



Universiteit  
Leiden  
The Netherlands

## Transformation and sublimation of interstellar ices: insights from laboratory experiments and astronomical observations

Carvalho Santos, J. de

### Citation

Carvalho Santos, J. de. (2025, July 2). *Transformation and sublimation of interstellar ices: insights from laboratory experiments and astronomical observations*. Retrieved from <https://hdl.handle.net/1887/4252309>

Version: Publisher's Version

License: [Licence agreement concerning inclusion of doctoral thesis in the Institutional Repository of the University of Leiden](#)

Downloaded from: <https://hdl.handle.net/1887/4252309>

**Note:** To cite this publication please use the final published version (if applicable).

# Transformation and sublimation of interstellar ices

Insights from laboratory experiments and astronomical  
observations

Proefschrift

ter verkrijging van  
de graad van doctor aan de Universiteit Leiden,  
op gezag van rector magnificus prof.dr.ir. H. Bijl,  
volgens besluit van het college voor promoties  
te verdedigen op woensdag 2 juli 2025  
klokke 10:00 uur  
door

Julia de Carvalho Santos

geboren te Rio de Janeiro, Brazilië  
in 1995

Promotores: Prof. dr. E. F. van Dishoeck  
Prof. dr. H. V. J. Linnartz †

Promotiecommissie: Prof. dr. I. A. G. Snellen  
Prof. dr. S. Viti  
Prof. dr. K. I. Öberg Harvard University  
Prof. dr. N. Watanabe Hokkaido University  
Prof. dr. L. Hornekær Aarhus University

ISBN:

Cover design: Camila Muffo Cafardo

*It is again among us, in a glass of milk. It is inserted in a very complex, long chain, yet such that almost all of its links are acceptable to the human body. It is swallowed; and since every living structure harbors a savage distrust toward every contribution of any material of living origin, the chain is meticulously broken apart and the fragments, one by one, are accepted or rejected. One, the one that concerns us, crosses the intestinal threshold and enters the bloodstream: it migrates, knocks at the door of a nerve cell, enters, and supplants the carbon which was part of it. This cell belongs to a brain, and it is my brain, the brain of me who is writing; and the cell in question, and within it the atom in question, is in charge of my writing, in a gigantic minuscule game which nobody has yet described. It is that which at this instant, issuing out of a labyrinthine tangle of yeses and nos, makes my hand run along a certain path on the paper, mark it with these volutes that are signs: a double snap, up and down, between two levels of energy, guides this hand of mine to impress on the paper this dot, here, this one.*

Carbon  
– The Periodic Table, by Primo Levi



# TABLE OF CONTENTS

<b>1</b>	<b>Introduction</b>	<b>1</b>
1.1	Star and planet formation . . . . .	2
1.1.1	Low-mass stars . . . . .	2
1.1.2	High-mass stars . . . . .	3
1.2	Interstellar chemistry . . . . .	4
1.2.1	Gas vs ice reactions . . . . .	4
1.2.2	Ice processes . . . . .	5
1.3	Chemical evolution through star and planet formation . . . . .	9
1.3.1	Prestellar phase . . . . .	9
1.3.2	Protostellar phase and beyond . . . . .	11
1.3.3	The missing sulfur problem . . . . .	13
1.4	Laboratory astrochemistry . . . . .	15
1.4.1	An overview of ice experiments . . . . .	15
1.4.2	SURFRESIDE <sup>3</sup> . . . . .	21
1.4.3	LISA . . . . .	22
1.4.4	SPACE-KITTEN . . . . .	23
1.5	Observational astrochemistry . . . . .	24
1.5.1	Submillimeter and millimeter observations . . . . .	24
1.5.1.1	ALMA . . . . .	25
1.5.1.2	APEX . . . . .	25
1.5.2	Infrared observations . . . . .	25
1.5.3	Fundamentals of radiative transfer . . . . .	26
1.6	This thesis . . . . .	27
1.6.1	Chapter summary . . . . .	27
1.6.2	Main conclusions and future directions . . . . .	31
<b>2</b>	<b>First experimental confirmation of the <math>\text{CH}_3\text{O} + \text{H}_2\text{CO} \rightarrow \text{CH}_3\text{OH}</math> + <math>\text{HCO}</math> reaction: expanding the <math>\text{CH}_3\text{OH}</math> formation mechanism in interstellar ices</b>	<b>35</b>
2.1	Introduction . . . . .	36
2.2	Experimental . . . . .	37
2.3	Results and Discussion . . . . .	37
2.4	Conclusions . . . . .	44
2.5	Appendix . . . . .	45
2.5.1	$\text{D}_2\text{CO}$ band strength estimation . . . . .	45
2.5.2	Experiment list . . . . .	45

<b>3</b>	<b>Resonant infrared irradiation of CO and CH<sub>3</sub>OH interstellar ices</b>	<b>49</b>
3.1	Introduction . . . . .	50
3.2	Experimental methods . . . . .	51
3.3	Results and discussion . . . . .	54
3.3.1	CH <sub>3</sub> OH . . . . .	54
3.3.1.1	Morphology . . . . .	54
3.3.1.2	Power-dependence analysis and photodesorption . . .	57
3.3.2	CO . . . . .	59
3.3.2.1	Morphology . . . . .	59
3.3.2.2	Photodesorption . . . . .	60
3.3.3	Mixtures . . . . .	62
3.3.3.1	Morphology . . . . .	62
3.3.3.2	Photodesorption . . . . .	64
3.4	Astrophysical implications . . . . .	65
3.5	Conclusions . . . . .	68
3.6	Acknowledgements . . . . .	68
3.7	Appendix . . . . .	69
3.7.1	Control IR spectra . . . . .	69
3.7.2	aCO ice stabilization . . . . .	69
3.7.3	Repeated irradiations on ice mixtures . . . . .	70
<b>4</b>	<b>Interaction of H<sub>2</sub>S with H atoms on grain surfaces under molecular cloud conditions</b>	<b>77</b>
4.1	Introduction . . . . .	78
4.2	Experimental methods . . . . .	79
4.3	Results and discussion . . . . .	81
4.3.1	H <sub>2</sub> S + H ice chemistry . . . . .	81
4.3.2	H-atom bombardment on H <sub>2</sub> S ice . . . . .	83
4.3.3	Kinetic analysis . . . . .	87
4.4	Astrophysical implications . . . . .	91
4.5	Conclusions . . . . .	92
4.6	Acknowledgements . . . . .	92
4.7	Appendix . . . . .	93
4.7.1	Determination of IR band strengths . . . . .	93
<b>5</b>	<b>H<sub>2</sub>S ice sublimation dynamics: experimentally constrained binding energies, entrapment efficiencies, and snowlines</b>	<b>95</b>
5.1	Introduction . . . . .	96
5.2	Methods . . . . .	97
5.2.1	The setup . . . . .	97
5.2.2	The experiments . . . . .	98
5.2.3	The analysis . . . . .	100
5.3	Results and discussion . . . . .	101
5.3.1	Binding energies . . . . .	101
5.3.1.1	H <sub>2</sub> S–H <sub>2</sub> S . . . . .	101
5.3.1.2	H <sub>2</sub> S–H <sub>2</sub> O . . . . .	103
5.3.1.3	Binding energies vs coverage . . . . .	105
5.3.2	Entrapment in H <sub>2</sub> O . . . . .	108
5.4	Astrophysical implications . . . . .	111

5.5	Conclusions . . . . .	114
5.6	Acknowledgements . . . . .	115
5.7	Appendix . . . . .	115
5.7.1	Submonolayer coverage estimation . . . . .	115
5.7.2	Pure H <sub>2</sub> S ice infrared features vs temperature . . . . .	115
5.7.3	Arrhenius plots . . . . .	116
5.7.4	Multilayer H <sub>2</sub> S ice fits with a temperature-dependent $\nu_{\text{TST}}$ . . . . .	116
5.7.5	Submonolayer fit with a single energy component . . . . .	116
5.7.6	QMS-TPD results for mixed H <sub>2</sub> O:H <sub>2</sub> S ices . . . . .	117
<b>6</b>	<b>Formation of carbonyl sulfide (OCS) via SH radicals in interstellar CO-rich ice under dense cloud conditions</b>	<b>121</b>
6.1	Introduction . . . . .	122
6.2	Experimental methods . . . . .	124
6.3	Results and discussion . . . . .	125
6.3.1	OCS formation . . . . .	125
6.3.2	Effects of larger CO fractions . . . . .	127
6.4	Astrophysical implications . . . . .	129
6.5	Conclusions . . . . .	130
6.6	Acknowledgements . . . . .	131
<b>7</b>	<b>Formation of S-bearing complex organic molecules in interstellar clouds via ice reactions with C<sub>2</sub>H<sub>2</sub>, HS, and atomic H</b>	<b>133</b>
7.1	Introduction . . . . .	134
7.2	Methods . . . . .	136
7.2.1	Experimental methods . . . . .	136
7.2.2	Computational methods . . . . .	139
7.3	Results and discussion . . . . .	139
7.3.1	CH <sub>2</sub> CHSH and CH <sub>3</sub> CH <sub>2</sub> SH . . . . .	139
7.3.2	H <sub>2</sub> S <sub>2</sub> and HSCH <sub>2</sub> CH <sub>2</sub> SH . . . . .	141
7.3.3	CH <sub>2</sub> CS and CH <sub>3</sub> CHS . . . . .	143
7.3.4	Computational results and chemical network . . . . .	145
7.4	Astrophysical implications . . . . .	149
7.5	Conclusions . . . . .	151
7.6	Acknowledgments . . . . .	152
<b>8</b>	<b>SO<sub>2</sub> and OCS toward high-mass protostars: a comparative study of ice and gas</b>	<b>153</b>
8.1	Introduction . . . . .	154
8.2	Observations and methods . . . . .	156
8.2.1	The observations . . . . .	156
8.2.2	Spectral analysis . . . . .	157
8.2.3	Isotope ratio calibration . . . . .	158
8.3	Results . . . . .	159
8.3.1	Morphology . . . . .	159
8.3.2	Fitting results . . . . .	159
8.3.3	Is <sup>34</sup> SO <sub>2</sub> optically thin? . . . . .	160
8.4	Discussion . . . . .	161
8.4.1	$N(\text{OCS})/N(\text{CH}_3\text{OH})$ . . . . .	161

8.4.2	$N(\text{SO}_2)/N(\text{CH}_3\text{OH})$ . . . . .	164
8.4.3	$\text{SO}_2$ versus OCS . . . . .	167
8.5	Conclusions . . . . .	168
8.6	Acknowledgments . . . . .	170
8.7	Appendix . . . . .	170
8.7.1	Example of an excluded source . . . . .	170
8.7.2	Source properties and observational parameters . . . . .	170
8.7.3	List of transitions . . . . .	172
8.7.4	Best-fit models for all sources . . . . .	172
8.7.5	Integrated intensity map of 693050 . . . . .	172
8.7.6	Best-fit parameters of $^{34}\text{SO}_2$ and $\text{O}^{13}\text{CS}$ . . . . .	172
8.7.7	FWHM and $V_{\text{lsr}}$ of $^{34}\text{SO}_2$ and $\text{O}^{13}\text{CS}$ compared to $\text{CH}_3\text{OH}$ . . . . .	175
8.7.8	Best-fit parameters of $^{33}\text{SO}_2$ . . . . .	175
8.7.9	Literature ratios . . . . .	175
8.7.10	$N(\text{SO}_2)/N(\text{OCS})$ . . . . .	175
<b>9</b>	<b>A spectral survey of <math>\text{CH}_3\text{CCH}</math> in the Hot Molecular Core G331.512-0.103</b> . . . . .	<b>181</b>
9.1	Introduction . . . . .	182
9.1.1	The source: G331.512-0.103 . . . . .	182
9.1.2	The molecule: Methyl acetylene . . . . .	183
9.2	Observations . . . . .	183
9.3	Results . . . . .	184
9.3.1	Line analysis of $\text{CH}_3\text{CCH}$ . . . . .	184
9.3.2	Rotational diagrams and physical properties . . . . .	186
9.3.3	Relative intensities . . . . .	189
9.3.4	Search for the $\text{CH}_3\text{CCH}$ isotopologues . . . . .	191
9.4	Discussion . . . . .	192
9.4.1	Origin of the emission . . . . .	192
9.4.2	Physical conditions: gas temperatures . . . . .	192
9.4.3	Kinematics . . . . .	195
9.4.4	$\text{CH}_3\text{CCH}$ abundances . . . . .	196
9.5	Chemical modeling . . . . .	198
9.6	Conclusions . . . . .	199
9.7	Acknowledgments . . . . .	201
9.8	Software . . . . .	201
	<b>Bibliography</b> . . . . .	<b>203</b>
	<b>Nederlandse samenvatting</b> . . . . .	<b>235</b>
	<b>English summary</b> . . . . .	<b>241</b>
	<b>Resumo em português</b> . . . . .	<b>247</b>
	<b>Publications</b> . . . . .	<b>253</b>
	<b>Curriculum Vitae</b> . . . . .	<b>255</b>
	<b>Acknowledgements</b> . . . . .	<b>257</b>