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# Excited CO Formation in Interstellar Molecular Clouds: Methyl Formate Photodissociation by Ultraviolet Radiation

Summary – Progress in astrochemistry is driven by observations. Typically, the molecules in the Interstellar Medium dark and dense clouds are studied by the infrared and millimeter spectroscopy by radiotelescopes. A careful analysis of their signatures in the spectra helps to characterize these regions where new stars and planets are born. The rotational transition lines of carbon monoxide, CO, are the most important tracer of molecular gas within molecular clouds. However, the accuracy of the interpretation of the detected signals depends on the quality of the kinetic models, used to simulate molecular environments, that in order to be reliable require accurate knowledge of the dynamics and reactive kinetics properties of the individual molecules. A certain lack of knowledge in current models surely affects reactive and dissociation processes involving complex organic molecules. For example, these can be exposed to far Ultra-Violet (FUV) radiation in photodissociation regions and also in the inner regions of molecular clouds (collision of cosmic rays with gas phase particles can results in UV emissions) and generate vibro-rotationally excited molecular fragments upon photodissociation, such as rotationally hot CO molecules. In this work we establish a possibly fruitful dialogue between the chemistry and astrophysics communities considering a molecular beam experiment of UV photodissociation of methyl formate, abundant and ubiquitous in space, as a source of accurate information about the generation of vibrationally and rotationally excited CO dissociation fragments in molecular clouds. The scheme can be extended to many complex organic molecules, for which experimental and theoretical photodissociation studies are feasible.

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#### Introduction

The advent of a new interdisciplinary field of scientific research, astrochemistry [1], as the investigation of the chemical nature of the Universe, originates from astronomical and radioastronomical observations and space mission data collections. The interpretation of the resulting ample phenomenology needs to be assisted by laboratory experiments and theoretical and computational modeling. This search has already led to the identification of a constantly increasing number of molecules, even complex organic molecules, but progress in space exploration and direct sampling promise further insight into the evolution of the universe, from a chemical point of view, since its formation up to the the generation of protobiological molecules.

In this respect, the discovery of amino-acids in meteorites, and possibly in other spatial environments, has contributed to the debate on the origin of the building blocks of life in space. The recent discovery of propylene oxide (PO) in the Interstellar Medium (ISM) [3] has induced large interest in spite that it is just a further addition to a now long list of molecules, being this molecule an ideal candidate as a prototype for studies aiming at elucidating the insurgence and establishment of homochirality since the origin and early evolution of life, an issue still lacking convincing explanations.

The trend in the discovery of Complex Organic Molecules (COMs) [4] confirm a diffuse presence in the Interstellar Medium (ISM), since besides protostellar hot cores and corinos, COMs are found at all stages of star formation, in cold cores, protoplanetary disks, shocks, jets and outflows [5].

Their widespread presence in the ISM suggests that in building kinetic models of spatial environments one should assess the role of COM breakings upon photodissociation, since such processes involve the production of the simple basic diatomic molecules such as, for example, carbon monoxide CO and the hydroxyl radical OH, generated in excited rotational and vibrational states.

The observation of molecules, in any astrophysical environment, relies upon experiments based on measurements of radiative spectra, but sufficiently high spectral resolution and sensitivity allow in principle to measure also absorption spectra from different rotational levels, including the ground state, permitting to probe the column density of the detected molecule, temperature and molecule abundances.

Carbon monoxide, a basic reactant for the formation of small organic molecules and aminoacids and, at the same time, the detectable product of their decomposition by photodissociation, is one of the most abundant molecules in space, with a specific relationship to hydrogen and a main tracer of molecular clouds, due to the ease of detection of its Ultraviolet (UV) and millimeter (mm) photon emission.

Privileged environments for CO generated by photodissociation are arguably regions of the ISM, so called "neutral", in which the gas heating and chemical processes are mostly regulated by far UV. These are termed Photo-Dissociation Regions (PDRs) and are the source of most of the non-stellar infrared (IR) and the millimeter and submillimeter CO emission from galaxies [6].

The importance of PDRs has become increasingly apparent with advances in Infra-Red (IR) and submillimeter astronomy. The IR emission from PDRs corresponds to rovibrational lines of  $H_2$ , rotational lines of CO, broad mid-IR features of polycyclic aromatic hydrocarbons (PAH) and a luminous underlying IR continuum from interstellar dust. The transition of H to  $H_2$  and C to CO actually occurs within PDRs. Comparison of observations with theoretical models of PDRs enables one to determine the density and temperature structure, the elemental abundances, the level of ionization, and the radiation field. Complex Organic Molecules (COMs) are abundant especially in the deep part of clouds, where actually the far UV radiation is more attenuated. In these regions, however, the effect of cosmic rays is the leading one, which causes the presence of secondary UV radiation, due to collisions with molecules (mainly  $H_2$ ).

If the temperature is sufficiently high, molecules, also the more complex ones, can be desorbed from grain surface.

Generation of excited CO molecules, could affect the emission spectra, which follow a proper excitation of the molecular emitting levels. The emitted radiation is directly linked to the population of the upper level (it may also depend on the population of the lower level) and to the physical and chemical properties of the environments located between the source and the observer. The presence of dust particles is an example of effect inducing additional absorption and scattering which may considerably alter the observed emitted spectrum.

In this work, we accont for molecular beam experiment of UV photodissociation of methyl formate, abundant and ubiquitous in space, as a source of accurate information about the generation of vibrationally and rotationally excited CO dissociation fragments in molecular clouds.

### Population of levels by collisional processes

The collisions between molecules are the basic processes leading to energy transfer and internal excitation and population of higher states. Their efficiency relies on the nature of the colliding partners, the chemical composition and the density of the medium and the local temperature, which influences statistically the average degree of excitation and, consequently, determines the intensities of the radiation emission. Other important mechanism can be effective, such as radiative and chemical level pumping. When relatively complex organic molecules are available, and photons with frequencies close to far-UV radiation are present, photodissociation might occur generating excited fragments, such as CO, OH or HCO. This scheme, is a mechanism that indirectly pumps radiation energy into the rotational and vibrational manifold of diatomic molecules, such as the tracer CO.

The level population in the conditions typical of the interstellar medium is generally not in line with a thermal distribution. For a given molecule, the assignment of a set of transitions allows to draw a so-called Boltzmann plot, reporting the logarithm of the column density, denoted as N(j) and corresponding to the *j*-level relative population divided by its statistical weight  $g_{j}$ , versus the related energies (often expressed in Kelvin). The corresponding points are aligned when thermodynamic equilibrium or local thermodynamic equilibrium (LTE) is fulfilled and the temperature is simply obtained from the slope of the curve.



Fig. 1 Boltzmann plots of data of rotational populations of vibrationally excited CO molecules (v = 1 and v = 2), from laser photodissociation of a molecular beam of methyl formate. Thermal bimodality is exhibited by changes in slopes (dashed lines are a guide for readers' eyes adapted from Ref. 7).

$$P(j) = g_j \frac{P(O)}{g_0} e^{-(E_j - E_0)/kT}$$

Fig. 1 shows an example of Boltzmann plot measured downstream of a molecular beam experiment involving photodissociation of methyl formate [7].

The drawback of such an idealized picture come from the low-density conditions typical of the interstellar medium, meaning low collision frequencies, which prevent molecular encounters to be the leading process in establishing thermal equilibrium, even locally, for the level population.

In other words, LTE is rarely fulfilled. Then, knowledge of the collisional rate coefficients involving the most abundant species, i.e. H,  $H_2$ , He, electrons and Carbon and Oxygen carrier molecules, such as the molecular tracer CO, is required to solve the coupled differential equations describing the evolution of the different excited states of each molecule. Under similar conditions, the interpretation of the

emission spectra to infer the physical and chemical properties of the molecular clouds also requires the simultaneous solution of the radiative transfer part, which contributes to de-excitation in competition with collisions.



Fig. 2 Reconstructed rotational quantum number distributions from the estimated rotational temperature values from Boltzmann deconvolutions. Two components, designated by  $T_{<}$  and  $T_{>}$ , are disentangled and attributed as arising from events emerging directly from pathways into the channel CH<sub>4</sub>OH + CO or from alternative paths along the radical channel adapted from Ref. 7.

To better understand the observational data, it is necessary to enhance the models including physical chemical networks containing gas-phase and grain-surface reactions. The determination of collisional rates for all the relevant interstellar molecules is therefore a major challenge in the interpretation of astrochemical observations. In the specific case outlined above, when photodissociation occurs, the network should include such processes and the correct share of single excited states in which the fragments are produced.

This situation is not limited to astrochemical models. In general, whatever the conditions, the modeling of gas phase systems requires an accurate description of the molecular energy transfer and photodissociation and reactive processes, which have to be carefully represented within the kinetic models. So many other research areas fields are included, such as combustion chemistry, chemistry of plasmas, gases under flow conditions (e.g. in aircraft and spacecraft design [8]). The additional obstacle here, is the lack of general and local equilibrium for any of the degrees of freedom, which prevents to assume statistical population averaging, and forces to

resort to a state-to-state level of details for the rate coefficients and to detailed dynamics simulations to obtain reactive mechanisms, branching ratios and dissociation pathways. Important attempts are currently being carried out in the gas dynamics community to develop kinetic models at a state-specific level [9-12].

The excitation and de-excitation of molecules, occurring upon collision, as well their decomposition patterns are strongly dependent on the features of the intermolecular potentials [10] and part of the efforts to improve the accuracy of models must be spent to obtain a realistic description of the intermolecular interactions. A further key point is that energy transfer is state-specific in its nature, since it depends on the initial quantum states of the colliding molecules, and this dependency is more pronounced when excited states are involved, as for hypersonic flows and high temperature plasmas, an aspect typical of planetary atmosphere chemistry [8].

#### Photossociation as a vibrational and rotational pumping mechanism

Besides collisional excitation, photodissociation processes of small and medium size molecules abundantly present in molecular clouds, can convert the UV radiation into significant amounts of vibrational and rotational energy of the preferred dissociation fragments, such as CO.

As an example, the methyl formate molecule (HCOOCH<sub>3</sub>) is one of the most abundant species in hot molecular cores [14]. Together with acetic acid and the sugar glycolaldehyde, these  $C_2H_4O_2$  molecules are the first triad of isomers detected in interstellar clouds. The abundance of methyl formate is an average of 100 times the amount of acetic acid, the second most abundant isomer and this must depend upon formation pathways and quantum yields of photodissociation. In the last ten years some significant experimental and theoretical studies of the photodissociation of methyl formate around the lower energy limit of the far-UV radiation, have been carried out (see e.g. Ref. [7,15]), showing that the main dissociation pathways involve CO fragment formation with a significant vibrational and rotational excitation. This suggests a possible role of such processes in determining the CO level population. Fig. 2 shows the rotational distribution of CO fragments from methyl formate photodissociated at 248 nm [7].

### Concluding remarks

Small organic molecules, e.g. methyl formate, are sources of excited molecular fragments, such as the tracer CO. Performing properly designed molecular beam experiments, assisted by theoretical and computational modeling, provide accurate rate coefficients of collisional energy transfer processes in the range of conditions typical of the interstellar medium. In particularly, experiments of photodissociation allow to reconstruct the energy disposal and the molecular vibro-rotational state distributions, enriching current astrochemical data base by updated kinetics and population data.

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