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FLUORESCENCE FROM $^1\Pi_u$ AND $^1\Sigma_u^+$ STATES OF MOLECULAR NITROGEN EXCITED WITH SYNCHROTRON RADIATION BETWEEN 12.4 eV AND 18.8 eV

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Fluorescence from $^1\Pi_u$ and $^1\Sigma_u^+$ States of Molecular Nitrogen excited with Synchrotron Radiation between 12.4 eV and 18.8 eV

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Abstract

Gaseous N_2 was excited with monochromatized Synchrotron radiation between 12.4 eV and 18.8 eV. Fluorescence photons with energies between 6.9 eV and 11.5 eV were monitored. The neutral states above the ionisation potential are found to decay radiatively to the N_2 ground state, but, as we suggest here, also with high probability to the N_2 ($a'^1\Pi_g$) excited state. Lifetimes between 0.2 nsec and 2 nsec were measured for selected excited states.

Introduction

Molecular fluorescence from some $^1\Pi_u$ and $^1\Sigma_u^+$ states of nitrogen has been investigated by electron impact excitation (1, 2). By dispersing the fluorescence different transitions were identified and cross-sections for electron impact were measured. The measurements reported here aim at a determination of the lower electronic level involved in fluorescence by means of a selective excitation of the upper level and applying symmetry selection rules. The fluorescence was not dispersed, but the experimental setup

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provided an energy window in the 6.9 eV to 11.5 eV region for fluorescence photons.

Experimental

Synchrotron light from the storage ring DORIS at HASYLAB (DESY, Hamburg) was monochromatized by a 1 m normal incidence monochromator in modified Wadsworth mounting (3, 4) with a wavelength resolution of 0.1 nm. The monochromatized light was focussed with a toroidal mirror onto an open aperture of a gas cell. Differential pumping allowed a pressure of 1.25 Pa (1×10^{-2} Torr) in the gas cell. Fluorescence was detected by a CsI-coated channel plate separated from the gas cell by a LiF-window. This combination served as a filter transmitting photons between 6.9 eV and 11.5 eV, only.

Photon bunches from DORIS for excitation had a pulse length of 150 psec (FWHM) (5). Repetition frequencies of 60 MHz and 10 MHz were used; they correspond to a deadtime of 16 nsec and 100 nsec between two light pulses, respectively. For the lifetime measurements a time-to-amplitude-converter (TAC) was started by the channel plate output pulse and stopped by the next bunch trigger pulse. The TAC output pulses were fed into a multichannel analyzer.

Results and Discussion

The fluorescence as a function of the wavelength of the exciting radiation is shown in figure 1 and compared with an absorption spectrum obtained by Gürtler et al. (6). These $^1\Pi_u$ and $^1\Sigma_u^+$ states below and above the first ionization potential (IP) at 15.581 eV emitting photons between 6.9 eV and 11.5 eV are listed in Tables 1 and 2, respectively.

States below the IP

The fluorescence observed here from states below the IP is attributed to a decay into vibrational states of the nitrogen ground state on the basis of its wavelength and due to the energy range accepted by the channel plate/LiF window combination. Radiation from decay to the a $^1\Pi_g$ state (T_o = 8.5489 eV (9)) and to the a" $^1\Sigma_g^+$ state (T_o = 12.254 eV (9)) cannot be detected. The $^1\Sigma_u^+$ states do not predissociate at low vibrational levels (10). The b' $^1\Sigma_u^+$ state has been reported to decay to the N_2 ground state (11, 12) and to the a $^1\Pi_g$ state (13-17). Predissociation at high vibrational levels v' = 20, 21, 22 has been reported (10).

In agreement with this observation we observe fluorescence decay to the ground state for v' = 0 - 19.

On the other hand, most of the $^1\Pi_u$ states undergo strong interaction with repulsive states leading to fast predissociation. The v' = 1, 5, 6 vibrational levels of the b $^1\Pi_u$ state have been reported (7, 8) to decay into the N_2 ground state and in the a $^1\Pi_g$ excited state. In addition, we see transitions b $^1\Pi_{g_u}$ (v' = 0,7) $\rightarrow$ $X^1\Sigma_g^+$. The c_3 $^1\Pi_u$ (v' = 0,2) states show a radiative decay into the a $^1\Pi_g$ state (18-20). Due to our energy window for fluorescence photons we cannot observe this decay to the N_2 ground state. For selected states below the IP the measured lifetimes are summarized in Table 3.

States above the IP

Most of the unidentified states of the Ogawa-Progressions (23) and the $nd\sigma_g$- and $ns\sigma_g$-Rydberg states (6) converging to the $B^2\Sigma_u^+$ ion state emit fluorescence photons with energy between 6.9 eV and 11.5 eV.

The lifetime measurements show two components: a short one with $\tau_1 \leq 5 \times 10^{-10}$ sec and a very long one with $\tau_2 >> 1 \times 10^{-6}$ sec. For the short lifetime we assume a decay into excited states with energies between 4.5 eV and 11 eV above the ground state energy. With $^1\Pi_u$ or $^1\Sigma_u^+$ symmetry for the states of the Ogawa-Progression, the lower level of the fast component could be the a $^1\Pi_g$ state or vibrational levels of the N_2 ground state with high quantum numbers (v' = 18). The states of the Ogawa-Progression and the B $^2\Sigma_u^+$ Rydberg states must have a large overlap with the zero

vibrational ground state level, as can be concluded from the large absorption cross-section (6). Consequently, the potential curves of these states must have a potential minimum not far from the ground state equilibrium internuclear distance and the repulsive part of the potential curve should cross the Franck-Condon-region. Such potential curves would also have a small overlap with v' = 18 levels of the ground state. Therefore, we propose the a $^1\Pi_g$ state as lower level for the fast radiative decay component. The a $^1\Pi_g$ state decays to the X $^1\Sigma_g^+$ ground state in $1.15 \pm 0.2 \times 10^{-4}$ sec (24). Photons of this transition fall in the right energy range and can be detected by the channel plate. We therefore assign the long fluorescence component observed after excitation of the neutral states above the IP to the a $\rightarrow$ X transition.

We cannot exclude the optically allowed decay of the a $^1\Pi_g$ state to the a' $^1\Sigma_u^-$ state. In this case, the long fluorescence component would correspond to the a' $\rightarrow$ X transition with a lifetime of 2 sec (25).

All neutral states above the IP autoionize (26). The various autoionization peaks are found to be very sharp. Dehmer and Chupka (26) report FWHM of equal or less their experimental resolution of 0.005 nm (0.7 meV). This corresponds to a lifetime of 10^{-12} sec or longer. In our fluorescence experiment we observe a decay of these states with lifetimes of less than 5×10^{-10}sec, where 2×10^{-10} sec is the experimental limit of our time resolution. This confines the range of the lifetimes for the Ogawa states to 10^{-12} sec to 10^{-10} sec.

A line shape analysis by Gürtler et al. (6) of the B $^2\Sigma_u^+$ Rydberg states resulted in half-widths between 9 meV and 41 meV corresponding to lifetimes of some 10^{-14} sec. Assuming a lifetime against radiative decay of 1×10^{-10}sec, one would hardly expect to observe fluorescence as a decay mechanism efficiently competing with an autoionization process with a lifetime in the order of 10^{-14} sec. On the other hand, these Rydberg states show up as strong peaks in the fluorescence spectrum (Fig. 1). Therefore, we assume that the total lifetime of these Rydberg states is longer than obtained from a line shape analysis in Ref. 6. The reason might be that the absorption peaks of the Rydberg states contains unresolved rotational structure.

Although autoionization is probably the most important decay mechanism, in this spectral range radiative decay of states above the IP into the a $^1\Pi_g$ state (or the a' $^1\Sigma_u^-$ state) can be clearly observed.

Wavelength resolved fluorescence experiments would be very useful to get more information of the decay channels of the high excited neutral states of nitrogen.

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Table 1

$^1\Pi_u$ and $^1\Sigma_u^+$ - states of molecular nitrogen below the first ionization potential (15.581 eV) emitting fluorescence photons between 6.9 eV and 11.5 eV. The second column gives published results (7,8).

	upper state	previous measurements
	v'	v'
b' $^1\Sigma_u^+$	1 - 19	1 - 9
b $^1\Pi_u$	0,1,5,6,7	1,5,6
c_4' $^1\Sigma_u^+$	0 - 4	0 - 4
c_3 $^1\Pi_u$	3,4	0,2
o_3 $^1\Pi_u$	2,4	-
Rydbergstates converging to the $X^2\Sigma_g^+$ ion state		
$3\sigma_g \rightarrow 4p\pi_u$	0	-
$3\sigma_g \rightarrow 5p\sigma_u$	0	-

Table 2

Neutral states of molecular nitrogen above the first ionization potential (15.581eV) emitting fluorescence photons between 6.9 eV and 11.5 eV. The values of the peak maxima are given adopting the data from Lofthus and Krupenie (9, Tab 46 b and c) and the absorption spectrum of Gürtler et al (6).

states	wavelength (nm)		assignment
unidentified states (Ogawa Progressions)	79.1 and 79.2		The symmetry of the Ogawa-Progression states is probably $^1\Pi_u$ or $^1\Sigma_u^+$
	78.60		
	78.36		
	78.15		
	77.58		
	77.15		
	76.87		
	76.48		
	76.32		
	76.1		
	75.8		
	75.43		
	74.75		
	74.4		
	73.75		
	73.3		
Rydberg states converging to the $B\ ^2\Sigma_u^+$ ion state	72.38	3(=n)	$2\sigma_u \rightarrow nd\sigma_g$ $^1\Pi_u$
	69.49	4	
	68.22	5	
	67.54	6	
	67.15	7	
	71.63	4	$2\sigma_u \rightarrow ns\sigma_g$ $^1\Pi_u$
	69.12	5	
	68.01	(6)	

Table 3

Lifetime of some $^1\Pi_u$ and $^1\Sigma_u^+$ -states of molecular nitrogen.

The error is estimated to be 15 %.

electronic state	lifetime (nsec)	previous measurements
b $^1\Pi_u$ v' = 0	0.27	
b $^1\Pi_u$ v' = 1	1.75	60[a]
c_4' $^1\Sigma_u^+$ v' = 0 and b' $^1\Sigma_u^+$ v' = 1	1.13	0.9 ± 0.2[b]
b' $^1\Sigma_u^+$ v' = 5	0.28	
c_4' $^1\Sigma_u^+$ v' = 2	0.65	
b' $^1\Sigma_u^+$ v' = 7	0.93	
o_3 $^1\Pi_u$ v' = 2	0.30	
b' $^1\Sigma_u^+$ v' = 9	0.71	
b' $^1\Sigma_u^+$ v' = 11	0.25	
b' $^1\Sigma_u^+$ v' = 12	0.25	
Rydbergstate $3\sigma_g \rightarrow 5p\sigma_u$	0.6	

a): Johnson (21) suggested that the lifetime of the First Negative System (τ = 59 nsec) was measured, which radiates in the same wavelength region.

b): Hesser and Dressler (22) gave the c_4' $^1\Sigma_u^+$ (v'=0)-state as uppel level.

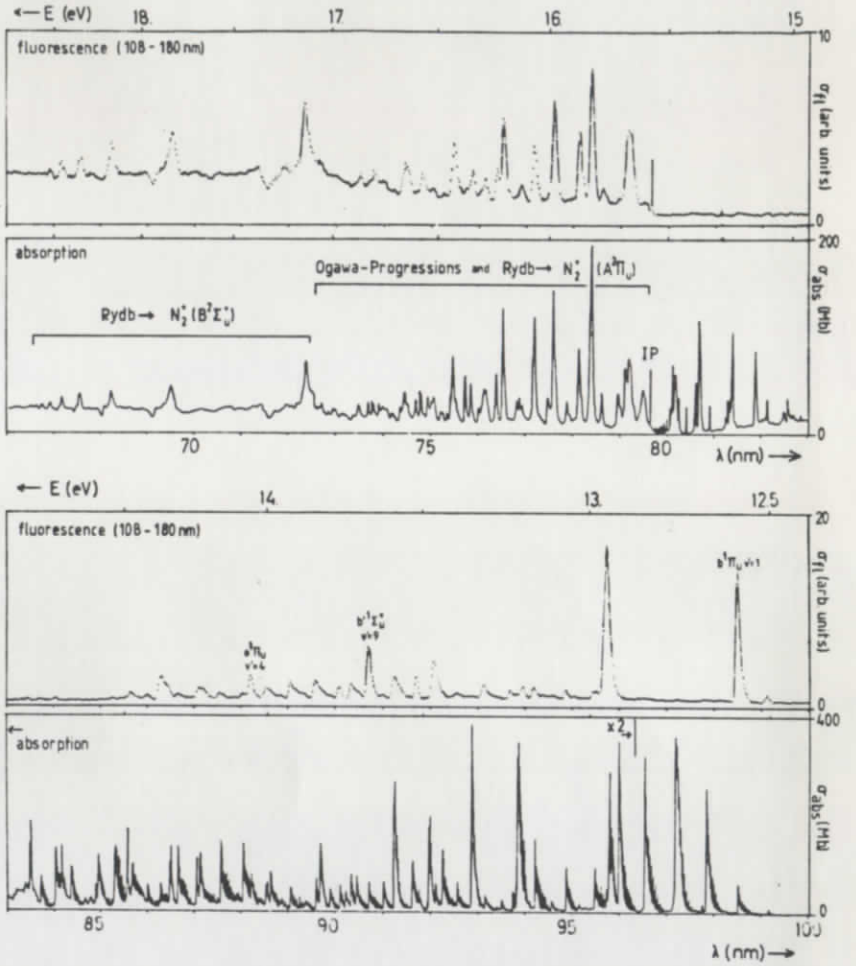

Fig. 1: Comparison between the fluorescence excitation spectrum (this work) and the N_2 absorption spectrum (6). In our experiment only photons with energies between 6.9 eV and 11.5 eV contribute to the fluorescence signal. The fluorescence spectrum is not corrected for the intensity variation with wavelength of the exciting light. For a more detailed assignment of the various absorption features, see Ref. 6.