



ELSEVIER

Journal of Molecular Structure 349 (1995) 17–20

Journal of
MOLECULAR
STRUCTURE

HIGH-VOLTAGE OPTICAL EMISSION IN BINARY GASEOUS MIXTURES OF N₂

Veysel Zengin^a, Ali Gökmen^a Sezai Dinçer^b and Şefik Süzer^c

^aChemistry Depart., Middle East Technical University, 06531 Ankara, Turkey

^bElectrical Engineering Depart., Gazi University, 06570 Ankara, Turkey

^cChemistry Depart., Bilkent University, 06533 Ankara, Turkey

Abstract

Optical emission in 1:1 binary gaseous mixtures under high voltage displays a varying character depending on pressure, applied voltage polarity, and chemical nature of the mixture. Under negative polarity, in pure N₂ and 50% mixture of Ar, O₂ and CO₂, emission stemming from N₂⁺ is enhanced relative to emission from neutral N₂. In mixtures of N₂ with gases containing halogens (CCl₄, CHCl₃, CH₂Cl₂, CF₃H, CF₂Cl₂ and SF₆) a reversal is observed, i.e. the N₂⁺ emission is suppressed. An enhancement factor is defined as the ratio of the emission under negative polarity to positive polarity to quantify this polarity dependence. This enhancement factor varies between 0.01 and 50 depending on the second component in the mixture.

Introduction

Discharges, carried out in air or even in commercial purity gases which are most of the time observed to contain impurity or trace levels of air and eventually molecular nitrogen and moisture, show optical emission due to species derived from molecular nitrogen via electron impact excitation, dissociation and ionization. This led to voluminous studies on the diagnostics of these systems using the optical emission as a tool, involving basic spectroscopic data for the interaction of electrons, ions, neutral particles with electron impact excited and/or ionized nitrogen. Optical characteristics (brightness, wavelength distribution etc.) of this glow will depend on the geometry, the chemical nature of the electrode and the surrounding atmosphere, and finally on the polarity of the applied field. It is the polarity dependence that will be focused in this contribution.

0022-2860/95/\$09.50 © 1995 Elsevier Science B.V. All rights reserved

SSDI 0022-2860(95)08698-6

Experimental

The basic components are a 40 mm diameter discharge chamber, an optical monochromator and a photomultiplier detection system. The high-voltage electrode is placed in the center of the chamber insulated via a ceramic feed-through. The tip of the electrode is also made out of stainless-steel and has a conical shape. The chamber is grounded and hence the geometry is best described as point-to-plane geometry. The gaseous mixtures are prepared by introducing each component to the desired partial pressures and several duplicate experiments are carried out to ensure reproducibility. The monochromator is Digikrom-240. The monochromator is controlled via a PC through its RS-232 connector. The photomultiplier detection system consists of a Hamamatsu R212 photomultiplier.

Results and Discussion

Figure 1 shows the spectrum of pure nitrogen under positive and negative polarities. Several features belonging to various neutral and ionic states are present in both polarities the intensities of which are functions of the applied field strength and pressure, hence it is better to analyze the dependency as V/P (V refers to voltage in units of volts and P to pressure in mbar). Notice, however, features due to the ionic states are very sensitive to the polarity of the electrode. These features are enhanced in negative polarity more than one order of magnitude. In part (c) of the figure sum of the intensities of the second positive system ($N_2 : B^3\Pi_g(v'') \leftarrow C^3\Pi_u(v')$) transitions are plotted against applied voltage divided by pressure (V/P) at both polarities on a log-log scale. The numbers in boxes refer to measured pressures. The expected linear relationship is easily depicted and the variation is independent of the polarity. In part (d) of the figure the sum of intensities belonging to N_2^+ of the first negative system ($N_2^+ : X^2\Sigma_g^+(v'') \leftarrow B^2\Sigma_u^+(v')$) are plotted in a similar manner. Although the voltage/pressure dependence is similar, there is a large difference between negative and positive polarity. The intensity of the lines belonging to ions are more than one order magnitude stronger under negative polarity. This enhancement persists in Ar+N₂ mixtures (Figure 2 (a)) but is much less pronounced and sometimes reversed in gases containing fluoro-chloro hydrocarbons (Figure 2 (b)).

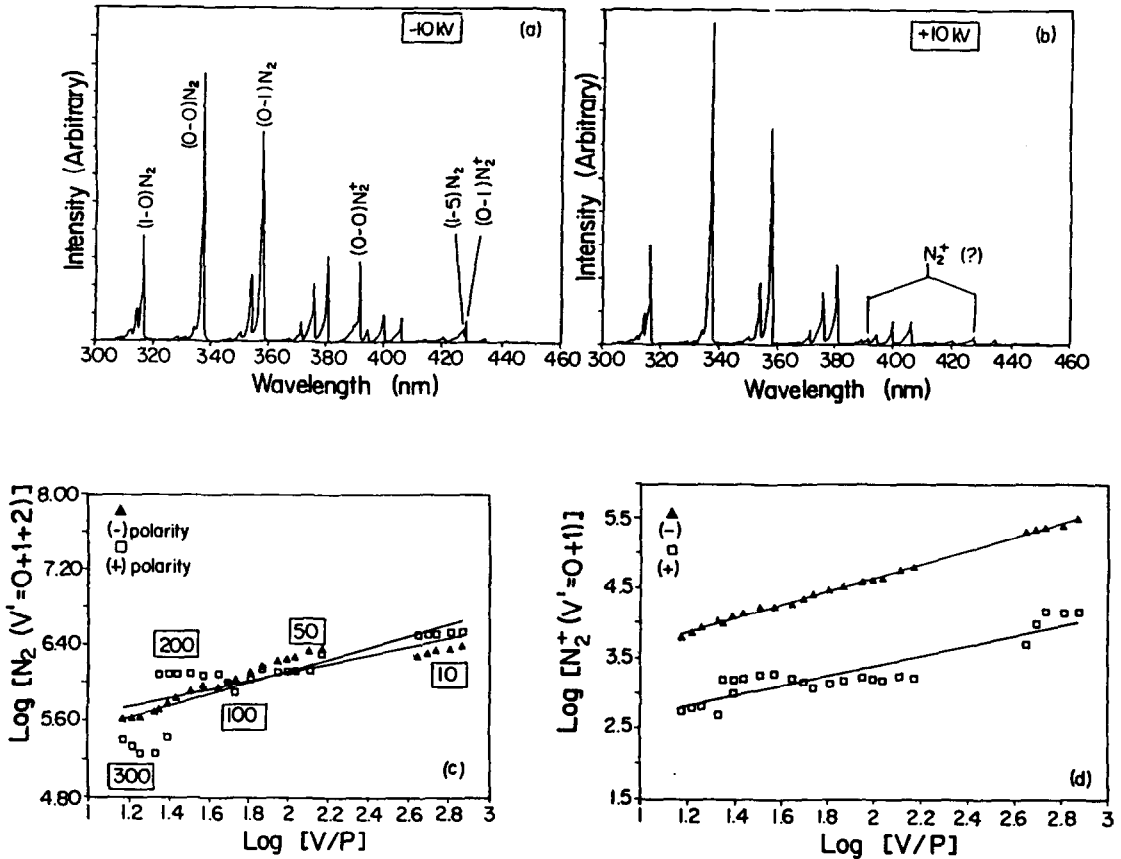


Figure 1. Optical emission spectrum of 300 mbar N_2 at (a) -10 kV and (b) at +10 kV. In part (c) of the figure sum of the intensities of the neutral lines at both positive and negative polarities are plotted against V/P on a log-log scale. The numbers in boxes refer to pressures in mbar. In part (d) lines belonging to N_2^+ at both polarities are plotted.

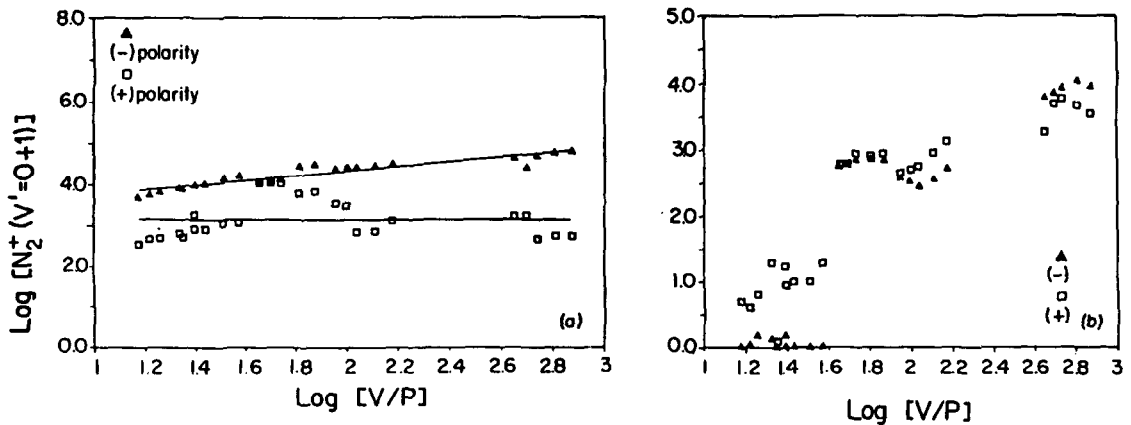


Figure 2. Sum of the intensities of the lines belonging to N_2^+ are plotted against V/P under both negative and positive polarities on a log-log scale for mixtures containing N_2 and (a) 50% Ar, (b) 50% CF_2Cl_2 .

We define an enhancement factor EF to quantify the polarity dependence of various gaseous mixtures. $EF = \text{Opt. Int. at (-) Polarity} / \text{Opt. Int. at (+) Polarity}$. The enhancement factors (and other related parameters) are given in Table I and vary between 0.1 and 5 for neutral N_2 emissions but the variation is much larger (between 0.01 and 50) for N_2^+ emissions. It is well known in gaseous dielectric studies that, due to formation of space charges in negative point-to-plane electrodes, the effective field value decreases so as to retard the breakdown of the dielectric medium whereas this space charge is absent in positive point-to-plane electrodes¹⁻³. In mixtures containing halogens (gaseous dielectrics) most of the electrons are slowed down or replaced by the heavier negative fragment ions hence production of highly excited or ionic species are retarded via electron impact.

References

- 1- L.G. Christophorou and L.A. Pinnaduwege, *IEEE Trans. Elec. Insul.* 25, (1990) 1.
- 2- T. Hibma and H.R. Zeller, *J. Appl. Phys.* 59, (1986) 1614.
- 3- M. Iwamoto, M. Fukuzawa and T. Hino, *IEEE Trans. Elec. Insul.* 22, (1987) 419.

Species	IP(a,d)	EA(a)	σ (b)	E.F.(c)		[$N_2^+(0-1)/N_2(1-5)$]	
				N_2^+	N_2	(-)Polarity	(+)Polarity
N_2+N_2	15.58	-1.6	-	25	1.5	1.2	0.08
N_2+Ar	15.76	-1	-	50	5	1.4	0.08
N_2+CO_2	13.77	3.8	2×10^{-18}	15	1.2	1.6	0.3
N_2+O_2	12.06	0.44	2×10^{-17}	4	1.5	1.5	0.6
$N_2+CF_2Cl_2$	12.3		5.4×10^{-17}	1	1	0.3	0.8
N_2+CF_3H	12.85	1.46	-	0.6	0.7	0.24	0.75
N_2+SF_6	15.67	1.43	1.3×10^{-15}	0.01	0.1	0.05	0.18
N_2+CCl_4	11.47	2.12	1.3×10^{-16}	0.5	1.3	0.4	0.8
N_2+CCl_3H	11.42	1.75	3.66×10^{-16}	0.5	0.8	0.4	0.85
$N_2+CCl_2H_2$	11.35		1.48×10^{-18}	0.5	1	0.4	0.8

(a) Ionization Potential Values (eV) are for the second component in the mixture, (b) Electron attachment cross sections ($cm^2/molec$), (c) Enhancement Factor, (d) CRC Handbook of Physics and Chemistry 67th Ed. 1987, CRC Press Inc., Boca Raton, Florida