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High Resolution Absorption Spectrum of Nitrogen in the Vacuum Ultraviolet

by

P. Gürtler
II. Institut für Experimentalphysik, Universität Hamburg
V. Saile
Sektion Physik der Universität München
E. E. Koch
Deutsches Elektronen-Synchrotron DESY, Hamburg

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P. Gürtler

II. Institut für Experimentalphysik, Universität Hamburg, Hamburg 50

V. Saile

Sektion Physik der Universität München, München 40

and E.E. Koch

Deutsches Elektronen-Synchrotron DESY, Hamburg 52

The photoabsorption cross section of molecular N_2 has been determined in the range from 10 - 35 eV utilizing the continuum of synchrotron radiation from the DORIS storage ring, a 3m normal incidence monochromator of 0.03 Å resolution and photoelectrical recording. New detailed features are observed which make possible a refined analysis of the valence-Rydberg interaction of the $b^1\Pi_u$-$c^1\Pi_u$, $b'^1\Sigma_u^+$-$c'^1\Sigma_u^+$ states as well as an improved analysis of Rydberg series leading to the $X^2\Sigma_g^+$, the $A^2\Pi_u$, the $B^2\Sigma_u^+$ and the $C^2\Sigma_u^+$ states of the N_2^+ ion.

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I. Introduction

The photoabsorption spectrum of molecular nitrogen has been studied by many investigators since the initial work by Lyman[1] and Hopfield[2]. The molecule absorbs strongly in the vacuum ultraviolet (VUV) at wavelength shorter than 1000 Å. Most of the structure in the fairly complex spectrum extending to shorter wavelength has been analyzed and assigned. A concise account of the constant improvement of the experimental techniques and refinement of the analysis including references to the relevant earlier work may be found in the paper by Carrol and Collins[3] and the detailed analysis given by Dressler[4]. Structure in the photoionization continuum of N_2 near 500 Å was first observed by Codling[5] and more recently a high resolution study of N_2 from 730 to 980 Å has been reported by Carter[6] (see also the analysis given in Ref. 7). The frequencies and intensities of transitions to Rydberg levels as well as autoionization processes have been investigated theoretically by Duzy and Berry[8,9].

In the present study we used for the first time the combination of a storage ring VUV-light source with a high resolution scanning monochromator for high resolution absorption studies. We present and discuss in this letter the spectrum of molecular N_2. The resulting refinement of the data is used for an assessment of the validity of calculations for highly excited Rydberg states and a discussion of the autoionization processes.

II. Results and Discussion

The absolute absorption cross section of N_2 is shown in Figs. 1 and 2 in the wavelength range 1000 Å to 400 Å corresponding to photon energies of 12 to 30 eV. These data have been obtained with synchrotron radiation from the DORIS storage ring at DESY[10] focussed onto the entrance slit of a 3m normal incidence monochromator with a vertical dispersion plane[11]. Sufficient intensity is available at the exit slit (10^7 photons per sec x 0.03 Å) for photoelectric recording of the

spectra with a resolution of 0.03 Å. High purity (99.997 %) N_2-gas from L'air Liquide has been used as sample gas without further purification. The gas pressure in the windlowless absorption cell with a path length of 60 cm ranged for these measurements from $1x10^{-1}$ to $1x10^{-4}$ Torr. It has been determined with a precision membrane-vacuummeter (Datametrix Model 531). Under these conditions the pressure in the monochromator stayed in the 10^{-8} Torr range. The light traversing the sample chamber was converted into longer wavelength photons by a sodium salicylate screen deposited on a glass window and detected by a photomultiplier (EMI 9804).

Parts of the spectrum shown in Figs. 1 and 2 have been measured previously[3-7] some of them even with higher resolution obtainable with photographic recording[3,7]. For the range 980 Å to 730 Å our results compare favorably with the data obtained by Carter[6] with somewhat lower resolution (0.04 Å). It is worth noting that we have no problems with emission lines from the light source and that the photoelectric recording at pressures $\gtrsim 10^{-2}$ Torr made possible to cover a large dynamical range in the cross section. For the range 790 Å to 720 Å our data can be compared to the photoionization cross section as determined by Berkowitz and Chupka[12a] with a resolution of 0.12 to 0.4 Å and Comes and Weber[12b] with $\Delta\lambda$=0.08 Å. Finally for wavelength <720 Å a cross section determination by Lee et al.[13] and the photographically recorded spectrum around 500 Å[5] are available for comparison. As far as the absolute values of the cross section are concerned there is good agreement with the data obtained by Carter[6], Huffman et al.[14] and Lee et al.[13].

Roughly speaking the spectrum shown in Figs. 1 and 2 can be devided into four parts: (1) For wavelengths λ > 795.9 Å many strong discrete bands with detailed resolved rotational fine structure forming several progressions are observed. For shorter wavelengths the discrete band absorption is superimposed on a back-

ground of continuous absorption. (2) In the range ∿795 Å to 730 Å sharp Rydberg bands show up with several vibrational progressions, however, without resolvable rotational lines. (3) Below ∿730 Å the spectrum is somewhat smoother with a fairly simple absorption and "apparent emission" structure. (4) Finally, at around 500 Å a quite regularily spaced vibrational progression is observed. The features (1) to (4) can be correlated to the three valence orbitals $3\sigma_g$ 2p with a binding energy of 15.5 eV, $1\pi_u$ 2p (16.8 eV) and $2\sigma_u$ 2s (18.6 eV) and a shake-up processes as observed in photoelectron spectroscopy (see e.g. Ref. 15 and the discussion below).

In the range below the first ionization potential (range 1) the absorption is caused by the two Rydberg series $3\sigma_g \rightarrow np\sigma_u$ ($c'^1\Sigma_u^+$) and $\rightarrow np\pi_u$ ($c^1\Pi_u$) and the valence excitations $b'^1\Sigma_u^+$ and $b^1\Pi_u$. The nature of these states and the perturbation of the valence states by the Rydberg excitations has been discussed in detail by Dressler[4]. We are able to determine these perturbation effects more quantitatively than previously possible by using the photoelectrically recorded spectrum. The results of our evaluation are displayed in Fig. 3 where the oscillator strengths for the vibrational bands have been plotted as well as the change in vibrational spacing ΔG as a function of the vibrational quantum number v'.[16] Fits for the rotational structure resulted in the same parameters as determined earlier from photographic recordings[7] and are discussed elsewhere[16]. Further evaluation of the perturbation effects along the lines developed by Leoni[17] are now possible having at hand precise experimentally determined absolute cross sections for these progressions.

For the Rydberg series in this range Duzy and Berry[8] have calculated oscillator strengths. Thus e.g. for the $np\sigma_u c'^1\Sigma_u^+$ series a minimum at n=8 is predicted which is mainly caused by the variation in configuration mixing with final state energy. Since from n=6 onwards the npσ and npπ series coalesce in the spectrum we cannot corroborate this prediction. We note that in the calculations[8] perturbations caused by the valence states close by, has not been considered. Finally it is

interesting to note that we can observe (unresolved π and σ) Rydberg series up to n=23. Stark-ionization experiments with DC-fields up to ≈600 V/cm (onset of discharge) did not show any field quenching effects on these highly excited Rydberg orbitals.[18]

For the range above the first ionization potential (range 2) we essentially recover the earlier results by Ogawa et al.[19], Berkowitz et al.[12a] and Comes et al.[12b]. No rotational structure exept for a slight asymmetric line profile is observed in this range due to autoionization effects. This spectral range has been discussed very recently in detail by Duzy and Berry[12]. Judging from the experimentally observed quantum defects we assign two series in this range in accordance with Lindholm namely a $1\pi_u \rightarrow ns\sigma_g$ ($^1\Pi_u$) series with δ = 1.05 and a $1\pi_u \rightarrow nd\sigma_g$ ($^1\Pi_u$) series with δ = 0.17. For the nsσ series the ab initio calculation by Duzy et al.[8] gives very good agreement whereas the energies for the ndσ series deviate from the experimentally determined values. This deviation is due to the quantum defect δ = 0.8 used for the calculations, which is considerably larger than the one determined experimentally (δ = 0.17). In this range we further assign for the first time two fairly strong progressions (see Fig. 1) with a ΔG value very similar to that of the $A^2\Pi_u$ ion-state. These may also belong to Rydberg excitations from the $1\pi_u$ orbital.

Autoionization manifests itself most clearly in the absorption spectrum for wavelength below 730 Å (range 3). In this range a $nd\sigma_g$ and a $ns\sigma_g$-type Rydberg series originating from the $2\sigma_u$ orbital converge to the $B^2\Sigma_u^+$ state of the N_2^+ ion. They interfere with the ionization continua of the $X^2\Sigma_g^+$ and the $A^2\Pi_u$ states causing characteristic line shapes and dips in the absorption cross section (Hopfields "apparent emission" lines[2]). Plummer et al.[21] could show in their recent determination of partial photoionization cross sections that the interference effects causing the absorption dips are far more pronounced in the partial cross section

for the $A^2\Sigma_u$ state than for the $X^2\Sigma_g^+$ state. Based on an analysis of the line shapes according to the Fano Cooper theory[22] we were able to locate the energetic positions of the bands unequivocally (see Figs. 1 and 2). Following from this analysis we now obtain series with almost constant quantum defects of $\delta = 0.15$ for the $nd\sigma_g$ series and $\delta = 0.94$ for the $ns\sigma_g$ series. The insert in Fig. 2 gives an example for a fit of the experimentally determined cross section with a Fano-Cooper Profile[22] for the $5d\sigma$ and $6s\sigma$ states.

From the parameters resulting from this fit for the 5d peak it can be seen that this state is strongly autoionizing. Its halfwidth of 20 meV corresponds to a autoionization rate of 3×10^{13} sec^{-1}. However, the overlap parameter is only small (6 %). Consequently the line shape is still fairly Lorentzian. For the $6s\sigma$ peak the situation is almost reverse. In this case we find a smaller autoionization rate of 2×10^{13} sec^{-1}, the overalp with the continuum is strong (53 %) and a characteristic minimum is resulting. We conclude from this together with the observation of Plummer et al.[21] that the $ns\sigma$ series strongly interacts with the continuum of the $A^2\Pi_u$ state. For the analysis given above two points have to be kept in mind which influence the line shape. First, the rotational structure can distort the line shape and secondly with decreasing separation between the $nd\sigma$ and the $(n+1)s\sigma$ states these states can interact in case they autoionize (although only partially) into the same continuum[23].

Finally we turn to the spectral range around 500 Å (range 4). Structure in the photoionization continuum at around this wavelength was first recorded photographically by Codling[5] and tentatively assigned to Rydberg series leading to the C state of N_2^+ at 23.6 eV. Our analysis of this range is shown in Fig. 2. The spectrum shows even asymmetric line shapes for some of the bands. The $C^2\Sigma_u^+$ state is reached from the ground state of N_2 by a two electron process where one electron

is removed from the 3σg orbital and another electron is excited from the $1\pi_u$ orbital into the unoccupied $1\pi_g$ orbital[24]. Codling assumed an nsσ type Rydberg series. Thus the one electron configuration of the intermediate state in autoionization is

$$(1\sigma_g)^2\ (1\sigma_u)^2\ (2\sigma_g)^2\ (2\sigma_u)^2\ (1\pi_u)^3\ (3\sigma_g)^1\ (1\pi_g)^1\ (ns\sigma)^1$$

We corroborate this assignment since the series shown in Fig. 2 has a $\delta \approx 0.9$ consistent with an s-type series. The limit to which this series converges has been determined in a recent photoemission study of the N_2 molecule[15]. In this study a band at≈24.9 eV was found corresponding to a shake-up process with the same configuration as given above except that the $(ns\sigma)^1$ electron is now in the continuum. Plummer et al.[21] show that this intermediate state autoionizes into the $X^2\Sigma_g^+$ and $A^2\Pi_u$ state but not into the $B^2\Sigma_u^+$ state of N_2^+ which energetically would also be possible.

The newley observed weak progression at around 630 Å (see Fig. 2) does not fit into the above mentioned s-like Rydberg series. It remains as jet unassigned.

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Figure captions

Fig. 1 Absolute absorption cross section of molecular nitrogen in the range 990 Å to 660 Å. For the assignments see text.

Fig. 2 Absolute absorption cross section of molecular nitrogen in the range 700 Å to 450 Å. The insert shows the 5dσ and 6sσ Rydberg excitation from the $2\sigma_u$ molecular orbital in an expanded scale together with a fitted line shape (see text).

Fig. 3 Numerical evaluation for the perturbations of the oscillator strengths $f(\nu')$ and spacings $\Delta G(\nu')$ for the progressions of the $b^1\Pi_u$ and $b'^1\Sigma_u^+$ valence states caused by the nearby Rydberg states $c^1\Pi_u$, n=3 (ν' = 0,1,2) and $c'^1\Sigma_u^+$, n=4,5 (ν' = 2,3,4), (ν' = 0,1) respectively. The dashed curves for $\Delta G(\nu')$ show the deperturbed cases as calculated by Leonie[17].

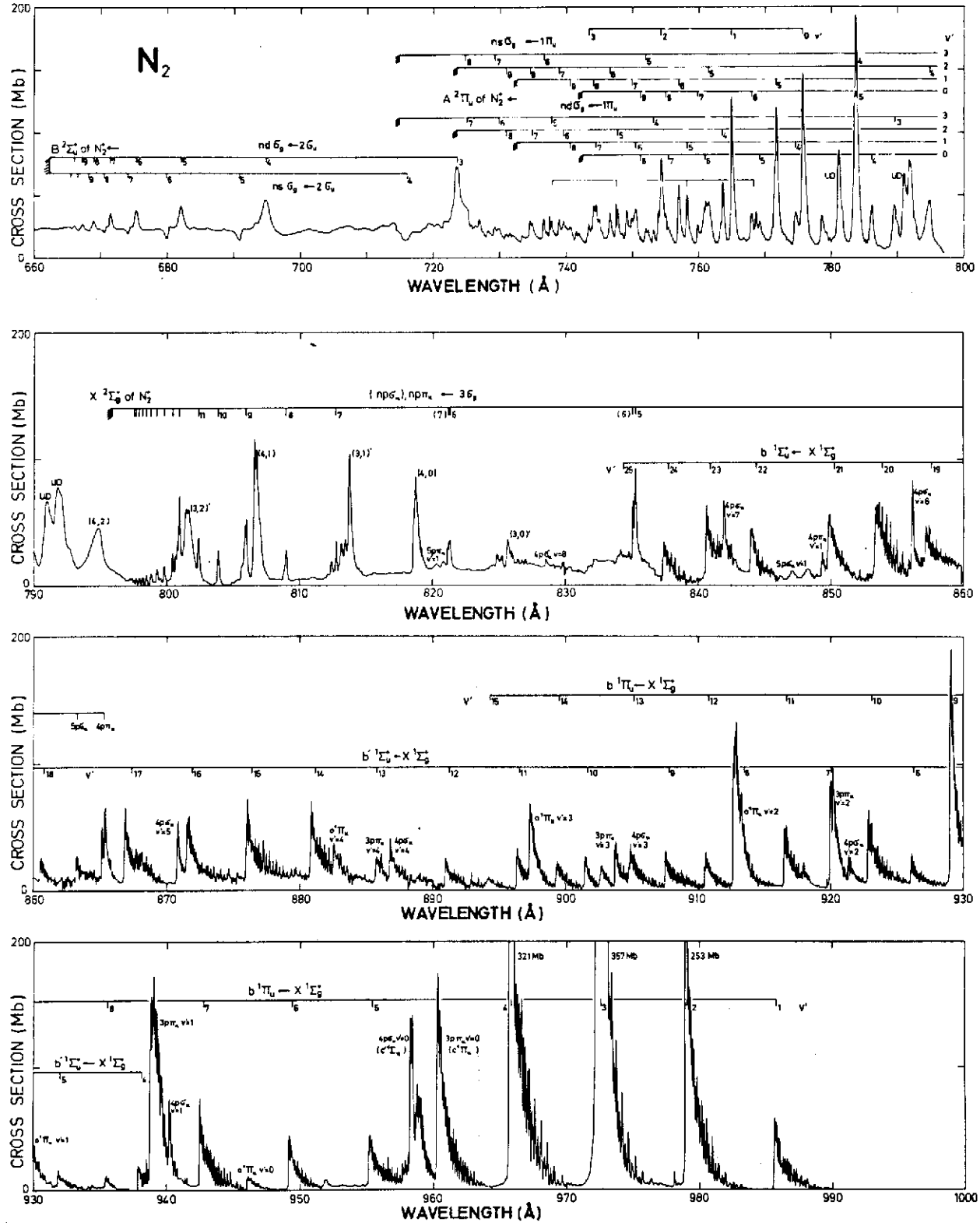

N2
CROSS SECTION (Mb)
WAVELENGTH (Å)
B 2Σu+ of N2+
A 2Πu of N2+
X 2Σg+ of N2+
b 1Σu+ ← X 1Σg+
b 1Πu — X 1Σg+
b' 1Σu+ — X 1Σg+
321 Mb
357 Mb
253 Mb

Fig. 1

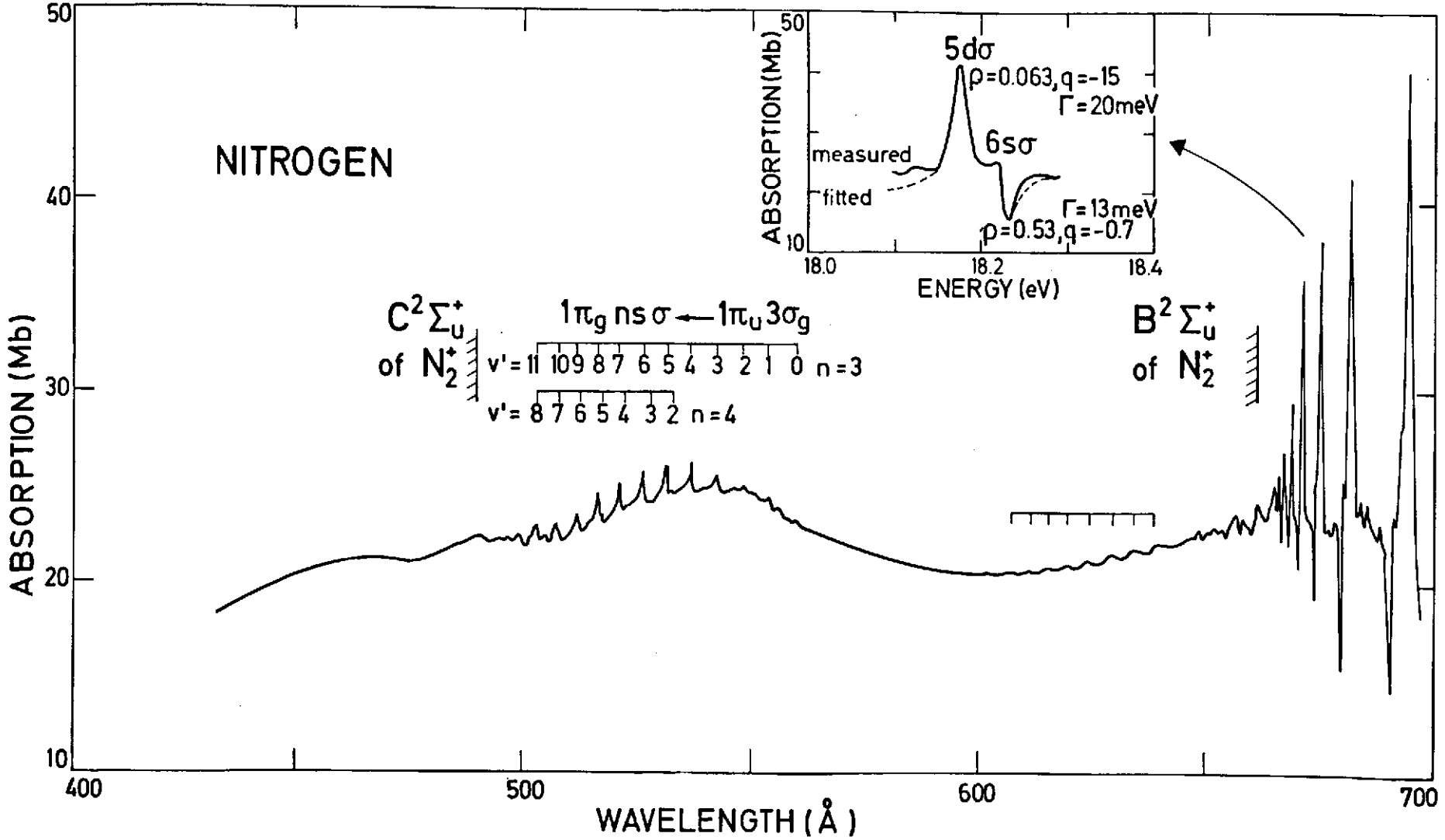
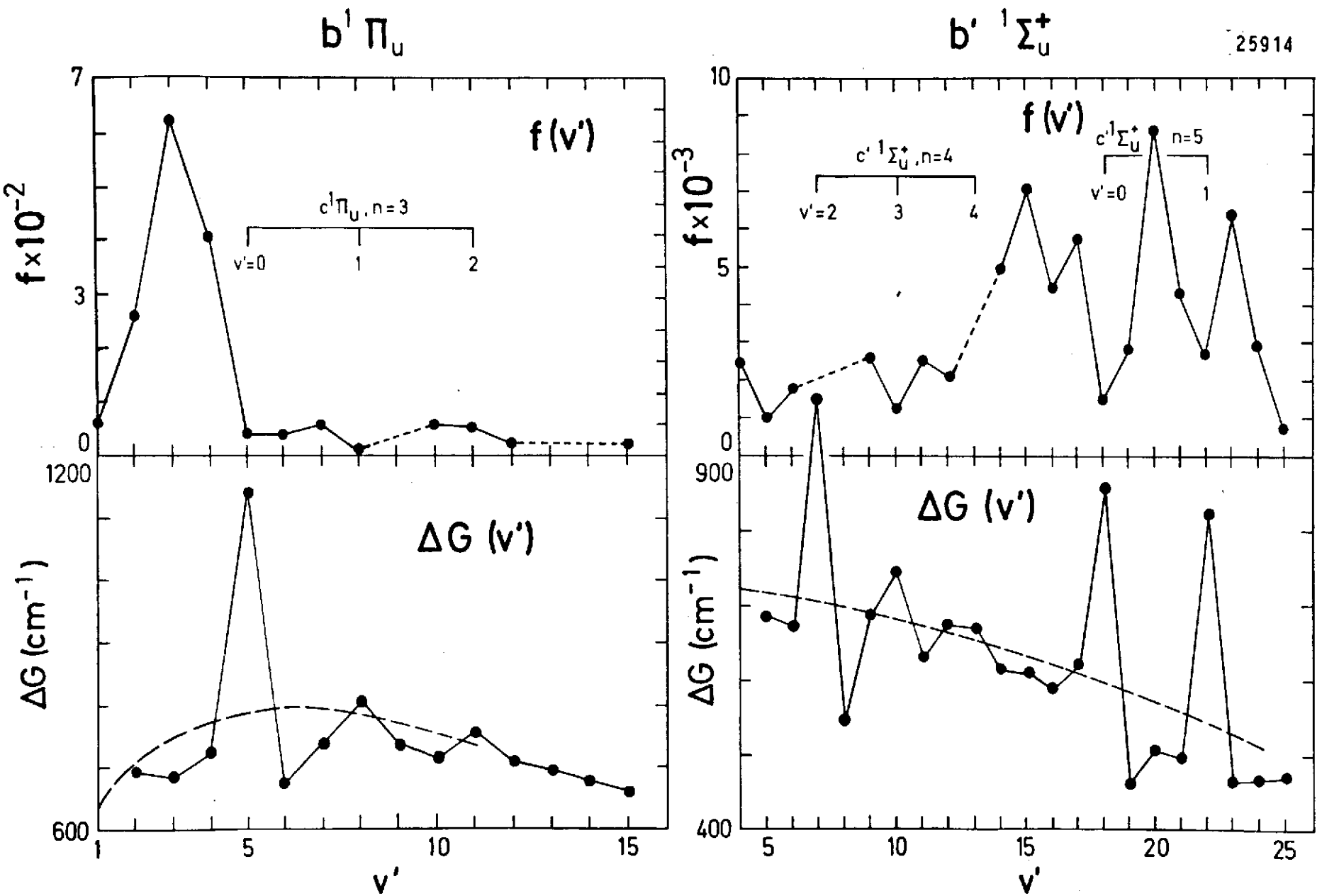

NITROGEN
ABSORPTION (Mb)
WAVELENGTH (Å)
50
40
30
20
10
400
500
600
700
ABSORPTION (Mb)
50
10
18.0
18.2
18.4
ENERGY (eV)
5dσ
ρ=0.063, q=-15
Γ=20meV
6sσ
measured
fitted
Γ=13meV
ρ=0.53, q=-0.7
C² Σ⁺u
of N₂⁺
1πg nsσ ← 1πu 3σg
v'= 11 10 9 8 7 6 5 4 3 2 1 0 n=3
v'= 8 7 6 5 4 3 2 n=4
B² Σ⁺u
of N₂⁺

Fig. 2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f(v')
f×10⁻²
c¹Π_u, n=3
v'=0
1
2
ΔG (v')
ΔG (cm⁻¹)
v'
b' ¹Σ⁺_u
f(v')
f×10⁻³
c'¹Σ⁺_u, n=4
v'=2
3
4
c¹Σ⁺_u
n=5
v'=0
1
ΔG (v')
ΔG (cm⁻¹)
v'

Fig. 3