

Experimental determination of ice sublimation energies

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Abstract

Current models about chemical evolution, both in planetary atmospheres and in pre-stellar clusters, need the knowledge of the release rate of certain substance to the atmosphere under study. Then, it is necessary to know the temperature at which occurs this process, as well as the energy involved. In this work we present the procedure used in our laboratory to determine the sublimation energy of different ices of astrophysical interest and the values obtained for CO₂.

1 Introduction

In Astrophysics, the study of ices is important due to the wide range of scenarios in which they are present. Their physical and chemical characteristics play an important role in the study of the interstellar medium (ISM). The assessment of the energy of sublimation allows us to improve our understanding of physical and/or chemical processes that take place where ices are present.

The energy of sublimation E_{sub} is defined as the change of energy between solid and gas phase of certain molecule. This value is important to determinate other thermodynamical parameters such as the reticular energy of ionic compounds, the energy of formation in gas phase from the energy of formation in condensed phase, or to estimate the sublimation rate, which is very important in determining the evolution of surfaces of astrophysical objects.

2 Experimental setup

The basic components are a high vacuum and low temperature system, a QCM, two lasers and a quadrupole mass spectrometer (QMS)[1]. The main component is a high vacuum

chamber ($P \leq 10^{-7}$ mbar) whose pressure conditions are obtained with a rotary pump ($\sim 10^{-3}$ mbar) backing a turbomolecular pump. A closed-cycle He cryostat acts as a cryopump providing a pressure in the chamber below 10^{-7} mbar.

In thermal contact of the cryostat second expansion stage (called cold finger) is located a sample holder that bears a QCM (gold plated surface) in thermal contact with the cold finger. Using a temperature controller (Oxford Instruments) it is possible to set the QCM at any temperature within the interval from 10 to 300 K or a ramp of temperature at a constant rate.

The gas coming from a pre-chamber enters the chamber and accretes onto the QCM. Its resonant frequency suffers a damping by the presence of a rigid attachment of mass to the gold surface. Assuming a thin, uniform, rigidly attached mass, the Sauerbrey Equation [2] relates the frequency to the mass loading through the expression: $\Delta f_0 = -S\Delta m$, where S is the Sauerbrey constant.

3 Experimental procedure

The experimental procedure is based in the following steps: firstly, cooling down the chamber up to the desired temperature of deposition (T_d); secondly, after T_d is stabilized for around two minutes, the ice is deposited for one minute (causing a sudden decrease of the frequency of QCM at constant temperature); thirdly, once the deposition is completed, the power supply is turned on and the system is warmed at constant rate of 1 K min^{-1} , until the ice is completely released from the sample-holder.

Sublimation can be considered as a desorption of a multilayer film from a surface, therefore the desorption kinetics are essentially independent of the coverage, i.e. as the surface molecules sublime, more molecules underneath are exposed. Consequently, the number of molecules in the interphase film-air remains constant. Therefore, the sublimation can be modelled as a zeroth-order desorption process described by the Polanyi-Wigner Equation:

$$r_{\text{des}} = -A \exp\left(-\frac{E}{RT}\right) n^0, \quad (1)$$

where A is the pre-exponential factor for sublimation, R is the constant of ideal gases, E is the activation energy barrier for sublimation, T is the temperature of the sample and n is the number of molecules on the surface.

From a graphical point of view, this kind of process displays a behavior characterized by an increase of the desorption rate exponentially with T , and a rapid drop when all molecules have desorbed. These features are shown in Fig. 1, which represents the derivative of the experimental frequency obtained from the QCM signal against temperature for CO_2 .

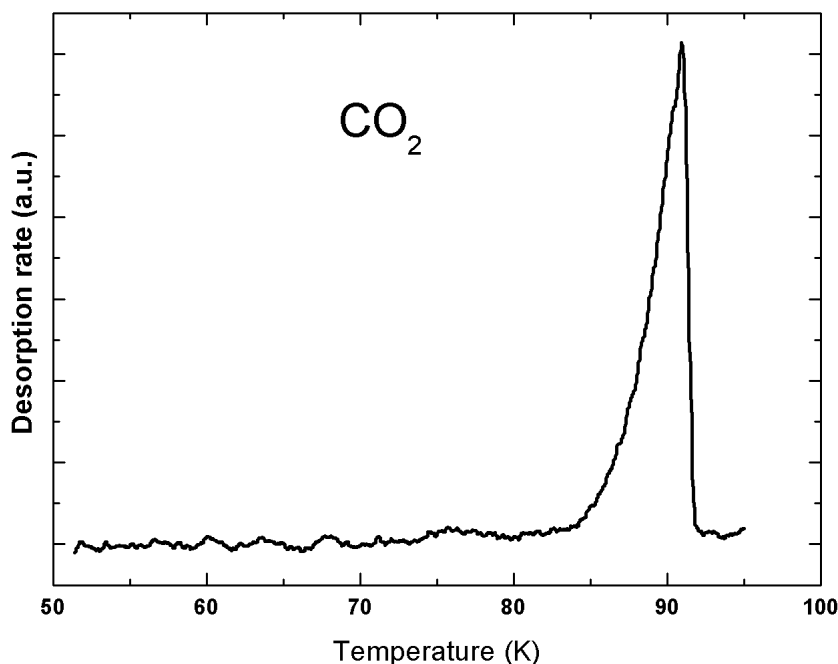


Figure 1: Experimental desorption rate (derivative of frequency signal of QCMB) versus T of CO_2 showing a typical zeroth-order desorption process.

4 Results and conclusions

These experiment of sublimation proceeds with approximately zeroth-order kinetics. Therefore, from Eq. 1 it is possible to infer that plots of $\ln(r_{\text{des}})$ versus $1/T$ from the QCMB signal during sublimation are linear (see Fig. 2). From the slope of linear fit to the experimental values we obtain the sublimation energy. For CO_2 we obtain $\Delta E_{\text{sub}} = 29.3 \pm 0.2 \text{ kJ mol}^{-1}$

This value is very close to that of bulk ice which can be found in the National Institute of Standards and Technology (NIST), despite the energy of sublimation has been obtained, in this case, at different temperatures from ours.

The procedure we have presented in this work allows us to obtain the energy of sublimation of ices at temperatures low enough to relate them to astrophysical scenarios as found in the interstellar medium, planetary icy surfaces, etc. Moreover, the procedure used is compatible with other analysis techniques used simultaneously, allowing us to measure simultaneously another parameters of the ice under study: the film thickness, the mass accreted from the frequency variation of the QCMB, the density and porosity.

Acknowledgments

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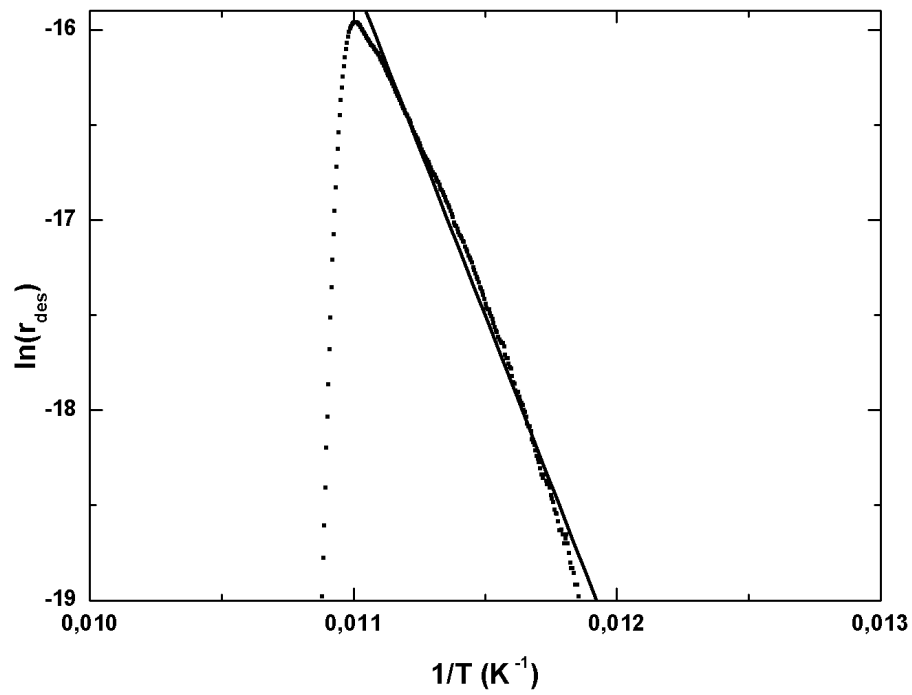


Figure 2: The $\ln(r_{\text{des}})$ versus $1/T$ (dotted line) and straight line fit.

References

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