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Transition Probabilities at Threshold for the Photoionization of Molecular Nitrogen

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TRANSITION PROBABILITIES AT THRESHOLD FOR THE PHOTOIONIZATION OF MOLECULAR NITROGEN*

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The relative transition probabilities at threshold for the photoemission of molecular nitrogen to vibrational levels of the $X(^2\Sigma_g^+)$, $A(^2\Pi_u)$ and $B(^2\Sigma_u^+)$ states of the N_2^+ ion have been determined with high resolution photoelectron resonance spectroscopy using synchrotron radiation. These threshold cross sections are found to be strongly influenced by ionizing Rydberg states which are not necessarily apparent in the absorption or photon spectrum of nitrogen. This interaction leads in the $X(^2\Sigma_g^+)$ state of N_2^+ to rotation-like structure in the observed vibrational transitions and in the $A(^2\Pi_u)$ state to a smooth but non-Franck Condon distribution of vibrational intensities. In addition to the cross section data, the molecular parameters for the X, A and B states of N_2 have been determined.

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1. Introduction

The role of ionizing Rydberg states in the photoionization of atoms and molecules at threshold has received considerable attention recently both theoretically[1-14] and experimentally[15-26]. It is well known from photoionization efficiency curves of molecules that autoionization often predominates and thus steps, which are usually attributed to direct ionization, are not apparent. From photoionization efficiency curves, however, the final states - the ion states to which the ionizing Rydberg states ionize - are not known.

Photoelectron spectroscopy (PES) on the other hand enables one to determine the locations of the ion states themselves and from the intensity data, corrected for analyser transmission function and angular effects, the branching ratios, or the distribution of final electronic states of the ion produced corresponding to the particular exciting photon wavelength used can be obtained[27-30]. In addition, with sufficient resolution, the vibrational intensity distribution within each electronic states can be determined.

In general, PES studies are made using 21.2 eV or 40.8 eV radiation to ionize the molecules and several such experiments have been performed in high resolution on nitrogen[31,32]. In order to study the wavelength dependence of the branching ratios for nitrogen several authors have employed the dispersed radiation emanating from a continuous or many line radiation source[33]. From such studies, and in particular for the case of O_2[15] it was found that the branching ratios obtained when the incident radiation excites an ionizing Rydberg state were often strongly effected along with the vibrational distributions observed. A detailed study of the role of autoionization in photoionization by means of PES at photon energies corresponding to well known Rydberg states has been carried out in the case of hydrogen and nitrogen.[17] From this study it appears that the role of autoionization differs

for the two molecules involved. That is, for hydrogen, vibrational relaxation of the Rydberg core seems to govern the choice of exit channels while for nitrogen two electron processes, configuration interaction, appears to dominate. In all of the PES studies made on nitrogen to date, photoionization has been studied at various energies above the particular ionization thresholds.

Calculations using multichannel quantum defect theory (MQDT)[1-5] have shown that an ionizing Rydberg state which lies in the vicinity of the threshold of the ion state to which it decays can strongly interact with the continuum and that the designation "direct ionization" and "autoionization" cease to be meaningful. That is, the photoionization cross section is not simply the sum of two processes but instead must be viewed as an entity in itself which is defined by more or fewer parameter depending on the number and nature of states which are in the range of the exciting radiation. For the rare gases, this effect has been calculated[1-5,25] and measured in detail over the range 0-50 meV above the threshold in photoionization[25]. Experimental studies have been also carried out in the case of molecular hydrogen.[18,23]

The primary intent of the present study is thus to measure the photoionization cross sections to the vibrational levels of the $X\ ^2\Sigma_g^+$, $A\ ^2\Pi_u$ and $B'^2\Sigma_u^+$ states of N_2^+ and to compare the relative amounts of both the electronic states produced and the vibrational distributions within these states with the results of photoelectron spectroscopy, photoion studies and photoabsorption studies in order to determine the nature of the photoionization process at threshold.

2. Experimental details

The present experiments were carried out at the Deutsches Elektronen-Synchrotron DESY in Hamburg, Germany. Synchrotron radiation from the storage ring DORIS was dispersed with a 3 meter scanning vacuum ultraviolet monochromator used at a resolution of 0.15 Å full width at half maximum (FWHM)[34]. The radiation emanating from the exit slit of the monochromator is calculated to be more than 98 % polarized but because the present electron measurements were made with a very narrow bandwidth at threshold (the electrons have zero kinetic energy) the effect of the polarization is estimated to be small[25]. The absolute wavelength calibration was made using rare gas and nitrogen absorption measurements.

The threshold electron analyzer has been previously described[22,35,36]. Electrons are drawn out of the photoionization region at an angle of 90° with respect to the photon beam and in the direction of the electric vector of the light. The bandpass of the detector was determined by measurement of the photoionization spectrum of argon (Fig. 1). A resolution of better than 0.003 eV FWHM was obtained - that is, the width of both the $^2P_{3/2}$ and the $^2P_{1/2}$ peaks correspond to the resolution of the photon monochromator. The argon spectrum also shows the effectiveness of the analyzer in rejecting energetic electrons as seen by the absence of autoionization peaks between the two ionization thresholds. Since the threshold electron analyzer is a passive device registering the presence of zero kinetic energy (threshold) electrons as the photon energy is scanned, no corrections of the transmission function of the analyser are necessary.

Convolution calculations[37-39] show that the photoionization thresholds correspond to a point on the leading edge of a peak at between 1/2 and 3/4 the peak height. The argon data substantiate this. The wavelengths given below were obtained in this way from the data.

The photon intensity was measured as photo-current using a sodium salicylate film to convert the photons in the 650 - 800 Å range studied to a band centered at about 4300 Å and a standard bialkali photomultiplier. The transmitted photon signal along with the threshold electron signal were simultaneously measured and stored in a PDP-11/45 computer. The photon wavelength was advanced at constant photon intensity so as to maintain constant electron counting statistics.

The absorption spectrum of nitrogen had been determined previously with the same monochromator but at a resolution of 0.03 Å u ng room temperature nitrogen[40]. Nitrogen was obtained from l'Air Liquide (99.997 % purity) and was used without further purification. The measurements were performed at room temperature with a nitrogen pressure of 5×10^{-5} Torr.

3. Experimental results

The threshold electron spectrum of nitrogen in the range 15.5 - 19.2 eV as well as the absorption spectrum over this range[40] are reproduced in figure 2. The relative intensities of the various transitions observed are as given in the figure. The locations of the ionization thresholds, the peak areas and the FWHM of each peak are given in Table 1. The peak areas were obtained by direct integration of the data stored in the computer. These areas are shown again in Table 2, in this case normalized to sum up to 1.00 for the particular electronic state involved. Also appearing in Table 2 are the measured vibrational intensity distributions from PES using 21.2 eV, 23.1 eV (averaged)[31], and 40.8 eV radiation[32] as well as results obtained in SF_6 electron trapping experiments.[26] In addition, calculated Franck-Condon factors for these three states of N_2^+ are shown[29,31,32]. It should be noted that for each transition observed in the present experiment, the photon energy is equal to the energy of the transition Molecule → Molecular Ion. In PES on the other hand, the photon energy exceeds the energy required for photoionization, and by differing amounts depending on the particular transition ob-

served. Thus the two types of experiments differ not only (a) in the threshold, non-threshold character but also (b) in that the present cross sections correspond to measurements with a fixed relationship to the transition energy, in this case $\Delta E = E_{Photon} - E_{\substack{Mol-Ion \\ Transition}} = 0$, and in PES this ΔE varies. The SF_6 electron trapping experiments are similar to the present results in these two aspects. The relative cross sections reported here may not be directly comparable with PES values because of point (b) above. Recently PES studies with synchrotron radiation as a light source have been made which enable one to determine the relative cross sections at a given energy above the threshold.[24] In these experiments the resolution was adjusted to yield the overall branching ratios rather than vibrational intensity distributions. These ratios are shown in Table 3 for photon energies of 5, 15 and 25 eV above the thresholds. The first and third values correspond roughly then to PES results for nitrogen using 21.2 eV and 40.8 eV radiation respectively.

Immediately discernable from the spectrum (Fig. 2) is the fact, that the peak forms for the $X\ ^2\Sigma_g^+$ ground state of N_2^+ are markedly different from those for the $A\ ^2\Pi_a$ state. This also shows up in the measured FWHM of the peaks as seen in Table 1. We will return to this point below.

The data presented in tables 1, 2 and 3 are an average obtained from three runs. The standard deviation of the scatter from run to run is also given in the tables where appropriate.

4. Discussion

4.1 Spectroscopic data

Birge-Sponer (ΔG 1/2) plots for the X and A states of N_2^+ have been made from the data given in Table 1 and are shown in Fig. 3. The molecular parameters obtained from least squares fits to these plots are given in Table 4 along

with data obtained from fluorescence emission spectroscopy[43]. It is important to note that the agreement between these two types of experiments (Table 4) indicates the lack of influence of non-zero volt electron processes on the observed spectra. The dissociation energies, obtained by linear extrapolation of the Birge-Sponer plots are in reasonable agreement with previously published results (Table 4).

4.2 Intensity data

The most striking features of the threshold electron spectrum are (1) the similarity in intensity (per vibrational level) of the three electronic states observed; (2) the extended vibrational progression observed in the X state which in addition shows rotationlike structure and (3) the smooth but non-Franck-Condon distribution of vibrational levels in both the X and A states (see below). The present spectrum is quite similar to that obtained in SF_6 electron trapping experiments[26].

Comparison of the 0-0 transitions to the X, A and B states of N_2^+ yields a relationship of 1.0:0.92:0.71 (peak areas) at the threshold as compared with 1.0:0.28:0.09 as obtained in photoelectron spectroscopy using the helium 21.21 eV and 23.1 eV radiation (results averaged) resonance line for excitation[31]. The SF_6 relationship of 1.0:0.54:0.19 lies in between the other results. The intensity distributions within each electronic state at threshold are very different from the PES results, the progressions in the X and A states being longer here and in the SF_6 data. The relative peak areas for all three states are given in Table 2 and are displayed graphically in Fig. 4 along with PES results[31,32], SF_6 electron trapping results[26] and calculated Franck-Condon factors.[41]

When one integrates the areas under the vibrational peaks in order to obtain the total relative threshold photoionization cross sections for the three electron states, one finds surprisingly that the results are similar to the comparable

PES results. The broad peaks and significant autoionization features present in the SF_6 electron trapping data prevented a comparison with these results.

At threshold one finds for X:A:B = 0.67:1.0:0.15 while from PES the following results are obtained depending primarily upon the excitation wavelength: At $h\nu$ = 21.2 eV ratios of 0.72:1.0:0.23[29] and 0.68:1.00:0.18[24] have been reported. At $h\nu$ = 40.8 eV, 0.66:1.00:0.23[32] and 0.48:1.00:0.22[29] and 0.62:1.00:0.27[24] have been obtained. It is not clear, why the ratios obtained in PES at 40.8 eV differ so from each other since at this photon energy, the electrons ejected from N_2 for all three states of N_2^+ (X,A,B) will have relatively similar energies of ca. 25 eV, 24 eV and 22 eV respectively. Thus, they will all be transmitted by the electron analyser to a similar extent, more so than at 21.2 eV excitation. The asymmetry factor β should be unimportant in these considerations since the PES measurements were made at 54.5° (magic angle).[44]

The similarity of the total threshold photoionization cross sections to the comparable PES results is surprising in view of the fact that at threshold, the manifold of ionizing Rydberg states is coupled with the ionization continuum altering the transition probabilities from the values at an energy well above threshold. In addition, it is expected that the extend of the interaction depends on the nature of the Rydberg states. This nature changes dramatically at the onset of the $A\ ^2\Pi_u$ state as is well known from the absorption spectrum of N_2[40]. The experimental observations suggest, that the overall transition moment to a particular electronic state of the ion is relatively insensitive to the details of the particular vibrational transitions and the related bound-continuum interactions. Indeed, measurements of the partial cross sections for the X, A and B ionic states continuously as a function of photon energy,

from a few electron volts above threshold to 50 eV[22], is quite smooth although the ratio at, for example 15 eV over the respective threshold (namely 0.93:1.00:0.23) differs from the aforementioned (Table 3). If sharp variations in the total cross sections were present, some of the resulting structure should show up in the experiments even though the photon and the electron resolution are only modest. Thus, although the contribution to the observed intensity distribution of the vibrational levels varies dramatically, the overall relative transition probability appears to be less influenced by single Rydberg states. We note in passing, that recent theoretical calculations of the partial cross sections for N_2[45] show a smooth variation with exciting photon energy.

With regard to the vibrational structure, the fine structure observed in the N_2^+-X state apparently reflects the sharply defind structure of the Rydberg states that lie in this region. That is not to say that the <u>observed</u> absorption are the ones that are affecting the threshold photoionization processes. That seems unlikely (see below). However, it is apparently the <u>nature</u> of Rydberg states in this region to be narrow and well defind. Furthermore the interaction between Rydberg states and states of the ion is determined not only by electronic nature of the states involved and their proximity to each other but also by the rotational selection rules.[23,26,46] Thus, it appears that particular rotational transitions are favored here but because of all of the conditions that must be fulfilled, they are irregularly favored leading to the jagged peaks observed. The peak areas for the transitions to the vibrational levels of the X state are given in Table 2 and graphically in Fig. 4. They are very different from those obtained in PES studies. The latter are in good agreement with calculated Franck-Condon factors, also shown in Table 2 and Fig. 4.

The form of the vibrational peaks in the N_2^+.A state as well as the intensity distribution are very different both from the X state and from PES results. The vibrational envelope looks very much like a normal Franck-Condon distribution, with the exception of the v=2 peak. However, the actual distribution deviates significantly from that obtained in PES and from the calculated results (Table 2,

Fig. 4). Comparison of the absorption peaks with the threshold electron peaks reveals no obvious correspondence. That is, in general the absorption maxima do not lie on top of the ion states and, as has been noted in the case of H_2^+ ($^2\Sigma_g^+$)[23]. Significant intensification of the threshold electron peaks often occurs where no Rydberg state is known to exist. Whether this results from the contribution of very broad but discrete Rydberg states as is known to occur in the case of argon atoms or from particular members of a dense manifold of weak and perhaps narrow Rydberg states which appear as a continuum in the absorption spectrum it not clear. However, the smooth nature of the vibrational envelope suggests that the latter alternative is probable since it would be a general effect without a strong dependence on the particular Rydberg states involved. That the spin-orbit splitting of 74.67 cm^{-1} (Ref. 43) is almost completely washed out in our spectrum also appears to result from this general effect. The reasoning is that (1) all of the peak intensities are enhanced by autoionization and yet (2) ordinary smooth rotational envelops are observed here as seen, for instance by the constant FWHM of the peaks. Thus there is no irregular enhancement of the rotational state intensities as was observed in the X $^2\Sigma_g^+$ transitions.

The B $^2\Sigma_u^+$ state is normal insofar as the vibrational peak intensities are concerned when compared with the PES results and with calculated Franck-Condon factors. The main deviation here from the PES experiments is the strong 0-0 transition which is comparable with those of the X and A states (see Table 1) even though, as previously mentioned, the total integrated intensities to each of the three electronic states are comparable with those obtained from PES.

5. Conclusions

From the experimental results published here and comparisons made between these results and results obtained on N_2 from absorption spectroscopy, photoelectron spectroscopy, and SF_6 electron trapping experiments it is clear that the interaction of ionizing Rydberg states with ionic states plays a significant role on the intensities observed at the photoionization threshold. What is particularly puzzleing is that although the spectra observed here differ extensively in peak form, peak intensity and in the length of the vibrational progressions from those obtained in PES, the relative integrated intensities over entire electronic states (X, A and B) are comparable.

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Table 1: Energy and intensity data taken from the threshold electron spectrum of N_2

v	λ (Å)	E (eV)	Peak Area (a.u.)[a]	Peak FWHM (Å)
			$X\ ^2\Sigma_g^+$	
0	796.0	15.576	67.7	0.28
1	782.4	15.847	75.1	0.88
2	769.4	16.115	52.0	(0.60)
3	757.1	16.376	29.9	0.35
4	745.4	16.633	14.9	0.72
			$A\ ^2\Pi_u$	
0	742.9	16.689	62.6	1.02
1	732.7	16.922	74.9	0.88
2	722.7	17.156	126.2	0.91
3	713.3	17.382	48.4	0.90
4	704.3	17.604	22.0	0.82
5	695.7	17.822	15.1	0.95
6	687.5	18.034	7.2	0.84
7	679.9	18.236	3.5	
			$B\ ^2\Sigma_u^+$	
0	661.4	18.746	48.2	0.85
1	650.9	19.048	5.0	

a) arbibtrary units normalized to constant photon intensity

Table 2: Measured and calculated vibrational intensity Distributions for the transitions N_2 $X^1\Sigma_g^+$ (v=0) → N_2^+ X,A,B

	v	At threshold (present work)[a]	(Ref. 26)	PES, hν=21 eV+23eV (Ref. 31)[a,c]	PES hν=40.8 eV (Ref. 32)[b,c]	Calculated (Ref. 41)	Calculated (Ref. 42)	Calculated (Ref. 29)
$X\ ^2\Sigma_g^+$	0	0.283	0.21	0.932	0.875	0.9046	0.915	0.9023
	1	0.313	0.54	0.065	0.107	0.08931	0.0796	0.0906
	2	0.217	0.17	0.003	0.018	0.00592	0.0049	0.0065
	3	0.125	0.05			0.00035	0.00028	
	4	0.062	0.03			0.000023	0.000016	
$A\ ^2\Pi_u$	0	0.172	0.20	0.260	0.274	0.2732	0.2746	0.2447
	1	0.206	0.25	0.298	0.314	0.3204	0.3195	0.3107
	2	0.347	0.39	0.227	0.206	0.2154	0.2148	0.2253
	3	0.133	0.12	0.130	0.115	0.1108	0.1107	0.1236
	4	0.060	0.05	0.057	0.054	0.04895	0.04894	0.0574
	5	0.052		0.021	0.025	0.01970	0.01971	0.0238
	6	0.020		0.007	0.012	0.00753	0.00749	0.0095
	7	0.010				0.00281	0.00275	
$B\ ^2\Sigma_u^+$	0	0.906		0.910	0.880	0.8864		0.8912
	1	0.094		0.090	0.120	0.1112	0.1070	0.1070

a) Peak areas

b) Peak heights

c) Measurements made at the magic angle (54.7°) to eliminate angular effects (Ref. 46)

Table 3: Relative production of the $X\ ^2\Sigma_g^+$, $A^2\Pi_u$ and $B^2\Sigma_u^+$ states of N_2^+

	At threshold (Present work)	PES 5 eV (Ref. 24)[a]	PES 15 eV (Ref. 24)[a]	PES 25 eV (Ref. 24)[a]	PES hν=21.2 eV (Ref. 24)[b,c]	PES hν=40.8 eV (Ref. 32)[b,d]
$X\ ^2\Sigma_g^+$	0.67	0.59	0.93	0.62	0.68	0.66
$A\ ^2\Pi_u$	1.00	1.00	1.00	1.00	1.00	1.00
$B\ ^2\Sigma_u^+$	0.15	0.17	0.23	0.27	0.18	0.22

a) Relative proportion of each state produced at the stated energy over the threshold of that state

b) Branching ratio: that is, the relative proportion of each state produced for a fixed incident photon energy

c) Corrected for angular effects

d) Measurements made at the "magic angle" thereby eliminating angular effects[47]

Figure captions

1. Threshold electron spectrum of argon with a photon resolution of 0.15 Å.

2. Absorption and threshold electron spectrum of N_2 over the range 805 Å - 650 Å.

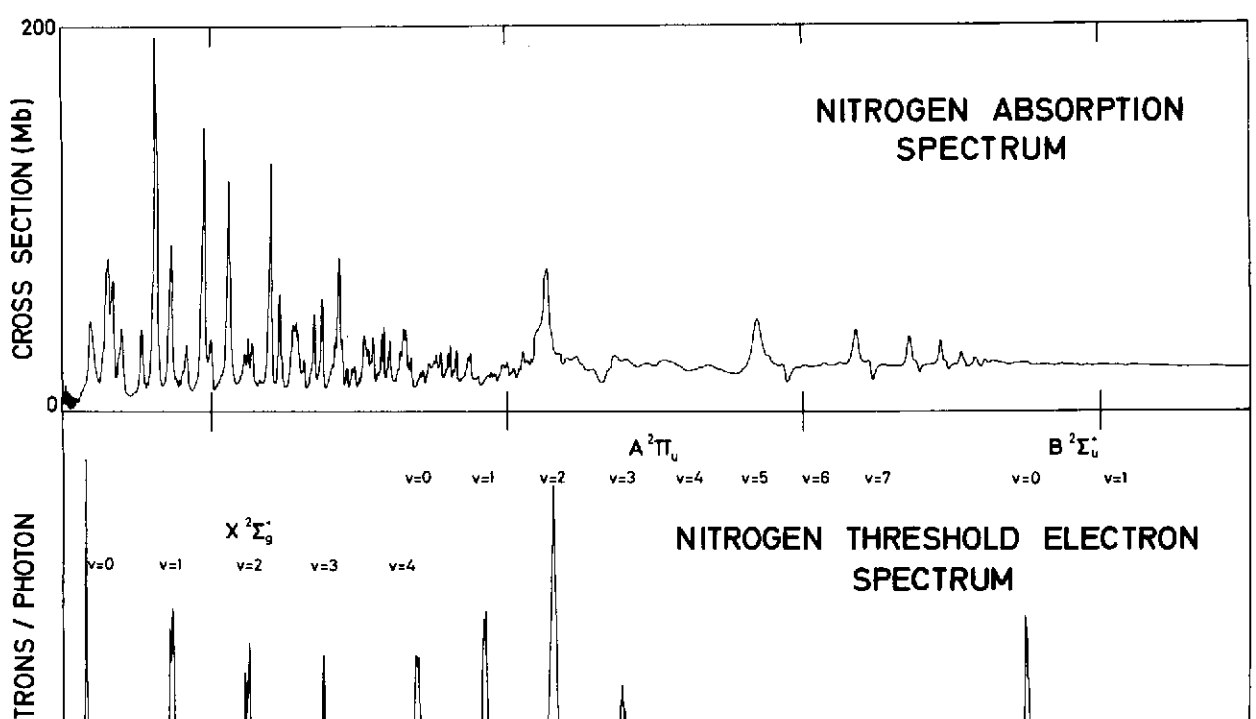
3. Birge-Sponer (ΔG 1/2) plots for the X $^2\Sigma_g^+$ and A $^2\Pi_u$ states of N_2^+. The crosses represent experimental values, the dashed curves show the fit used for the analysis.

4. Vibrational intensity distributions for the transitions N_2 X $^1\Sigma_g^+$ (v=0) → N_2^+ X $^2\Sigma_g^+$, A $^2\Pi_u$, B $^2\Sigma_u^+$. (a) Measured at threshold (this work). (b) SF_6 electron trapping results, (c) PES with 21.2 eV and 23.1 eV photons (results averaged), (Practically identical with the 40.8 eV PES results, see Table 2), (d) calculated Franck-Condon factors (Ref. 41). All data taken from Table 2.

Table 4: Molecular parameters relating to the X $^2\Sigma_g^+$, A $^2\Pi_u$ and B $^2\Sigma_u^+$ states of N_2^+

	T_o (cm^{-1})	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	$\omega_e y_e$ (cm^{-1})	D^o (cm^{-1})	A_e (cm^{-1})
Present work						
X $^2\Sigma_g^+$	125701	2218	14.0	-0.73	64[illegible]9	
A $^2\Pi_u$	134808	1934	13.9	-0.62	56717	a)
B $^2\Sigma_u^+$	151155	2436				
Fluorescence studies (Ref. 43)						
X $^2\Sigma_g^+$	125667.5	2207.00	16.0	-0.040	70273	
A $^2\Pi_u$	134683.9	1903.53	15.011		61256	-74.67
B $^2\Sigma_u^+$	151233.5	2419.84	23.19		44706	

a) the spin-orbit splitting in the threshold electron experiments is barely discernable (Fig. 2)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CROSS SECTION (Mb)
0
NITROGEN ABSORPTION SPECTRUM
A $^2\Pi_u$
B $^2\Sigma_u^+$
v=0 v=1 v=2 v=3 v=4 v=5 v=6 v=7
v=0 v=1
X $^2\Sigma_g^+$
v=0 v=1 v=2 v=3 v=4
NITROGEN THRESHOLD ELECTRON SPECTRUM
ELECTRONS / PHOTON
16
17
18
19
ENERGY (eV)

Fig. 2

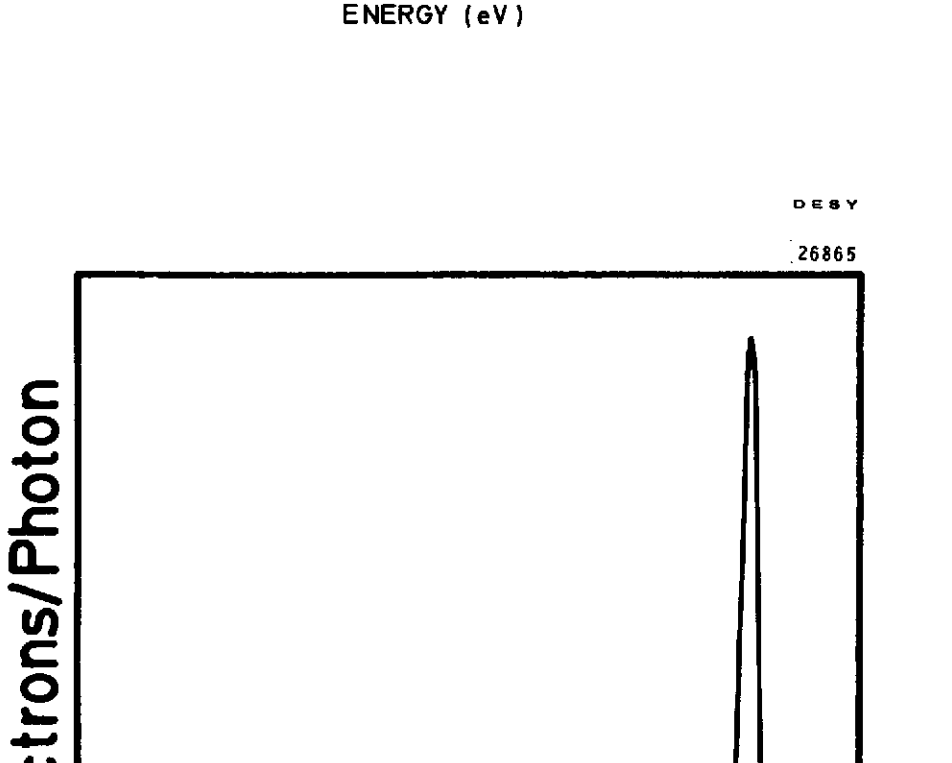
DESY
26865
Electrons/Photon
16.100
15.900
15.700
ENERGY (eV)

Fig. 1

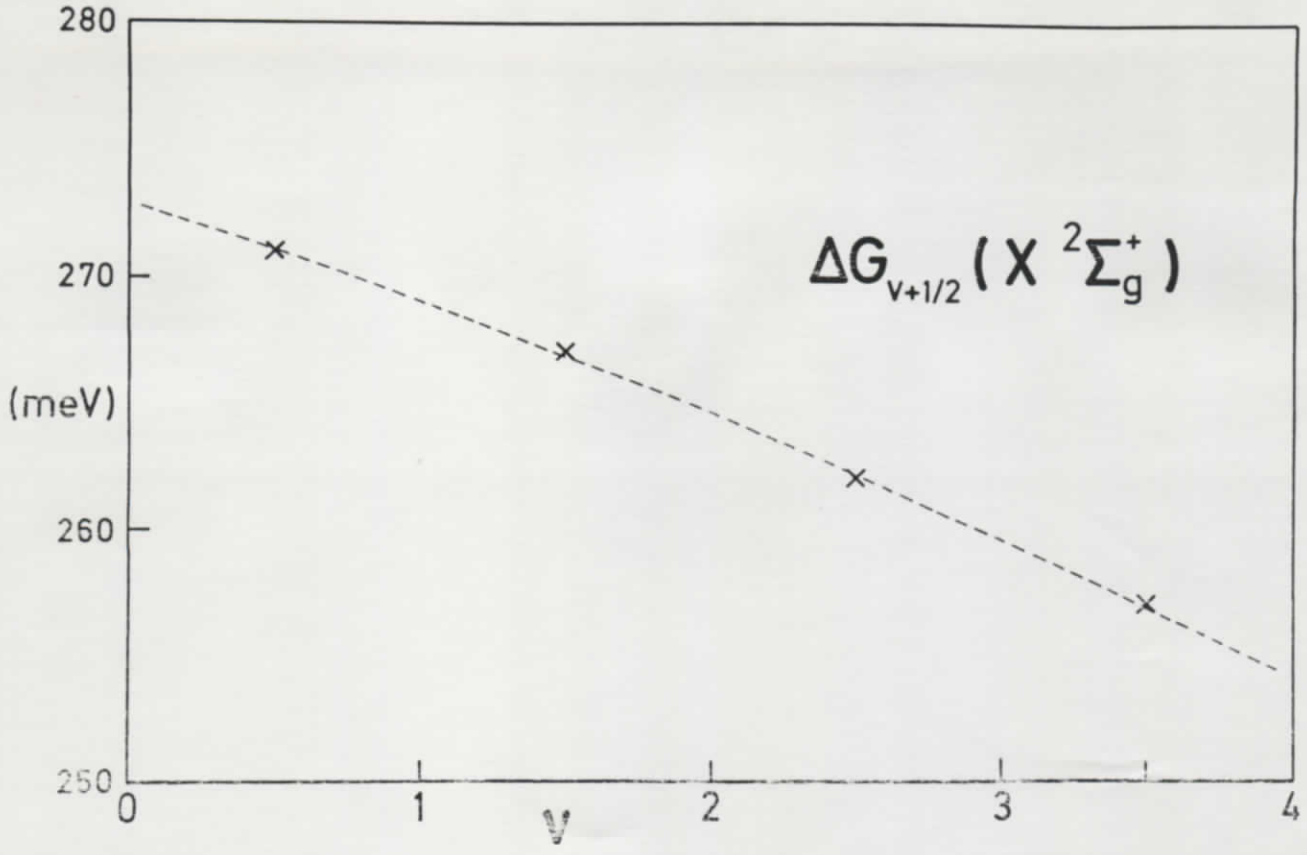
280
270
260
250
(meV)
0
1
2
3
4
v
$\Delta G_{v+1/2}(X\ ^2\Sigma_g^+)$

Fig. 3a

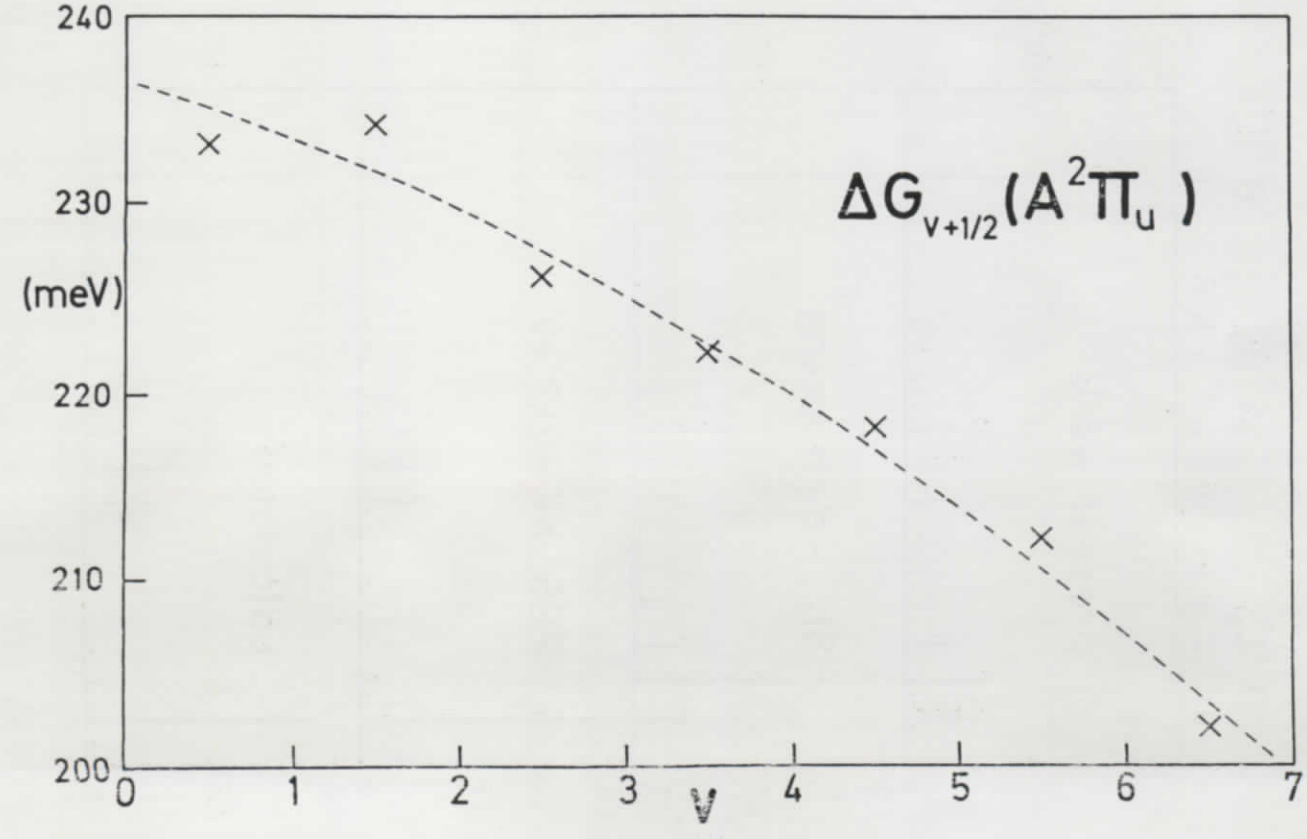
240
230
220
210
200
(meV)
0
1
2
3
4
5
6
7
v
$\Delta G_{v+1/2}(A^2\Pi_u)$

Fig. 3b

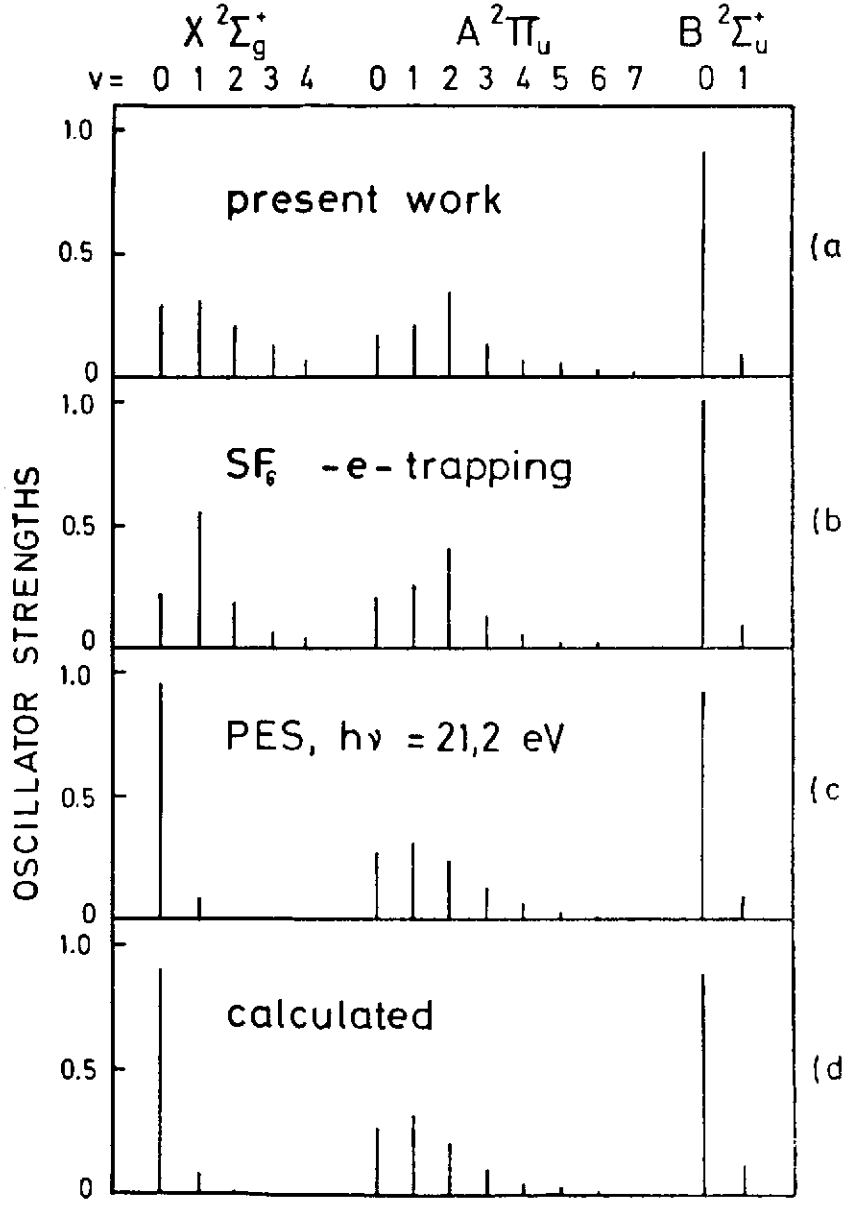
X $^2\Sigma_g^+$
A $^2\Pi_u$
B $^2\Sigma_u^+$
v= 0 1 2 3 4 0 1 2 3 4 5 6 7 0 1
OSCILLATOR STRENGTHS
1.0
0.5
0
present work
(a
SF_6 -e- trapping
(b
PES, hν = 21,2 eV
(c
calculated
(d

Fig. 4