

LETTER TO THE EDITOR

Photoelectron study of electronic autoionization in rotationally cooled N₂: the $n = 6$ member of the Hopfield series

K Ueda†||, J B West†, M A Hayes†, M R F Siggel†, A C Parr‡ and J L Dehmer§

† Daresbury Laboratory, Daresbury, Warrington WA4 4AD, UK

‡ National Institute of Standards and Technology, Gaithersburg, MD 20899, USA

§ Argonne National Laboratory, Argonne, IL 60439, USA

Received 2 July 1993

Abstract. We report preliminary results of a study of the Hopfield series in rotationally cooled molecular nitrogen. By using angle resolved electron spectroscopy in combination with synchrotron radiation, partial cross sections and asymmetry parameters for formation of the vibrationally resolved X and A states of N₂⁺ were measured in the region of the $n = 6$ member of the Hopfield bands. The results are compared with earlier *ab initio* MQDT calculations and reflect qualitative agreement for the X ²Σ_g⁺ decay channel, but sharp disagreement for the A ²Π_u decay channel.

In the absorption spectrum of N₂ in the wavelength range 660–730 Å, there are two prominent autoionizing Rydberg series converging to the $v^+ = 0$ level of the B ²Σ_u⁺ state of N₂⁺. Of the two prominent series, one shows broad absorption peaks, whereas the other shows ‘window’ profiles ($q \sim 0$ in terms of Fano’s profile index; Fano 1961). These two series, first observed by Hopfield (1930a, b), are often called the Hopfield ‘absorption’ and ‘emission’ series.

The Hopfield series have been investigated extensively by a number of groups; the references below are given as examples. An absolute photoabsorption cross section was measured by Gürtler *et al* (1977) at a resolution of 0.03 Å, a relative photoionization cross section by Dehmer *et al* (1984) at a resolution of 0.023 Å, and a well resolved photographic absorption spectrum by Baig and Connerade (1986). Vibrationally resolved partial cross sections for production of the N₂⁺ X ²Σ_g⁺ and A ²Π_u states were measured by Morin *et al* (1983) and vibrational branching ratios and photoelectron asymmetry parameters for production of the N₂⁺ X and A states by Parr *et al* (1981) and West *et al* (1981); the photon-energy resolution of these measurements was 0.5–0.8 Å.

A theoretical investigation was carried out by Raoult *et al* (1983) using multichannel quantum defect theory (MQDT; see for example Greene and Jungen 1985) combined with *ab initio* calculations for the MQDT parameters; based on their theoretical analysis Raoult *et al* concluded that the Hopfield ‘absorption’ series corresponds to excitation to the (B ²Σ_u⁺) n ‘d’σ states and the ‘emission’ series to an overlap of the (B ²Σ_u⁺) $nd\pi$ and ($n - 1$)‘s’σ, where ‘s’ and ‘d’ indicate the dominant contribution to the l -mixed Rydberg

|| On leave from the Research Institute for Scientific Measurements, Tohoku University, Sendai 980, Japan.

states. Raoult *et al* (1983) also compared their vibrationally unresolved partial cross sections σ and asymmetry parameters β with experimental results by Morin *et al* (1983) and West *et al* (1981); the agreement was in general satisfactory in view of the complexity of the processes involved. One particular problem remained outstanding: Raoult *et al* compared their results with the experimental results for $n = 3$ because the partial cross sections and photoelectron asymmetry parameters had been best characterized for this member. However, the $n = 3$ resonances are heavily contaminated by high Rydberg members converging to the $v^+ \geq 2$ levels of the $A^2\Pi_u$ state of N_2^+ , and this throws some doubt on the comparison with the theoretical calculations, as West *et al* (1981) and Raoult *et al* (1983) pointed out. The purpose of this experiment, therefore, was to measure partial cross sections and asymmetry parameters for the higher n members, taking advantage of the better resolution available to us compared to that used in the earlier experiment. Moreover, quite recently, high-resolution (0.008–0.02 Å) absolute photoabsorption cross section measurements for jet-cooled N_2 , as well as room-temperature N_2 , have been made by Huber *et al* (1993). They clearly demonstrated that the resonance shapes of the Hopfield series result from the superposition of a large number of rovibronic transitions, rather than simple Beutler–Fano profiles. Only the rotationally cooled spectra show the strikingly regular patterns of the ‘absorption’ and ‘emission’ series, in qualitative agreement with the MQDT predictions (Raoult *et al* 1983, Greene and Jungen 1985).

In our experiment we have focused our attention on the high- n members ($n = 5$ to 8) of the Hopfield series. To minimize the rotational structure, we have used a cooled sample obtained by a supersonic expansion. The experimental set-up and procedure were essentially the same as those used in previous measurements (see for example West *et al* 1990, Dehmer *et al* 1992). Briefly, the experiment was carried out on a 5 m normal-incidence monochromator (Holland *et al* 1989) at the Daresbury Synchrotron Radiation Source. The monochromator band pass was set to 4–7 meV depending on the resolution necessary for observing the resonance structures. Using a 2 mm ID glass capillary, a monochromatized photon beam was brought into the interaction region of the angle-resolving photoelectron spectrometer system. This system comprised two hemispherical analysers equipped with area detectors of the resistive anode type. One analyser was fixed and aligned along the E -vector of the incident radiation; the other was rotatable about the incident light beam axis. The angular acceptance of each analyser was limited by an aperture in the entrance lens to approximately $\pm 2^\circ$. Pass energies were set to 5 eV and the resulting electron resolutions were ~ 50 meV for both analysers. A complete description of the electron spectrometer system has been given by Parr *et al* (1984).

The most important difference from the previous experiments was the use of a supersonic jet. Pure N_2 sample gas was introduced into the interaction region through a pinhole of 25 μm diameter located ~ 3 mm below the interaction point. The stagnation pressure was $\sim 9 \times 10^4$ Pa. The whole experimental chamber was pumped by a 10 000 l s^{-1} cryopump and the ambient pressure was $\sim 7 \times 10^{-3}$ Pa during the measurements.

The transmission function of each electron spectrometer was calibrated as a function of photoelectron energy by using the known photoionization cross sections from Marr and West (1976) and the angular distributions of Ar measured by Holland *et al* (1982). The well known expression

$$\frac{d\sigma}{d\theta} = \frac{\sigma}{4\pi} \left(1 + \frac{\beta}{4} (3p \cos 2\theta + 1) \right)$$

was used in the process of determining the energy calibration, as well as to determine the relative values of the partial cross section σ and asymmetry parameter β of the sample

gas. The angle θ was measured with respect to the E -vector of the incoming radiation. The polarization p of the incident light was monitored periodically by a reflection analyser incorporating three gold coated mirrors that was attached to the rotating electron analyser and was 0.59 ± 0.02 for the wavelength range concerned. Normalization to the incident photon flux was carried out using the incident flux monitor, a tungsten mesh in the polarization analyser. Further details are given by Dehmer *et al* (1992) and references therein.

Using the equations for a free jet expansion and the parameters of our experiment, we calculated a lower limit to the temperature of the jet of 3 K. Because of the assumption of ideal conditions in this calculation, we also investigated the degree of cooling achieved by measuring the total photoionization cross section for the N_2 Hopfield series in the vicinity of the $n = 8$ member using a cooled N_2 beam and a 'room-temperature' effusive beam. The photon resolution was $\sim 0.15 \text{ \AA}$ or 4 meV. We could clearly see a dip in the cross section corresponding to the Hopfield 'emission' series for the cooled N_2 , whereas we could hardly see the dip for the 'room-temperature' N_2 . Also, the 'absorption' resonance was wider at room temperature than at the jet-cooled temperature. From the resemblance of our jet-cooled spectrum to the absorption spectrum of the jet-cooled N_2 observed by Huber *et al* (1993), we estimate the rotational temperature achieved in our experiment was below 20 K.

We present in figure 1 the results obtained in the vicinity of the $n = 6$ resonance of the Hopfield series, and compare the present results with the theoretical predictions of Raoult *et al* (1983). Specifically, figure 1 shows the partial cross sections σ_X and σ_A for the $X^2\Sigma_g^+$ and $A^2\Pi_u$ states of N_2^+ , respectively, formed by summing over all the vibrational levels observed (i.e. $v^+ = 0$ to 3 for the X state and $v^+ = 0$ to 6 for the A state), and some vibrationally resolved asymmetry parameters β ($v^+ = 0-2$ for the X state; $v^+ = 1$ and 3 and β averaged over $v^+ = 0-6$ for the B state). We calibrated the photon energy scale using the peak wavelengths of the Hopfield 'absorption' series for the jet-cooled N_2 given by Huber *et al* (1993). We normalized the measured relative cross sections to the off resonance absolute photoabsorption cross section of 23 Mb measured by Huber *et al* (1993), and assumed the photoionization efficiency was close to unity in the region of the Hopfield series. No errors are shown for the cross section data, because our statistical error was very small; from the measurements of Huber *et al* we estimate the error in the absolute scale to be $\sim \pm 5\%$. The error bars shown for the β -parameter data represent a ± 1 sigma deviation from the mean value.

The broken curves in figure 1 were constructed using the theoretical calculations by Raoult *et al* (1983). Since they performed *ab initio* calculations only for the $n = 3$ Hopfield bands, we reproduced the results for $n = 6$ from their figures 4 and 6 using a Rydberg scaling procedure, in which the photon energy scale is replaced by an effective quantum number scale, and we assumed the MQDT parameters have no energy dependence. A slight energy shift (-0.005 eV) was necessary to match the position of the 'absorption' resonance calculated for $n = 6$ with that of Huber *et al*. The gaps shown in the broken curves occur because the theoretical data are given over a range of less than one for the effective quantum number; we considered it reasonable to draw a smooth line through the gaps, since no structure is expected here. It should be noted also that the calculations by Raoult *et al* were 'purely electronic', i.e. neglected the rotational motion of the molecule as well as vibration.

In the measured partial cross section σ_X , a pronounced peak can be clearly seen at the location of the absorption resonance, whereas only a weak variation can be recognized at the location of the emission resonance. The calculation of Raoult *et al* (1983) predicts the strong absorption feature well. The cross section, 4.3 Mb, calculated for the direct photoionization is smaller than the experimental off-resonance cross section $\sim 8 \text{ Mb}$. Also,

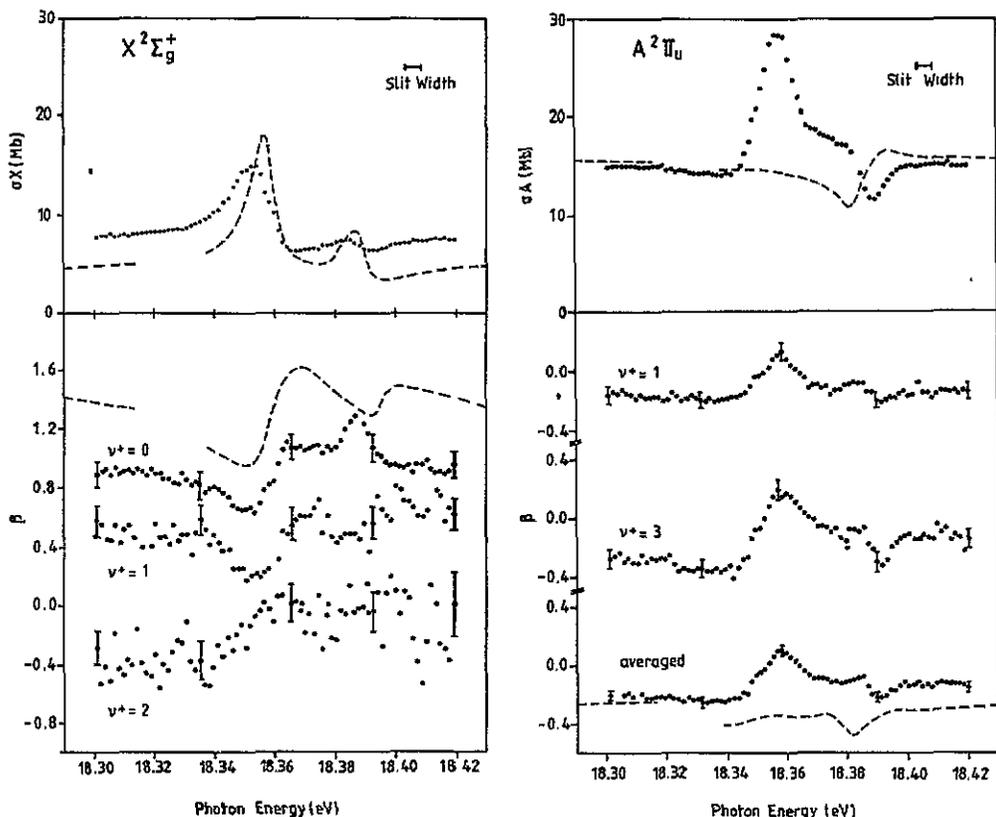


Figure 1. Partial cross sections σ_X and σ_A , for populating the $X^2\Sigma_g^+$ and $A^2\Pi_u$ states, respectively, of N_2^+ , formed by summing over all the vibrational levels observed (i.e. $v^+ = 0$ to 3 for the X state and $v^+ = 0$ to 6 for the A state); vibrationally resolved asymmetry parameters β for populating the $v^+ = 0-2$ levels of the X state, the $v^+ = 1$ and 3 levels of the A state and β averaged over the $v^+ = 0-6$ levels of the A state. All data were taken in the vicinity of the $n = 6$ member of the N_2 Hopfield bands using a jet-cooled sample. The photon resolution was ~ 5 meV. The broken curves correspond to the theoretical calculations by Raoult *et al* (1983), reproduced from their figures 4 and 6 for the $n = 3$ resonance using a Rydberg scaling procedure (see text).

the calculation is less satisfactory in the vicinity of the emission resonance. As Raoult *et al* pointed out, the emission resonance is composed of the two Rydberg states $n d\pi_g$ and $(n-1) 's'\sigma_g$ and the calculation is very sensitive to the locations of these two states.

The measured photoelectron asymmetry parameters β for the X state also exhibit structure at the locations of the two resonances. The β curve for each vibrational level v^+ exhibits a dip in the vicinity of the $6'd\sigma$ absorption resonance. Its spectral profile is asymmetric, reflecting the competition between the asymptotic phases. The asymmetric profile of the β curve changes dramatically from $v^+ = 1$ to $v^+ = 2$. In the vicinity of the emission resonance, on the other hand, the β curve exhibits a peak for $v^+ = 0$ and almost no structure for $v^+ = 1$ and 2. These observations for the two resonance features are in general consistent with the previous observations by Parr *et al* (1981) for the $n = 3$ Hopfield band.

The purely electronic β curve calculated by Raoult *et al* for the X state is compared

with the measured β for $v^+ = 0$ for this state; the effect of electronic autoionization is expected to be largest in the $v^+ = 0$ continuum because its vibrational wavefunction is expected to have the largest overlap with the $B^2\Sigma_u^+ v^+ = 0$ vibrational wavefunction. The β value calculated for direct photoionization is 1.4, to be compared with the measured off-resonance value of ~ 0.95 . The calculated β curve in the vicinity of the $n'd'\sigma$ absorption resonance is in fair agreement with the present experimental results, exhibiting a prominent dip. According to the calculation by Raoult *et al* the $(B^2\Sigma_u^+)n'd'\sigma$ state autoionizes preferentially to the $\epsilon f\sigma$ continuum associated with the X state. Thus, at the $n'd'\sigma$ resonance, β is expected to decrease from the off-resonance value towards the geometrical value, 0.53, for the $\epsilon f\sigma$ single channel (Thiel 1982). Indeed, the experimental β value decreases from ~ 0.95 to ~ 0.65 at the resonance, whereas the theoretical β value decreases from 1.4 to ~ 1 . This semiquantitative agreement supports the theoretical prediction that channel interaction is much stronger between the $(B^2\Sigma_u^+)n'd'\sigma$ and $(X^2\Sigma_g^+)\epsilon f\sigma$ channels than between the $(B^2\Sigma_u^+)\epsilon'd'\sigma$ and $(X^2\Sigma_g^+)\epsilon p\sigma$ channels. The agreement between the theoretical calculation and the measurement is poor in the vicinity of the emission resonance, as was the case for the partial cross section.

In the measured partial cross section σ_A for the A state we see strong enhancement and depletion at the locations of absorption and emission resonances, respectively. The calculation of Raoult *et al* predicts the emission resonance, though the sign of the profile index q for the emission resonance is different for the calculated and measured partial cross sections. The calculated off-resonance cross section shows good agreement with the measured one. The most significant discrepancy between experiment and theory is the response of the $A^2\Pi_u$ cross section at the $(B^2\Sigma_u^+)n'd'\sigma$ resonance. This has been seen in previous experiments (Plummer *et al* 1977, Morin *et al* 1983), but our experiment shows a much stronger enhancement than is evident from the earlier measurements. In the model of Raoult *et al* l -uncoupling is neglected, and it can be seen from table 3 of their paper that of the many outgoing channels leaving the N_2^+ ion in the $A^2\Pi_u$ state, the $(B^2\Sigma_u^+)n'd'\sigma$ channel couples predominantly with the $(A^2\Pi_u)\epsilon d\pi$ channel, although even in this case the degree of coupling is small. The discrepancy could therefore be attributed to an underestimate of the coupling between the $(A^2\Pi_u)\epsilon d\pi$ and the $(B^2\Sigma_u^+)\epsilon'd'\sigma$ channels in the theoretical calculation; it should also be noted that the neglect of l -uncoupling could be invalid, particularly at higher n values.

Each of the measured β curves for the different vibrational levels of the A state exhibits a prominent peak in the vicinity of the absorption resonance and a weak dip in the vicinity of the emission resonance. These features were not clearly observed in the previous observations (West *et al* 1981). These features gradually become more prominent as one goes from $v^+ = 0$ to $v^+ = 6$ but the profiles are similar for different v^+ , in contrast to the case for the X state vibrational levels, where the β curve changes significantly with v^+ . The purely electronic β calculated by Raoult *et al* (1983) is compared with our measured β averaged over the vibrational levels $v^+ = 0$ to 6. The sloping parts of the theoretical curve in the off-resonance regions are probably an artefact resulting from reproducing these data from the published figures in Raoult *et al*. We would expect the curves to be constant here, with the β value calculated for direct photoionization of -0.235 , in good agreement with our measured off-resonance value of ~ -0.2 . The theoretical calculation predicts the small dip at the emission resonance well, but underestimates the resonance effect at the $n'd'\sigma$ absorption resonance. As discussed above in connection with the partial cross section, the most probable outgoing channel responsible for this resonance effect is $(A^2\Pi_u)\epsilon d\pi$. If the $(B^2\Sigma_u^+)n'd'\sigma$ state autoionizes predominantly into the $(A^2\Pi_u)\epsilon d\pi$ continuum, the β value at the $n'd'\sigma$ resonance is expected to approach the geometrical value, 0.29, for

the single channel $\varepsilon d\pi$. Indeed the measured β increases from -0.2 to ~ 0.15 . Thus, the observed increase of β at the $n'd'\sigma$ resonance is consistent with the strong channel interaction between the $(B^2\Sigma_u^+)$ $\varepsilon'd'\sigma$ and $(A^2\Pi_u)$ $\varepsilon d\pi$ channels proposed above.

In conclusion, these measurements demonstrate that although the purely electronic MQDT calculations do predict the general features of the experiment, detailed agreement is lacking. One of the major reasons is probably due to the strength of channel interaction between the $(B^2\Sigma_u^+)$ $\varepsilon'd'\sigma$ and $(A^2\Pi_u)$ $\varepsilon d\pi$ channels, underestimated in the calculation. This study also illustrates the general importance of measuring complementary observables (σ , β) for all available electronic and vibrational (and rotational where possible) ionization channels in order to gain insight into the resonant photoionization dynamics and provide a definitive test for theoretical approaches. A full analysis including our measurements for the $n = 5, 7$ and 8 members of the Hopfield bands is currently in progress.

We are grateful to Dr K P Huber for providing us with a copy of his results prior to publication. This work was supported in part by the US Department of Energy, Office of Energy Research, Office of Health and Environment Research, under contract W-31-109-Eng-38, and by the Science and Engineering Research Council (UK). One of us (KU) wishes to thank the British Council for financial support.

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