

**Screenplay for the 2nd Practical Task: Analysis by FTIR Spectroscopy
(Fourier Transform Infrared Spectroscopy - Infrared spectroscopy by Fourier Transform)**

1. INTRODUCTION

Materials such as water, carbon monoxide, carbon dioxide, methane and ammonia are very abundant in the universe and are often in the form of interstellar grains or condensed on the surface of comets and satellites of the solar system. Mixtures of these astrophysical gills are under permanent bombing by stellar winds and cosmic radiation, causing erosion and chemical reactions.

One of the most plausible hypotheses for the origin of life is based on the processes of chemical evolution, according to which chemical reactions promoted a gradual increase in the complexity and organization of the substances that make up living beings, resulting in the generation of increasingly complex organic molecules, with the end result its life itself. Therefore, to test the validity of this hypothesis, one should show how from simple inorganic substances supposedly existing at the time of formation of our planet or in planetary atmospheres, more complex substances of biological interest, such as amino acids and sugars, can be synthesized. Using a gas mixture composed of CH_4 , NH_3 , H_2 , H_2O along with electric discharges to simulate rays in the atmosphere it was possible to produce amino acids and other complex organic compounds.

The data to be analyzed in this task were obtained in experiments performed in the laboratory with the N_2O molecule using analysis techniques to determine the modifications in the concentration of chemical species on nitrous oxide ice. Infrared spectrometry was employed by Fourier Transform (FTIR). The analyzes were performed at the CDAP (Recherche Sur Les Ions, Les Matières et La Photonique) laboratory that operates next to the Ganil (Grand Accélérateur National D'Ions Lourds) laboratory located in Caen, Normandy, France.

2- Infrared spectroscopy

Infrared spectroscopy is based on the observation that chemical bonds have specific frequencies to which they vibrate, at well-defined energy levels. These vibration frequencies, or resonance frequencies, are determined by the form of the molecule, their energy levels and the mass of the atoms that constitute it. The resonance frequencies of a chemical connection are related, in the first approach, with the force of the connection and the mass of the atoms at each end. Thus, each vibration frequency may correspond to a specific type of chemical bonding.

The vibration of atoms inside a molecule has energy consistent with the region of the electromagnetic spectrum corresponding to the infrared (100 to 10000 cm^{-1}). A normal vibration mode is one in which each nucleus performs a simple harmonic oscillation around its equilibrium position. Atoms in a molecule are never immovable. In practice, the number of normal vibration modes does not always correspond to the number of bands observed in the spectrum. This is due to the existence of vibrations of the same energy (degeneration), presenting the same frequency and, consequently, the same position in the spectrum.

2.1 - Fourier's transform spectrometer

When infrared radiation crosses the sample to be analyzed, the transmitted radiation is compared to the one obtained in the absence of sample. The spectrometer records the result in the form of an absorption band. The band intensity is measured by transmittance or absorbance. The transmittance is defined by the ratio between the transmitted energy and the energy incident in the analyzed sample and the absorbance is the logarithm at base ten of the reciprocal of transmission:

$$T = E_t / E_i \quad A = \log 1 / T \quad \text{eq. 1}$$

The possibility of two different compounds having the same infrared spectrum is unlikely. For this reason, each organic function presents a “fingerprint” region in the spectrum in the range 500 – 4000 cm⁻¹. A highly sensitive spectrometer is the Fourier transform spectrometer (FTIR), which employs a Michelson interferometer[3]. With this spectrometer it is possible:

- i) identify the new chemical species formed in the annealing of condensed water;
- ii) determine the rates of synthesis and formation of organic compounds;
- iii) characterize the spectroscopic optics of thin films of new organic compounds.

2.2 – N₂O Vibrational Modes

N₂O has a certain degree of importance in the greenhouse effect, as its three main vibrational modes are active in the infrared to some degree, which makes it capable of absorbing and “scattering” the heat resulting from infrared radiation originating from the Earth, before it escapes into space. The N₂O molecule is linear and its characteristic vibrations are very similar to those of CO₂. The vibrational modes shown in figure 1 are based on measurements by infrared spectroscopy.

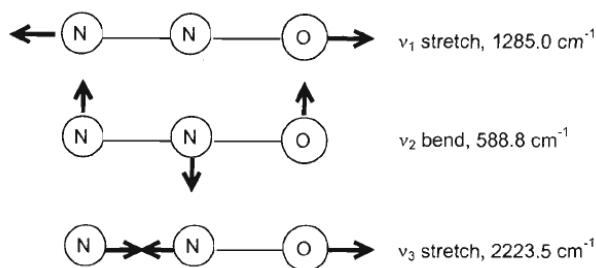


Figure 1 - Main Vibrational Modes of N₂O with the absorption peak values for the gas phase.

3-Experimental Procedure

We use a sample mixtures system (Figure 2), a Fourier transform spectrometer in the infrared (FTIR) and a computer for data analysis obtained by the FTIR. In the analysis of the spectra, the OMNIC® programs were used, which processes the data obtained in the FTIR and performs its In-Situ analysis, removing the initial background before the measurements, and for the elaboration of the graphs and spectra analysis was used the Origin® program.

In order to simulate the astrophysical environment, the yines were formed in ultra high vacuum cameras coupled to the Irrsud light lines on the ganyl heavy ion accelerator, from the condensation of gas on previously cool surfaces for 10 k -order temperatures. Infrared spectroscopy of irradiated molecules), allows to regulate the temperature of the sample between 11 and 300 k, radiate it with heavy ions and perform infrared absorption measures in transmission. It is composed of:

- (i) a creature with a sample holder and temperature sensors that allow the control of the sample temperature;
- ii) a gas and
- iii) a vacuum chamber where the samples are radiated and analyzed. As shown in the scheme of Figure 2 below.

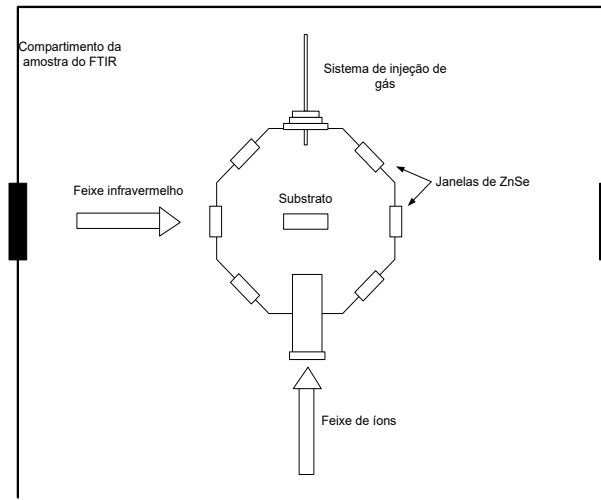


Figure 2.

Gas samples are deposited on a polished Znse surface (transparent to infrared) previously cooled to 11 K. The ice are bombarded by heavy ion beams with 1 and 10 MEV/U energies. In-Situ analyzes will be performed by an infrared spectrometer by Fourier Transform (FTIR) in different ions fluories. Further details of the experimental step can be seen in the work published by the group previously [attached literature].

From the evolution of spine density (abundance) obtained by infrared spectrum analysis, dissociation shock sections and sputtering rates for different molecular species will be determined. The presence of new peaks in the spectra go according to fluency when compared to previous studies will indicate the formation of new species on ice due to irradiation. To confirm and quantify complex organic species, after irradiation and subsequent slow heating of samples to room temperature, organic waste will be analyzed former SITU by chromatographic techniques according to protocols employed in similar investigations.

Molecular column density (n) in the sample (molecules/cm²) is another factor that determines the intensity of the band. The equation that relates column density to absorbance is given by the expression:

$$N = \frac{2,3}{A} \int (\alpha) d\kappa \quad \text{eq. 2}$$

where the integral is performed at the corresponding spectral band wavelength. In equation 2 quantity A is called integrated absorbance in cm/molecule (or simply a-value). It is a fundamental physical property of the molecule that depends on $(\partial m / \partial r)^2$. Integrated absorbance is an absolute measure of absorbance to a given molecule in a specific wave number. For example, CO₂'s antisymmetric vibration produces a band at 2345 cm⁻¹ whose integrated absorbance is worth 7.6 x 10⁻¹⁷ cm/molecule. The deformation vibration of the CO₂ molecule (660 cm⁻¹) has an integrated absorbance of 1.1 x 10⁻¹⁷ cm/molecule.

4- Dinâmica da densidade de coluna de gelos irradiados em vácuo

Be a flow beam ϕ (number of projectiles per unit area and per unit of time) by focusing perpendicularly on a layer of ice of thick x and density ρ . The column density is defined by $N = \rho x$ and is generally expressed in molecules by cm². Fluency f (number of projectiles per unit area) is defined by $F = \phi \Delta t$ where Δt is the duration of irradiation.

Soon,

$$\frac{dN}{dt} = \phi \frac{dN}{dF} \quad \text{eq. 3}$$

Among the various ice-induced processes by irradiation of energy ions stand out the destruction of the molecule, sputtering (desorption) of the surface and chemical reactions. The first two processes contribute to the reduction of the abundance of the molecule on ice while the latter is related to the formation of new molecular species. The term molecular destruction is related to the “disappearance” of the molecule on ice, either by dissociation or by synthesis of another molecule (in the case of carbon monoxide: $\text{CO} + \text{O} \rightarrow \text{CO}_2$). Both destruction and molecular bundles formation are characterized by shock sections (σ_d e σ_f respectively) that represent the probability in which such processes may occur by passing the ion. Each projectile removes an average number γ of target molecules called desorption performance, which produces a crater whose typical dimension (radius or depth) is given by length δ .

These will be the parameters we will study in the next classes.

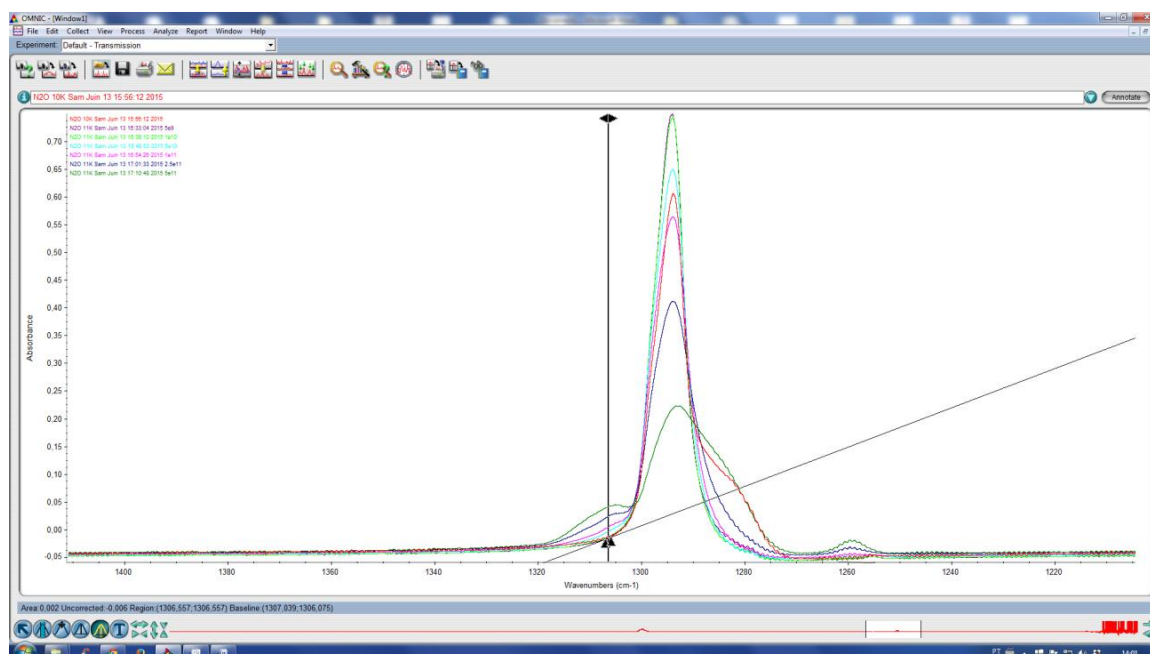
ROAD MAP

Analysis in the OMNIC program of N_2O data radiated with XE to 90 MEV.

1) Using the OMNIC program:

- Open the spectrum without radiating to determine the thickness of the movie formed.
- eliminate the noise range and correct the baseline (delete the previous spectrum).
- Choose the 3 peaks contained in the Fulvio-2009 article [5] (Table 4). Determine their area and calculate the column density using the A-Value of the table and the EQ. 2.

Note: The third most intensity band of the N_2O (589 cm^{-1} ν_2) was not analyzed in Fulvio [5].



2) Determination of ice thickness

As this value determines the thickness of the ice with the excel file - Ref. [7]:

| Dose | |
|-----------------|----------|
| Se (keV/μm) | 4.0 |
| ρ (g/cm³) | 0.500 |
| M (g/mol) | 16.042 |
| F (ion/cm²) | 1.40E+16 |
| dose (eV/molec) | 29.84 |
| dose (MGy) | 179.43 |

| Thickness of the sample (l) | |
|-----------------------------|----------|
| N (molec/cm²) | 1.45E+18 |
| M (g/mol) | 44.000 |
| ρ (g/cm³) | 1.170 |
| l (μm) | 0.91 |

| Wavenumber / wavelength converter | |
|-----------------------------------|------|
| Wavenumber (cm⁻¹) | 4527 |
| Wavelength (μm) | 2.21 |

| Initial Cross Section / G converter | |
|-------------------------------------|----------|
| Se (keV/μm) | 4908.0 |
| ρ (g/cm³) | 0.800 |
| M (g/mol) | 17.031 |
| σ (cm²) | 6.44E-14 |
| G (molec/100 eV) | 3.71 |

| Rate of Adsorption | |
|----------------------|----------|
| sticking probability | 1.0 |
| pressure (mbar) | 1.00E-06 |
| molecule mass (kg) | 2.99E-26 |
| Temperature (K) | 300 |
| R (molec/cm²/s) | 3.58E+14 |

| Thickness from interference fringes | |
|-------------------------------------|--------|
| v1 - v2 (cm⁻¹) | 19.000 |
| n | 1.200 |
| l (μm) | 219.30 |

| density converter | |
|-------------------|----------|
| ρ (g/cm³) | 0.800 |
| M (g/mol) | 17.031 |
| ρ (molec/μm³) | 2.83E+10 |

| Beam Current / Flux converter | |
|-------------------------------|----------|
| Beam Current (nA/cm²) | 30.0 |
| Charge state | 18 |
| Flux (ion/cm²/s) | 1.04E+10 |

| Molar Masses | |
|--------------|--------|
| CH4 | 16.042 |
| NH3 | 17.031 |
| H2O | 18.015 |
| CO | 28.010 |
| CH3OH | 32.040 |

a) Use for such determination the density of N2O to 11K given in Fulvio 2009 article. Make this calculation for the 3 bands of the article with A-Value.

b) As these values check through the SRI program (seen in the previous class) as the beam behaves in a KEV/microns unit.

We will know through these data whether or not the beam has been implemented in the sample.



3) Band analysis for the unredded sample (father bands) and the correspondent for irradiation in the various fluencies

3.1- Identify through the omnic program the peaks of the data below (not irradiated sample) and check with those described in Fulvio 2009 [5] - Table 3. What are the corresponded substances? What can we classify as contaminants? Note: Search the bands that are not in the table in the literature.

Bands for the peaks at: 589, 1166, 1295, 2239, 2581, 3380, 3706

3.2 -Determine the areas of the bands corresponding to these peaks.

3.3 - Determine the areas of the bands corresponding to these peaks to the various irradiation fluencies.

3.4 - Make the graphs with these values in the Origin Program:

3.3.1 - Chart area x fluency

3.3.2 - Column density chart (n) x fluency

3.5 - Compare the results obtained from the graphics with the work of Fulvio 2009 [5], Figure 4B of the article.

4) Child band analysis for the sample irradiated with various fluency values

4.1- Identify through the Ominic program the evolution of the bands with the peaks given below, from the sample not radiated to irradiation with the highest fluency value. What are the corresponded substances?

Bands Son for the peaks at: 781, 1040, 1702, 1718, 2139

4.2 - Determine the areas of the bands corresponding to these peaks.

4.3 - Make the graphs with these values in the Origin Program:

4.3.1 - Chart area x fluency

4.3.2 - Column Density Chart (n) X Fluency

5) Prepare and deliver task report.

RERERENCES:

1 – OMNIC software

2 – SRIM / TRIM software

3 – Origin Software

4 - Fulvio, D. et all – **Novel measurements of refractive index, density mid-infrared integrated band strengths for solid O₂, N₂O, and NO₂:N₂O₄ mixtures.** Molecular and Biomolecular Spectroscopy. Spectrochimica Acta, 2009. p.1007–1013.

5 - Molecular and Biomolecular Spectroscopy. Spectrochimica Acta, 2009. p.1007–1013.

6 - Ices calculations dose v1 Bordalo – Planilha

7 - Catalogo NIST (National Institute of Standards and Technology) disponível no Livro de Química na Web.

8 - Corey S. Jamieson, Chris J. Bennett, Alexander M. Mebel and Ralf I. Kaiser - **Investigating The Mechanism For The Formation Of Nitrous Oxide[N₂O(X 1₊)] In Extraterrestrial Ices.**The Astrophysical Journal,624:436–447,2005 May 1.

9 - Andrzej Lapinski, Jens Spanget-Larsen, Jacek Waluk, and J. George Radziszewski - Vibrations of nitrous oxide: **Matrix isolation Fourier transform infrared spectroscopy of twelve N 2 O isotopomers.** The Journal of Chemical Physics 115, 1757 (2001); doi: 10.1063/1.1383031.

10 - S. Ioppolo, G. Fedoseev, M. Minissale, E. Congiu, F. Dulieu and H. Linnartz* - **Solid state chemistry of nitrogen oxides – Part II: surface consumption of NO₂.** Royal Society of Chemistry - Phys.Chem.Chem.Phys., 2014, 16, 8270.

11 - Perry A. Gerakines and Reggie L. Hudson - **First Infrared Band Strengths For Amorphous Co₂, An Overlooked Component Of Interstellar Ices.** Astrochemistry Laboratory, NASA Goddard Space Flight Center, Greenbelt, MD 20771 USA. published 2015 July 28.