ATOMIC AND MOLECULAR BEAMS FROM ELECTRICAL DISCHARGES: THEIR CHARACTERIZATION AND APPLICATIONS USEFUL FOR PLASMA DIAGNOSTIC AND CHEMICAL MODELING

B.Brunetti*, D.Cappelletti, S.Falcinelli*, G.Liuti, and F.Pirani*

*Istituto per le Tecnologie Chimiche, Facoltà di Ingegneria
Università di Perugia, 06123 Perugia,   ITALY*

**Dipartimento di Chimica, Università di Perugia
06123   Perugia,   ITALY*

Abstract
A plasma diagnostic technique is reported based on magnetic analysis of molecular beams. The case of metastable nitrogen molecules is considered in more detail together with scattering data with xenon. The possible use of atomic and molecular beams for the clean-up of metal surfaces is suggested.

Introduction
The knowledge of weak intermolecular interaction features, usually determined by the parameters of an intermolecular potential, is among the critical information necessary for many modeling computations in complex systems such as plasmas, lasers, combustions, atmospheric chemistry and physics.

The molecular beam scattering technique is one of the most powerful experimental methods to obtain information on the intermolecular potential. In the last two decades dramatic improvements have been achieved in beam scattering studies of atoms, other than rare gases, and metastable species with various molecules and with surfaces. An interesting experimental

development is the characterization of a beam containing paramagnetic particles by magnetic analysis [1]. As the beam is produced from an electrical discharge in molecular gases, it is necessary to characterize its composition because several atomic and molecular species may be present in different electronic excited states. These atoms and molecules may therefore show different paramagnetism. The characterization of a beam containing paramagnetic particles is performed using a Stern-Gerlach magnetic selector inserted along the beam path. The analysis of the beam transmittance performed as a function of the magnetic field strength and of the beam velocity allows an identification of the various species living at different times after they have left the beam source. Therefore magnetic analysis of a beam is a powerful and quite general plasma diagnostic technique.

In this work we will use this method for the diagnostics of discharge generated plasmas in N_2 and O_2 and we will also present the results of scattering experiments of metastable N_2 with xenon [2]. Also it will be suggested the possibility of using discharge generated atomic beams, such as H or O, to restore to original conditions metal surfaces modified either by oxidation or by coating with organic chemicals under mild and at the same time strictly controlled conditions, especially regarding the size of the interaction area.

Apparatus

The experimental apparatus where beam diagnostic and the scattering experiments have been performed is basically the same used over the years for magnetic analysis of various open shell atomic beams and for the study of the interaction of many systems [2] (Fig. 1).

For N_2, the beam containing the metastable nitrogen molecules is produced from a microwave discharge in an approximatively 50% He-N_2 mixture at about 800 Pa total pressure. Some experiments were carried out using pure nitrogen at the same total pressure to extend the measurements to a wider velocity range and for signal comparison especially regarding N_2^* detection.

For O_2, the beam containing the metastable oxygen molecules is produced in the same discharge in pure oxygen at about 300 Pa.

The beam is velocity selected with a resolution of ~5% fwhm and the velocity distribution appears to be slightly supersonic for both N_2 and O_2 allowing beam diagnostics in a satisfactorily wide velocity range, which for

N_2 is between about 0.9 km·s^{-1} and 1.90 km·s^{-1} and for O_2 between 0.47 km·s^{-1} and 1.45 km·s^{-1}.

As usual, beam detection is performed by a quadrupole mass spectrometer kept in a ultra high vacuum chamber. For detection of N_2^* the mass spectrometer ionizer is kept off and the metastable species are detected by electron ejection from the mass spectrometer ion collector following the impact of the excited particles. This is possible considering the relatively high energy of the lowest metastable state of N_2 (6.2 eV) and the similar electron ejection efficiency of different metals when hit by energetic particles. For O_2 detection the usual mass spectrometric operating conditions are used.

Plasma diagnostics

In electrical discharges electronically excited and long lived states of atoms, molecules and radicals can be produced. As will be shown, the present experimental technique is relevant for the diagnostic of discharge generated plasma.

The characterization of a beam containing paramagnetic particles is performed using a Stern-Gerlach magnetic selector in Rabi configuration, inserted along the beam path. The action of an inhomogenous field on a beam composed of paramagnetic particles of the same mass and velocity is to induce different deflection of these particles, depending on the values of their effective magnetic moments. Accordingly the measured beam transmittance, defined as the ratio between the beam intensity with and without the magnetic field I_B/I, is determined by the effective magnetic moments which are strongly dependent on the electronic state of the molecule. The analysis of the beam transmittance performed as a function of the magnetic field strength and of the beam velocity should allow an identification of the various species living at different times after they have left the beam source.

In the case of a He-N_2 discharge, nitrogen can be present in the beam excited to several different long lived metastable states. Under the conditions of the present experiment these include the A $^3\Sigma^+_u$, W $^3\Delta_u$ and A' $^5\Sigma^+_g$ states. Other possible excited N_2 molecules are less important either because they are in small concentration or because their lifetimes are too short; metastable nitrogen atoms can also be present although not relevant in the present case because their energy is too low for detection. In Fig. 2 the beam transmittance measured as a funtion of the magnetic field strength obtained at three selected beam velocities is shown. By measuring the change in concentration of the A' $^5\Sigma^+_g$ it has been possible to evaluate a mean collision

free lifetime of $4.5\pm1\cdot10^{-4}$ s for this state. It should be emphasized that this value is not in disagreement with values previously obtained [2] and that it has been measured by completely different methods from those usually adopted for this kind of measurements.

The technique has been applied to the analysis of a superthermal beam of O_2 molecules produced in a microwave discharge at a source temperature of about 900 K. Typical beam transmittance results are shown in Fig. 3; the presence of a certain amount of the metastable $^1\Delta_g$ state in the superthermal beam can be reveald because its paramagnetic character is quite different from that of the $^3\Sigma^-_g$ state. An estimated concentration of 15% of the metastable molecule can be estimated. This estimated value holds at all the studied beam velocities in agreement with the known long lifetime of the metastable state.

Scattering data and interaction potential for N_2^*-Xe

The magnetically analyzed beam can be used to perform scattering experiments. As usual the cross section is measured by the attenuation of the velocity selected beam in a scattering chamber filled with xenon kept at a pressure of about 0.1 Pa and cooled at solid air temperature to decrease the averaging effect on glory oscillation due to the thermal motion of the target gas. It is interesting to note that it is possible to measure ground state nitrogen-xenon cross sections under the same experimental conditions by just switching the mass spectrometer ionizer on, focussed on the nitrogen mass. Therefore the ratio of N_2^*-Xe to N_2-Xe cross sections can be given with high accuracy. The absolute cross sections are obtained by internal calibration based on a flow method and on the absolute value of He-Ar total cross section. The data show several well developed high frequency glory extrema in both systems. As it is well known, from these direct information on the potential well features can be obtained. For the data analysis we employ the usual parametrization for the interaction potential and standard computing techniques for the calculations. From the analysis the long range effective dipole-dipole constant C_0, the well depth ε and location R_m are obtained. They are reported in Table 1 for both systems. In addition, from the potential parameters ε and R_m and from the ratio of the long range constants it is possible to extract the average polarizability of N_2^* using the recently developed correlation formulas between potential parameters and polarizabilities of interacting partners [3]. A value of 2.2 ± 0.1 Å^3 is obtained.

Table 1   Potential parameters for N_2 (X $^1\Sigma^+_g$)-Xe and N_2 (A $^3\Sigma^+_u$)-Xe

	N_2 (X $^1\Sigma^+_g$)-Xe	N_2 (A $^3\Sigma^+_u$)-Xe
ε (meV)	13.70	21.70
R_m (Å)	4.05	4.20
C_0 (meV Å^6)	$1.07 \cdot 10^5$	$1.23 \cdot 10^5$

Atomic beam scattering from surfaces

It is known that treating corroded metals inside a low pressure hydrogen plasma removes efficiently surface oxides and chlorides. This technique has been applied to the restoration of metal artifacts [4]. The treatment proposed here consists in exposing the metal surface, positioned inside a vacuum apparatus, to a beam containing H atoms or, if cleaning of the surface from organic coatings has to be achieved, to a beam containing O atoms. This method has some positive features. First, since the beam contains atoms mostly in the ground state, small concentrations of excited atoms and molecules and negligible concentrations of charged particles, the treatment is generally very mild. Furthermore and more important, since the beam size can vary between less than one millimeter to a few millimeters, the treatment can be localized on a specific site of the surface. Tests have been performed in an apparatus basically similar to the one shown in Fig. 1. The sample, either an oxide coated metal surface or an araldite coated surface, is positioned at about 2 mm from the beam source and is exposed to a beam containing respectively H atoms or O atoms. Significant changes of the surface are observed especially regarding the weight loss in the case of araldite removal. In conclusion we feel that this technique represents a significant extension of the use of a weak plasma.

References
[1] V.Aquilanti, D.Ascenzi, D.Cappelletti, and F.Pirani *J.Chin.Chem.Soc.* (1995) in press.
[2] D.Cappelletti, G.Liuti, E.Luzzatti, and F.Pirani *J.Chem.Phys.* **101**, 1225 (1994).
[3] R.Cambi, D.Cappelletti, G.Liuti, and F.Pirani *J.Chem.Phys.* **95**, 1852 (1991).
[4] J.Patscheider and S.Veprek, *Studies in Conservation*, **31**, 29 (1986).
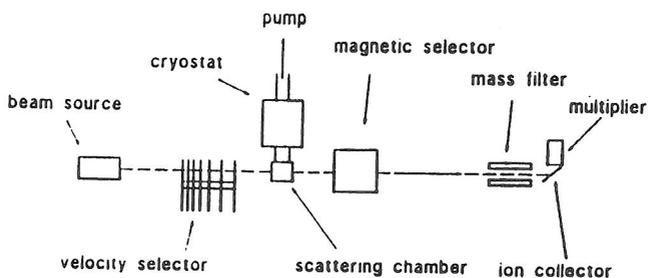
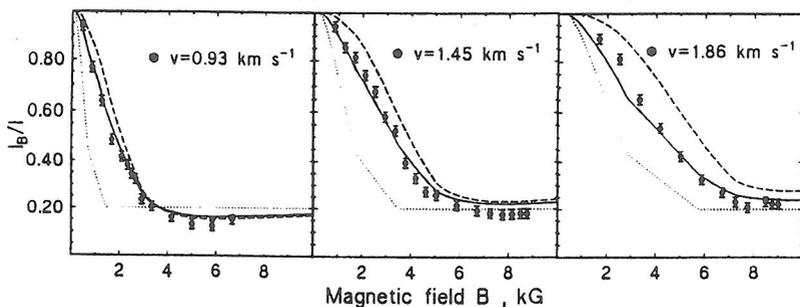FIG. 1. Schematic view of the apparatus used in the present experiments.

FIG. 2. Transmittance of the N_2^* molecular beam at three velocities. The dashed and dotted curves represent the transmittance of a beam composed by A $^3\Sigma_u^+$ N_2 molecules (dashed) and by A$'$ $^5\Sigma_g^+$ N_2 molecules (dotted). The continuous curves are the best fit ones obtained from those of pure A molecules with an increasing concentration of A$'$ molecules.
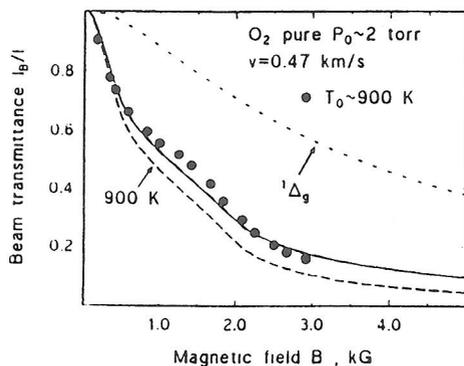

FIG. 3. Transmittance of the O_2 beam. The long dashed and dashed curves are the transmittances of a beam composed of 100% $^3\Sigma_g^-$ and $^1\Delta_g$ O_2 molecules respectively. The full line is the best fit calculation with a concentration of 15% of the $^1\Delta_g$ state in the beam.