak which coincides with the $5d\delta_g$ ($v' = 2$) transition at 16.606 eV. A peak is evident at 16.69 eV which coincides with shallow minima in the $v = 0$ and $v = 1$ data; there does not appear to be any feature in the photoionisation spectrum which coincides with this.

Although small differences can be perceived between the β -parameters for the $nd\sigma$ and $nd\delta$ series, Lefebvre-Brion and Yoshino [5] have suggested that both series should be assigned $nd\delta$, i.e. the Ogawa and Tanaka series should be reassigned from $nd\sigma$ to $nd\delta$ but should maintain the triplet assignment $^3\Pi_u$. Perhaps the qualitative similarity between the β -parameters for these two series lends some support to this. Lefebvre-Brion and Yoshino assign the "P" series to $nd\sigma$ $^1\Pi_u$; certainly these members cause substantial dips in the β -parameter, behaving rather differently from the "I" and "II" series, indicating that they are of different character. The higher vibrational members of these series, though generally weaker in the photoionisation spectrum, should become more prominent in our measurements for the higher vibrational states of the ion. The $5d\delta_g$ ($v' = 2$) is more prominent in our $v = 2$ measurements, corresponding to a pronounced

peak in β ; however $5d\sigma_g$ ($v' = 2$) corresponds to a minimum, and they both correspond to minima in our $v = 1$ measurements, as does $4d\sigma_g$ ($v' = 2$). Unfortunately the higher n members of these vibrational progressions are outside the range of our measurements, and a definite pattern is hard to discern.

4. Conclusion

Based on the measurements presented here, we are able to give some support for recent suggestions for the reassignments of Worley's third series and the Ogawa-Tanaka series. Further analysis, particularly of the β -parameters, will depend on theoretical calculations, hopefully encouraged by the fact that such detailed measurements are now available.

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