

The reactions of atomic oxygen with unsaturated hydrocarbons and their relevance in the interstellar hydrocarbon growth



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Introduction:

The observation of highly unsaturated organic molecules (e.g. polyynes, and cyanopolyynes) in the interstellar medium (and in other extraterrestrial environments such as the atmosphere of Saturn's moon Titan) poses the question of how these molecules can survive in media rich in molecular and atomic hydrogen as well as other atomic and radical species. From a chemical point of view, indeed, each unsaturated C-C bond is a potential site for addition reactions, especially if one considers the electrophilic nature of the atomic and molecular radicals abundant in the interstellar medium. Part of this puzzle is actually explained by the fact that the reactions of polyynes and other unsaturated hydrocarbons (alkenes, dienes) with several atomic and radical species (such as atomic carbon or CH, C₂H, C₃ and CN radicals) do not destroy the C-atom skeleton of unsaturated species, but rather elongate it. Oxygen-containing highly unsaturated species have not been identified so far in interstellar objects, with the only exceptions being HCCO, ketene (CH₂=C=O), vinyl alcohol (CH₂=CHOH) and propynal (HC≡CCHO). Oxygen in C-rich environments appears, instead, to be mostly locked in CO, H₂CO and H₂O species.¹

In our laboratory we have started a systematic investigation of several reactions involving atomic oxygen and unsaturated hydrocarbons (C₂H₂, C₂H₄, CH₂CCH, CH₂=C=CH₂, CH₃CH=CH₂, C₂H₃CH=CH₂) by means of the crossed molecular beam technique with mass spectrometric detection and time-of-flight analysis. The experimental results are discussed in the light of electronic structure calculations of the underlying PESs and related statistical or dynamical calculations.²

Experimental:

We have investigated the dynamics of the O(³P) + unsaturated hydrocarbons reactions by the crossed molecular beams method in its "universal" arrangement with mass spectrometric (MS) detection, exploiting soft electron ionization (at 17 eV). From product angular and velocity distribution measurements in the lab frame at different m/z ratios we have identified the primary product channels reported in the tables below, derived the product angular and translational energy distributions in the center-of-mass frame, and determined the branching ratios (BRs).

Theoretical:

Theoretically, the triplet and singlet PESs of the O(³P) + propyne and O(³P) + propene reactions were investigated at the CASPT2 and CCSD(T) levels, with extension to the complete basis set limit. Branching ratios were determined integrating the 1D master equation, accounting explicitly for the possibility of intersystem crossing (ISC) between the triplet and singlet potential energy surfaces, at 300 K (room temperature) and for the conditions of the CMB experiments (E_c = 9.3 kcal/mol). For the reaction between O(³P) + ethylene, the calculations employ a previous singlet PES that is a fit using a basis of permutationally invariant polynomials in Morse-like variables in all the internuclear distances to roughly 200,000 electronic energies. A PES for the triplet state was developed for this study. This PES is a permutationally invariant fit to roughly 52,000 ab initio energies computed with the coupled cluster method with account of single and double excitations, and perturbative treatment of triple excitations [CCSD(T)], as implemented in the MOLPRO suite of codes. For the calculations regarding the reaction between O(³P) + acetylene see [13].

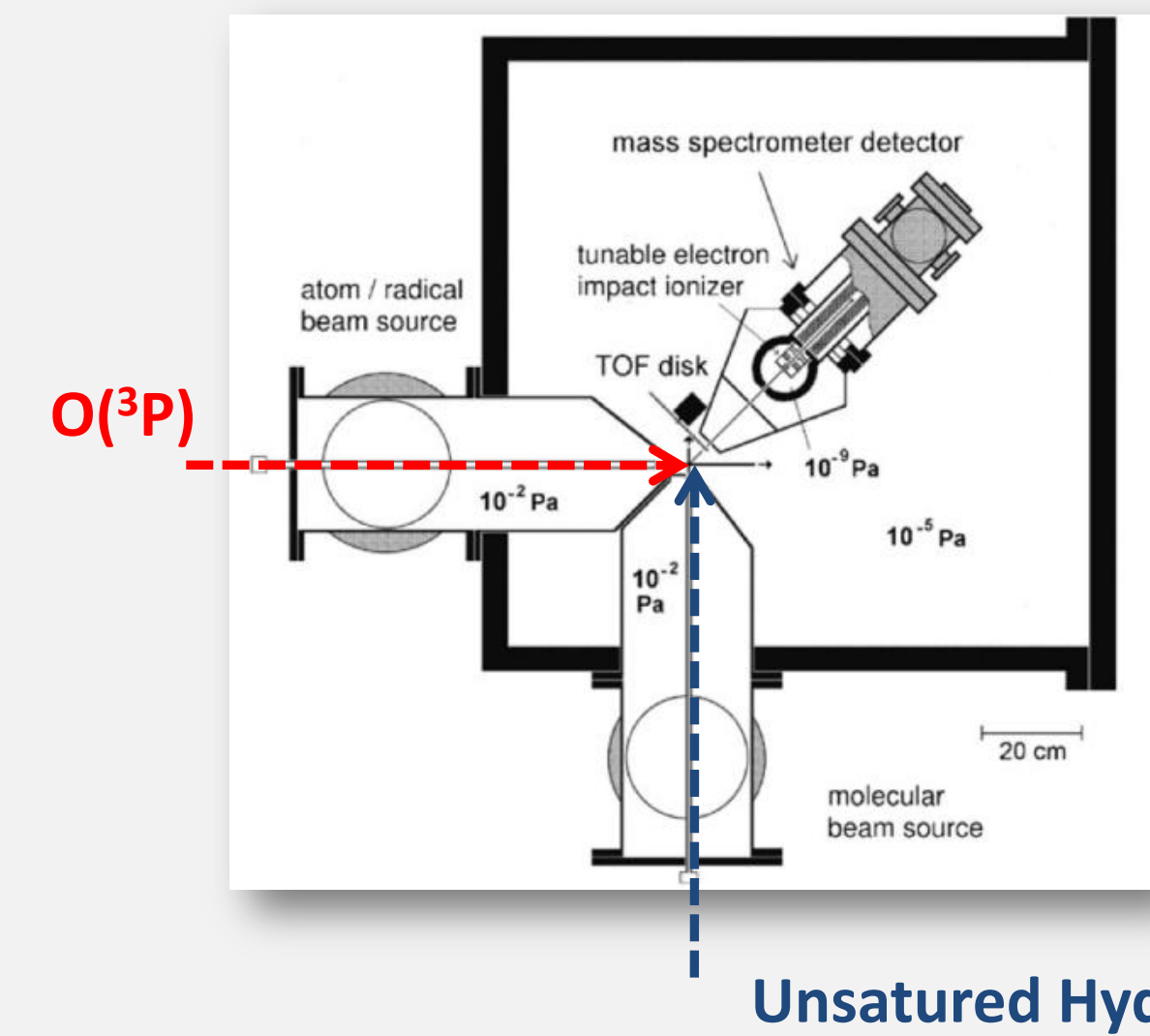
EXPERIMENTAL TECHNIQUE:

(Perugia CMB)

What we measure:

Intensity of the products as a function of their:

- scattering angle (Θ)
- velocity (time of flight distribution)



- Continuous supersonic beams of reactants, crossing angle 90° (even 45° and 135°)
- RF discharge source for atomic oxygen beam
- Rotating mass spectrometer (MS) detector with tunable electron impact ionizer (soft-ionization)
- TOF pseudo-random disk for time-of-flight analysis

Unsaturated Hydrocarbon

What we learn:

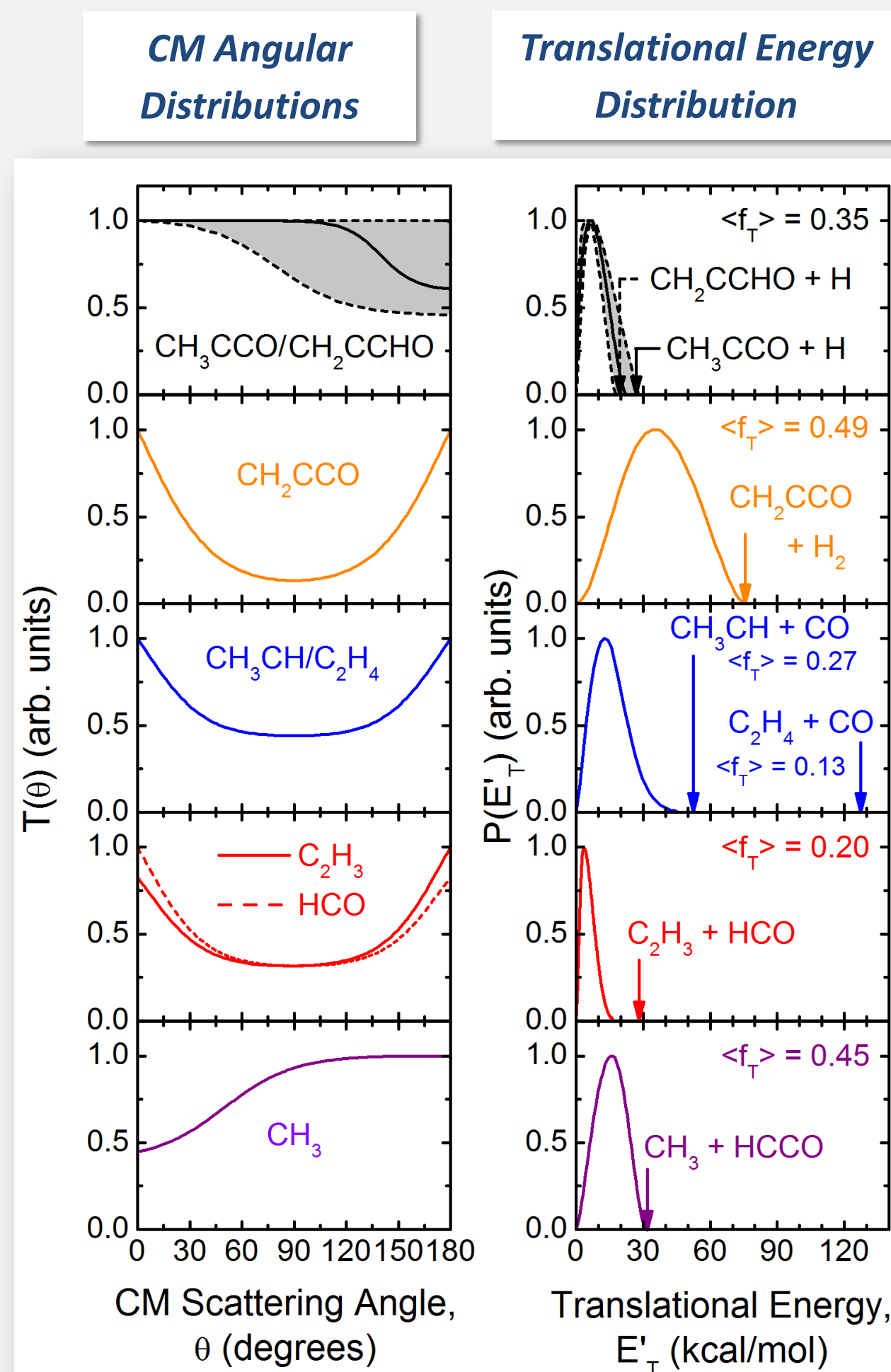
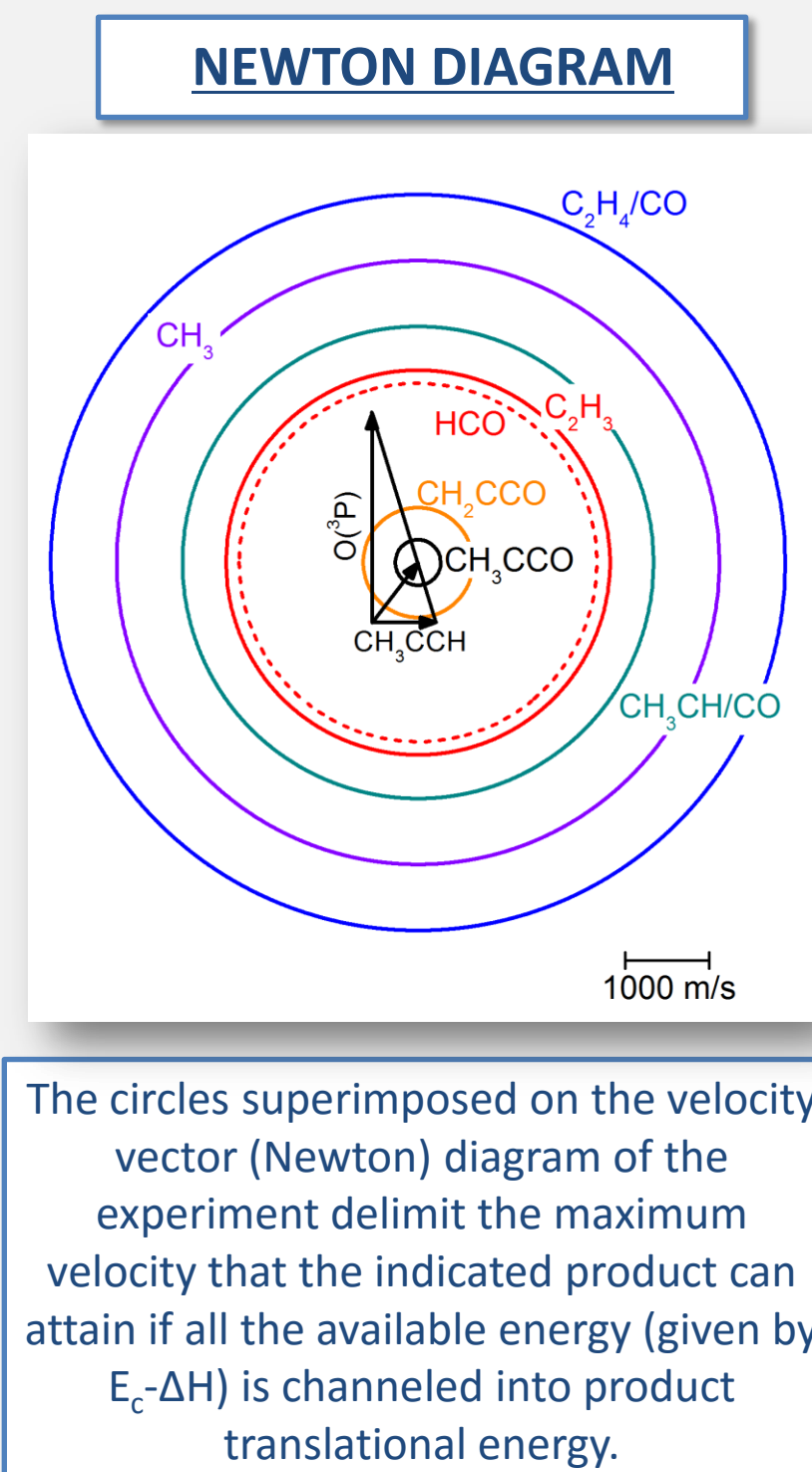
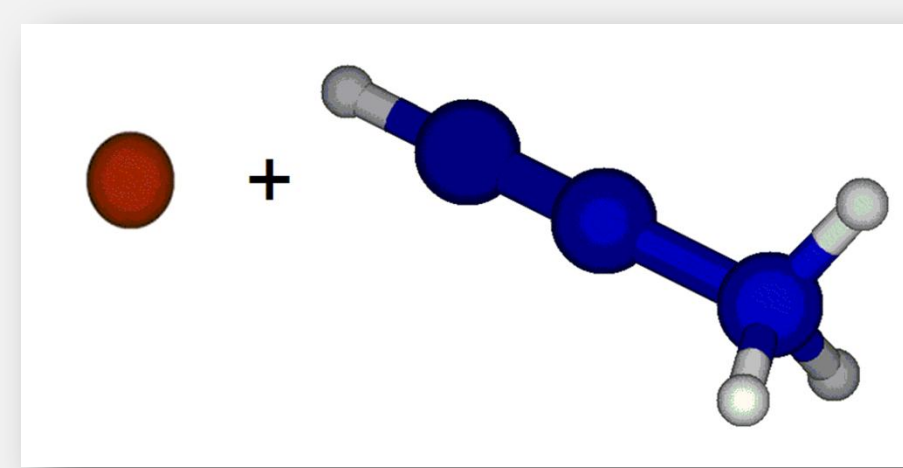
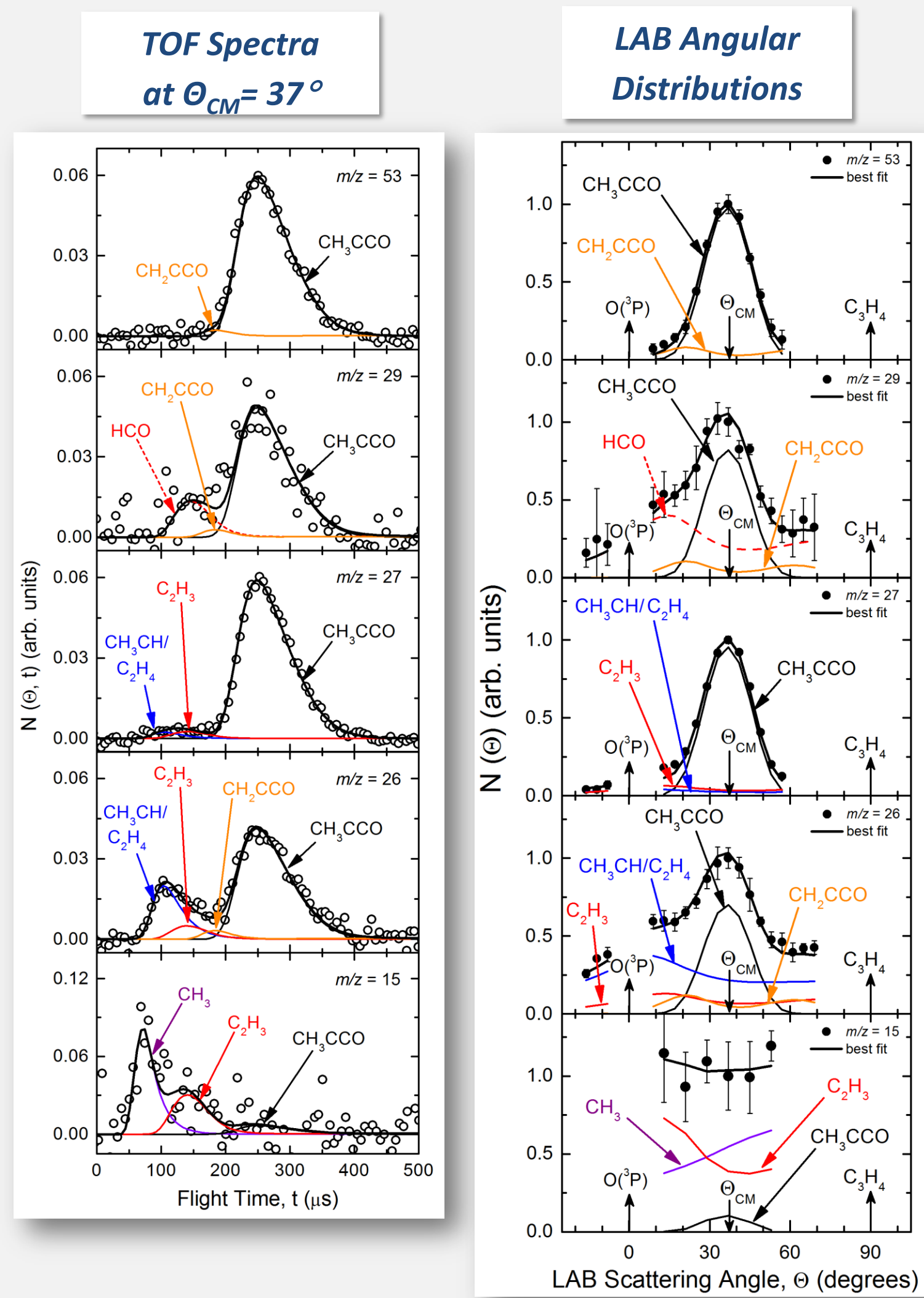
- Identity of primary products and their yields
- Intermediate life-time
- Micro-mechanism
- Energy release

We have been able to observe **six open channels** and to determine their branching ratio under the same experimental conditions

O(³ P) + CH ₃ CCH	Branching ratios as obtained from CMB experiments at E _c =9.2 kcal/mol [15,16] and from kinetics experiments at 300 K [18], compared with theoretical (RRKM/ME) predictions from this work on coupled triplet and singlet PESs [17].				
Reaction Channel	ΔH ₀ ^o (kcal/mol)	CMB Expt E _c = 9.2 kcal/mol [15,16]	RRKM/ME Calculations E _c = 9.2 kcal/mol [17]	Kinetics work 300 K [18]	RRKM/ME Calculations 300 K [17]
H + CH ₃ CCHO	-13.4	0.04	0.225	0.05	0.06
CH ₃ + HCCO	-22.1	0.10	0.13	0.1	0.16
C ₂ H ₃ + HCO	-19.0	0.11	0.159 (0.145-0.04T)	0.28	0.18
CH ₃ CH/C ₂ H ₄ + CO	-115.1	0.74	0.33 (0.305-0.03T)	0.39	0.50
C ₂ H ₂ + H ₂ + CO	-76.7	-	0.05	0.19	0.09
H ₂ + CH ₃ CCHO	-66.5	0.01	-	<0.01	-

Uncertainties on B.R.s are of about ±30-50%

The O(³P) + CH₃CCH reaction



The O(³P) + C₂H₄ reaction

O(³ P) + C ₂ H ₄	Branching ratios as obtained from CMB experiments at E _c = 8.4 kcal/mol compared with theoretical (QCT-SH) predictions from [11] on coupled triplet and singlet PESs.		
Reaction Channel	ΔH ₀ ^o (kcal/mol)	CMB Expt E _c = 8.4 kcal/mol [11]	QCT-SH calculations E _c = 8.4 kcal/mol [11]
H + CH ₂ CHO	-16.9	0.30	0.28
CH ₂ + H ₂ CO	-6.9	0.20	0.08
CH ₃ + HCO	-27.0	0.34	0.49
H + CH ₃ CO	-27.2	0.03	0.10
H ₂ + CH ₂ CO	-85.1	0.13	0.05

Uncertainties on B.R.s are of about ±20-33%

The O(³P) + C₂H₂ reaction

O(³ P) + C ₂ H ₂	Branching ratios as obtained from CMB experiments at E _c = 8.2 kcal/mol [12] compared with theoretical (QCT-SH) predictions [13].		
Reaction Channel	ΔH ₀ ^o (kcal/mol)	CMB Expt E _c = 8.2 kcal/mol [12]	QCT-SH calculations E _c = 8.2 kcal/mol [13]
H + HCCO	-19.7	0.79	0.80
CH ₂ + H ₂ CO	-47.5	0.21	0.10

Uncertainties on B.R.s are of about ±6-23%

The O(³P) + CH₃CHCH₂ reaction

O(³ P) + CH ₃ CHCH ₂	Branching ratios as obtained from CMB experiments at E _c = 9.3 kcal/mol and from kinetics experiments at 300 K [10], compared with theoretical (RRKM/ME) predictions on coupled triplet and singlet PESs [9].				
Reaction Channel	ΔH ₀ ^o (kcal/mol)	CMB Work E _c = 9.3 kcal/mol [9]	RRKM/ME Calculations E _c = 9.3 kcal/mol [9]	Kinetics work 300 K [10]	RRKM/ME Calculations 300K [9]
H + CH ₃ CHCHO	-17.2	0.07	0.261	0.46	0.159 (0.358)
H + CH ₃ COCH ₂	-18.3	0.05	0.010	-	0.003 (0.006)
CH ₃ + CH ₂ CHO/CH ₂ CO	-25.1	0.32	0.326	0.28 (1.0)	0.442 (1.0)
³ CH ₃ CH + H ₂ CO	-76.3	0.44	0.321	-	0.065 (0.212)
¹ C ₂ H ₄ + H ₂ CO	-5.4	-	0	(0.27) ^a	0
H ₂ + CH ₃ CHCO	-78.8	0.03	0.011	0.014 (0.05)	0.018 (0.041)
C ₂ H ₃ + HCO	-24.8	0.09	0.07	0.25 (0.91)	0.283 (0.640)

Uncertainties on B.R.s are of about ±30-50%
The value between parentheses is the branching ratio relative to methyl + CH₂CHO/CH₂CO channel^a assigned as secondary product, potentially a primary product

The O(³P) + CH₂CCH₂ reaction

O(³ P) + CH ₂ CCH ₂	Branching ratios as obtained from CMB experiments at E _c = 9.4 kcal/mol [4,14]	
Reaction Channel	ΔH ₀ ^o (kcal/mol)	CMB Work E _c = 9.4 kcal/mol [2]
H + CH ₂ =C-CHO	-14.0	1.5
³ CH ₂ + CH ₂ CO	-24.4	6
C ₂ H ₃ + HCO	-24.0	6.5
C ₂ H ₂ + H ₂ CO	-77.6	9
C ₂ H ₄ + CO	-119.6	77

Uncertainties on B.R.s are of about ±20%

Dependence of ISC on molecular complexity and structure :

It can be noticed that ISC, while is negligible in the simplest system O + acetylene, becomes very important (~75%) in methyl-acetylene (propyne), in which an acetylenic H atom is replaced by CH₃ group or in O + ethylene. According to Nguyen et al., the lack of an efficient ISC in the O(³P) + C₂H₂ reaction can be attributed to (i) the faster (with respect to O + C₂H₂) chemical decomposition of the chemically activated triplet trans-HCCHO adduct and (ii) the narrow geometry range of the HCCHO triplet and singlet surface crossing seams. It may be interesting and useful to correlate the extent of ISC in related systems with the relative stability of the initial triplet intermediates. For O(³P) + propene, despite the fact that the triplet diradicals CH₃CH₂O/CH₃CHOCH₂ have a stability of -23.7 kcal/mol, slightly larger than the value of -90 kJ/mol of the triplet diradical C₂H₄O in O(³P) + C₂H₄, their probability of ISC to the corresponding singlet species is considerably lower than in O + C₂H₄, presumably because a very significant fraction of the reactive flux goes from the more abundant CH₃CH₂O triplet intermediate to the CH₃CH + H₂CO products. In contrast, ISC in O(³P) + CH₂CCH₂ appears to be larger than in O(³P) + ethylene because the corresponding triplet diradical intermediates are much more stable (more than -60 kcal/mol) with respect to the O + ethylene and O + propene cases. So, despite the presence in O + allene of competitive C-C bond cleavage channels on the triplet PES, as in O + propene, the much longer lifetime of the triplet intermediate makes much higher the probability of ISC. All this suggests caution in extrapolating the extent of ISC along a series, because it appears to be all matter of relative rates of competing pathways, which in turn depend on the detailed topology of the triplet/singlet PESs.

Extent of intersystem crossing

Reaction Channel	E _c (kcal/mol)	Experiment (%)	Theory (%)
O(³ P) + C ₂ H ₄	8.2	Negligible	11
O(³ P) + C ₂ H ₂	8.4	51	64
O(³ P) + CH ₃ CCH	9.2	85	49
O(³ P) + CH ₃ CHCH ₂	9.2	≥ 22	22
O(³ P) + CH ₂ CCH ₂	9.4	92	-

Extent of ISC for the various reactions investigated, from CMB experiments and from theory (QCT-SH calculations for O + C₂H₂ and O + C₂H₄, and statistical calculations for O + CH₃CHCH₂ and O + CH₃CCH) on coupled triplet/singlet PESs, at the indicated collision energies.

Astrochemistry implications:

Atomic oxygen is an important player in the ISM chemistry because oxygen is the most abundant element after hydrogen and helium. In the modelling of cold/warm interstellar objects the reactions of O(³P) with simple organic molecules (including small unsaturated hydrocarbons) or radicals need to be included, as they affect the molecular abundances. For instance, the reaction between atomic oxygen and the CH₂OCH₂ radical is the only viable route of methyl formate formation in the gas phase.³ Until recently,⁴ however, limited and simplistic information about these reactions were included in the models. Very recently, the results of our studies on some of the discussed reactions have been introduced in models which simulate the chemistry of the interstellar objects by Occhiogrosso et al.⁵ The effects of this more accurate chemical network representing the reactions of atomic oxygen with several unsaturated hydrocarbons on both warm and cold regions of the ISM has been examined.⁶ A conclusion of that study is that towards hot cores/corinos atomic oxygen easily degrades unsaturated hydrocarbons directly to CO or to its precursor species (such as HCCO or HCO) and destroys the double or triple bond of alkenes and alkynes. This is the reason why O-rich interstellar environments are not characterised by the presence of large unsaturated hydrocarbons or PAHs polycyclic aromatic hydrocarbons). In contrast, in O-poor and C-rich objects, hydrocarbon growth can occur to a large extent. In the revised model Occhiogrosso et al.⁵ also highlight the main contribution from other reaction channels not included in the previous databases: ketyl and vinoxy radicals are among the new significant species that should be considered in the modelling. A more general conclusion put forth by that study is that, if we wish to fully understand the formation of the numerous organic species detected in the ISM, the intricate chemistry that leads to their formation and destruction should be treated in detail. The necessary information can mainly come from experimental/theoretical studies of the type reviewed here. Finally, some implications of the present results have been already verified in the modelling of hydrocarbon-rich planetary atmospheres, such as that of Titan, where a little amount of oxygen compounds are present.^{7,8} The reactions of atomic oxygen with acetylene and ethylene represent important steps toward the formation of the observed CO.

Acknowledgments:

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