High resolution molecular spectroscopy for astrochemistry and cosmology

José Rachid Mohallem

Departamento de Física, Universidade Federal de Minas Gerais

LAtME
Laboratório de Átomos e Moléculas Especiais

Departamento de Física, ICEx, UFMG

Molecular astrophysics - Astrochemistry

Astroquímica (ou **Astrofísica Molecular**) é uma área interdisciplinar que estuda a evolução química do Universo, focando especialmente o meio interestelar. Reações químicas envolvidas nos variados mecanismos de formação de moléculas, abundância de elementos e isótopos, interação com a radiação, são processos ou temas de interesse na área. A relação a **Cosmologia** é imediata: do tripé de sustentação da teoria do Big-Bang, dois pés têm relação com a astroquímica.

As atividades nessa área podem ser:

Observacionais → Identificação de moléculas através de seus espectros de radio e infravermelho.

Teóricas → Modelos, propostas de rotas de formação e cálculos para explicar as observações e experimentos.

E**xperimentais** → Simulação de comportamentos de moléculas em meios específicos (Ex: fase gasosa na atmosfera de planetas e fase condensada, gelos astrofísicos em poeira, planetas etc.).

A identificação de moléculas ocorre em: Meio interestelar, gases pré-galáticos, discos proto-estelares, atmosferas de planetas, etc

Molecular astrophysics - Astrochemistry

Composição da "matéria" cósmica: Matéria e energia escuras (95%), átomos e moléculas (5%). Desse total, H e He (98%), outros elementos leves (2%). Apesar disso, a procura por moléculas maiores, possivelmente biológicas, é da maior importância. As primeiras moléculas poliatômicas descobertas foram NH_3 (1968), H_2O (69), H_2CO (a primeira orgânica, 69), CO e CH_3OH (70) HCN, HCOOH e H_2NCHO (71). Desde então mais de 200 moléculas foram identificadas no meio interestelar por radioastronomia.

Grandes desafios atuais (C. Puzzarini):

1. A busca por novas moléculas

2. Reatividade química (mecanismos de formação em condições extremas)

3. Origem da vida (conexão com a existência de moléculas orgânicas?)

Relation with Cosmology

HeH^+: A PRIMEIRA MOLÉCULA DO UNIVERSO

- Após o Big-Bang, 13.8 bilhões de anos atrás, nos primeiros trilionésimos de segundo havia uma sopa cósmica de quarks, elétrons, fótons..., tão “quente” que nem mesmo os quarks podiam se juntar para formar núcleos, eram expulsos pelos fótons.

- O universo se expandiu e sua temperatura caiu progressivamente.

- Prótons e nêutrons foram formados com 1 centésimo de segundo da vida do universo. Após 3 minutos os núcleos atômicos leves se formaram, H^+, He^{++} e Li^{+++}.

-Na chamada Era da Recombinação, 380 mil anos após o Big-Bang os primeiros átomos se formaram. Embora os núcleos mais leves tenham naturalmente se formado primeiro, no caso de átomos, i. e., núcleos capturando elétrons, o que decide é uma combinação de abundância com o potencial de ionização:

Atom	Li2+	Li+	He+	He	H	Li
I_p (eV)	122.4	75.6	54.4	24.6	13.6	5.4

P. ex., o primeiro átomo neutro surgiu na reação $He^+ + e^- \rightarrow He + \nu$

Relation with Cosmology

-Quando a temperatura do Universo atingiu 4000 K, surgiram as primeiras moléculas.

- O HeH+ (hidro-hélio) foi a primeira molécula a aparecer, segundo a rota $H^+ + He \rightarrow HeH^+ + \nu$

Isto porque o He foi o primeiro átomo neutro formado e a sua abundância e a do hidrogênio eram determinantes. Era o início da química.

- Elementos mais pesados que o Carbono foram produzidos em estrelas.

- Desde 1970 pesquisas sugeriam que o íon hidro-hélio deveria existir em quantidades significativas nos gases incandescentes ejetados pela morte de estrelas semelhantes ao Sol, que criam condições similares às do universo primitivo.

- A equipe alemã liderada por Rolf Güsten desenvolveu um espectrômetro capaz de detectar a radiação infravermelha de uma molécula individual no espaço. A molécula foi encontrada numa nebulosa planetária a 3 mil anos-luz da Terra. nebulosa NGC 7027, na constelação do Cisne

Relation with Cosmology

- **Nebulosas** em que a contaminação por elementos produzidos posteriormente por estrelas é baixa, são bastante representativas da abundância química do início do universo. Conta também o fato de que nebulosas planetárias, estágios finais de estrelas de pouca massa (como o sol), são ambientes propícios.

- Especula-se que as transições rovibracionais das moléculas primordiais desempenharam papel relevante no resfriamento do Universo posterior a 4000 K.

- Além disso, identificar essas moléculas é um dos sustentáculos da teoria cosmológica do Big-Bang.

1 eV = 8100 cm^{-1}
1 cm^{-1} = 0.00012 eV

The motivation of our research

- The first formed molecules are very important to the astrophysics of the primordial universe and star formation.

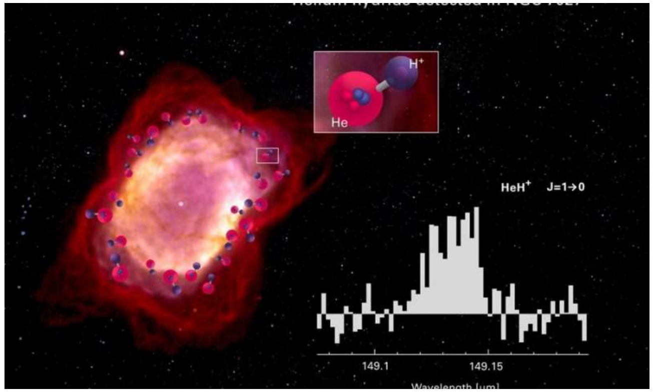
  H_2^+, H_2, HeH^+, LiH^+, LiH, H_3^+,... and isotopologues

- Experiments are very accurate but limited to few transitions!

- Astrophysicists need the full sets of transitions (<u>the linelists</u>) with increasing accuracy.

↓

ACCURATE COMPUTATIONS OF FULL LINELISTS (beyond BO)



Güsten at al., Nature **568**, 357 (2019)
Astrophysical detection of helium hydride ion, HeH^+

Frequency Measurements of HeH^+ and HeD^+ Transitions

Unit : MHz

$0.00001\ cm^{-1}$

$1\ cm^{-1} = 0.000124\ eV$

HeH^+ Transition	This Work	Other's Work	Diff.
P(4)	78 366 569.24 (2.74)	78 366 632.91 (59.96)[a]	-63.67
P(3)	80 795 499.71 (0.91)	80 795 499.88 (0.99)[b]	-0.17
P(2)	83 096 617.73 (0.77)	83 096 617.69 (1.34)[b]	0.04
P(1)	85 258 146.24 (0.66)	85 258 146.86 (0.35)[b]	-0.62
R(0)	89 115 533.00 (0.48)	89 115 533.66 (1.38)[b]	-0.66
R(1)	90 788 379.66 (0.37)	90 788 380.66 (0.40)[b]	-1.00
R(2)	92 275 879.49 (0.52)	92 275 879.63 (0.77)[b]	-0.14
R(3)	93 567 523.03 (0.68)	93 567 523.38 (0.92)[b]	-0.35
R(4)	94 653 352.58 (4.05)	94 653 373.83 (59.96)[a]	-21.25
HeD^+ Transition			
R(2)	72453181.5 (2.0)	72453241 (150)[c]	-59.5
R(3)	73344784.1 (3.1)	73344764 (150)[c]	20.1
R(4)	74144694.9 (2.7)	74144730 (150)[c]	-35.1

New experiments from Shy's group (Taiwan)

a. P. Bernath and T. Amano, Phys. Rev. Lett. **48**, 20 (1982).

b. A. J. Perry, J. N. Hodges, C. R. Markus, G. S. Kocheril, and B. J. McCall, J. Chem. Phys. **141**, 101101 (2014).

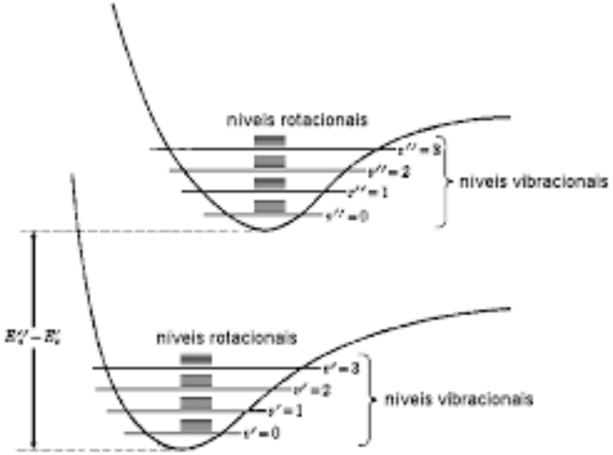
c. M. W. Crofton, R. S. Altman, N. N. Haese, and T. Oka, J. Chem. Phys. **91**, 5882 (1989).

How to reach 10^{-1}-10^{-2} cm^{-1} accuracy in rovibrational levels

MO (CI, MPT,...) or DFT-based EE methods are not capable of reaching this accuracy

Full-body calculations (nuclei and electrons on the same footing) are not viable for excited states.

1. Explicitly correlated BO calculations (PEC) + corrections
2. Solution of the rovibrational equation for the PEC



How to reach 10^{-1}-10^{-2} cm^{-1} accuracy in rovibrational levels

BO hierarchy of approximations:

1. BO PEC (PES) variational calculations with explicitly correlated GTFs

   Accuracy of 0.002 cm^{-1} in the BO points but errors of dozens of cm^{-1} in the rovibrational energy levels

2. Adiabatic (DBOC) corrections on the PEC

   Amounts to about 10^2 cm^{-1} and contribute 10^0 - 10^1 cm^{-1} to the energy levels

3. Relativistic + QED corrections on the PEC

$$E = E_{nr} + \alpha^2 E_{rel,bp} + \alpha^3 E_{qed}$$

One order of magnitude smaller than DBOC but important for high quantum numbers

⟶ Results are still units of cm^{-1} far from experimental values

The explanation is the absence of non-adiabatic corrections to the energy levels themselves!

Non-adiabatic effects

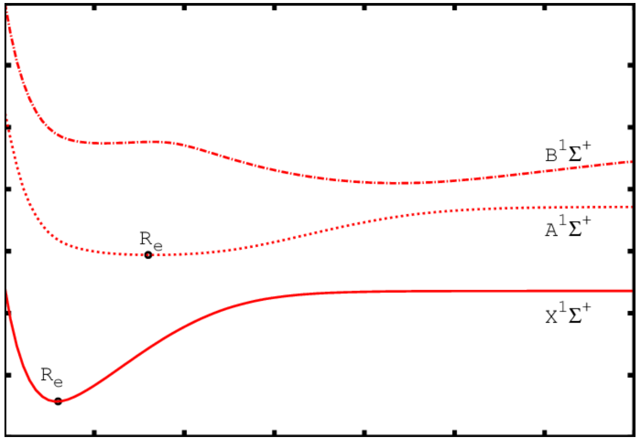
Two types: from avoided crossings and from electron dragging!

In the coupled nuclear equations,

$$\left(-\frac{1}{2\mu}\frac{d^2}{dR^2}+\frac{J(J+1)}{2\mu R^2}+E_{kk}(R)-E\right)\chi_k(R)=-\sum_{l\neq k}\frac{(\boldsymbol{\nabla}_{\boldsymbol{R}})_{kl}.\boldsymbol{\nabla}_{\boldsymbol{R}}}{\mu}\chi_l(R)$$

$$\left(-\frac{1}{2\mu_{vib}(R)}\frac{d^2}{dR^2}+\frac{J(J+1)}{2\mu_{rot}(R)R^2}+E_{kk}(R)-E_{vJ}\right)\chi_k(R)=0$$

Variable reduced mass demands new techniques for the solution of this equation! (colaboration with A. Alijah, Reims)



Previous applications

- Empirical use of atomic masses for vibrations and nuclear masses for rotations; constant fractional masses (2/3 of electron mass for each nucleus of H_3^+)

Formal (2- electron systems):

- Bunker & Moss, Herman & Asgharian, Pachucki & Komasa:
  Obtained formal transformations, leading to non physical vibrational masses

- Kutzelnigg was the first to consider the question of "which masses are vibrating and rotating in a molecule" [Mol. Phys. **105**, 2627 (2007)

Real masses of variable electron fractions added to nuclei (our group):

- Separation of motions of core and valence electrons in a molecule
  [Mohallem et al. CPL **501**, 575 (2011)]
- Masses based on diagonal Mulliken populations or VB coefficients
  [Diniz et al. CPL **633**, 89 (2015)]

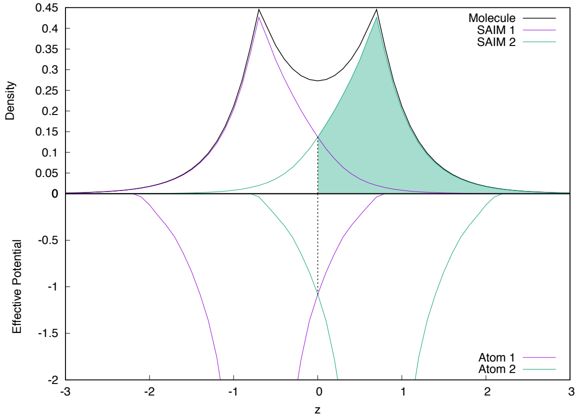
- No general empirical method for core masses until then!

The stockholder AIM approach for vibrational core masses (general)[2]

Problem: How to fractionate de electronic density in order to identify electronic cores?

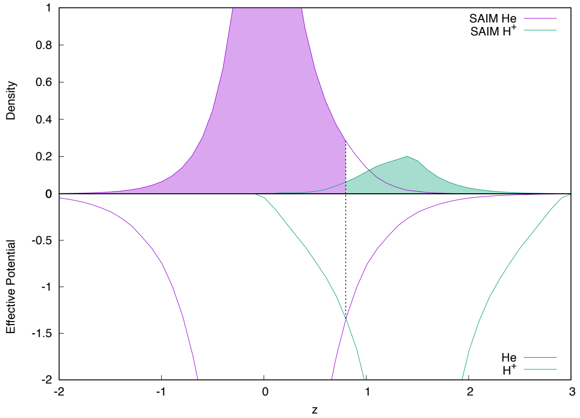
Solution: Hirschfeld (stockholder) AIM[1] imitate real atoms in a molecule
Effective electrostatic potentials separate core and valence fractions[2]

FIG 1



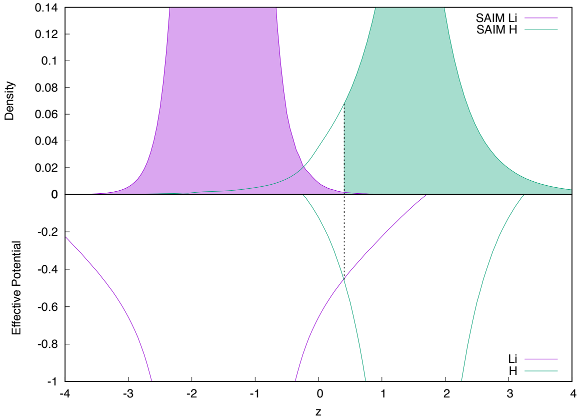
H_2

FIG 4



HeH^+

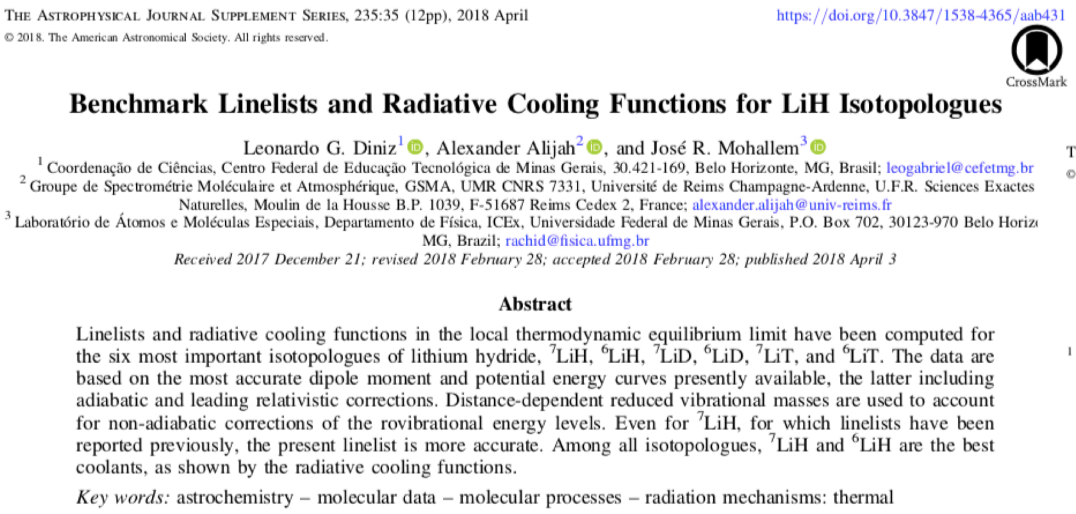
FIG 6



LiH

1. F. Hirschfeld, Theo. Chim. Acta **44**, 129 (1977)
2. Amaral and Mohallem, J. Chem. Phys. **146**, 194103 (2017)

Produced linelists (under 10^{-1} cm^{-1})



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Benchmark Linelists and Radiative Cooling Functions for LiH Isotopologues

Leonardo G. Diniz[1], Alexander Alijah[2], and José R. Mohallem[3]
[1] Coordenação de Ciências, Centro Federal de Educação Tecnológica de Minas Gerais, 30.421-169, Belo Horizonte, MG, Brasil; leogabriel@cefetmg.br
[2] Groupe de Spectrométrie Moléculaire et Atmosphérique, GSMA, UMR CNRS 7331, Université de Reims Champagne-Ardenne, U.F.R. Sciences Exactes Naturelles, Moulin de la Housse B.P. 1039, F-51687 Reims Cedex 2, France; alexander.alijah@univ-reims.fr
[3] Laboratório de Átomos e Moléculas Especiais, Departamento de Física, ICEx, Universidade Federal de Minas Gerais, P.O. Box 702, 30123-970 Belo Horiz
MG, Brazil; rachid@fisica.ufmg.br

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Abstract

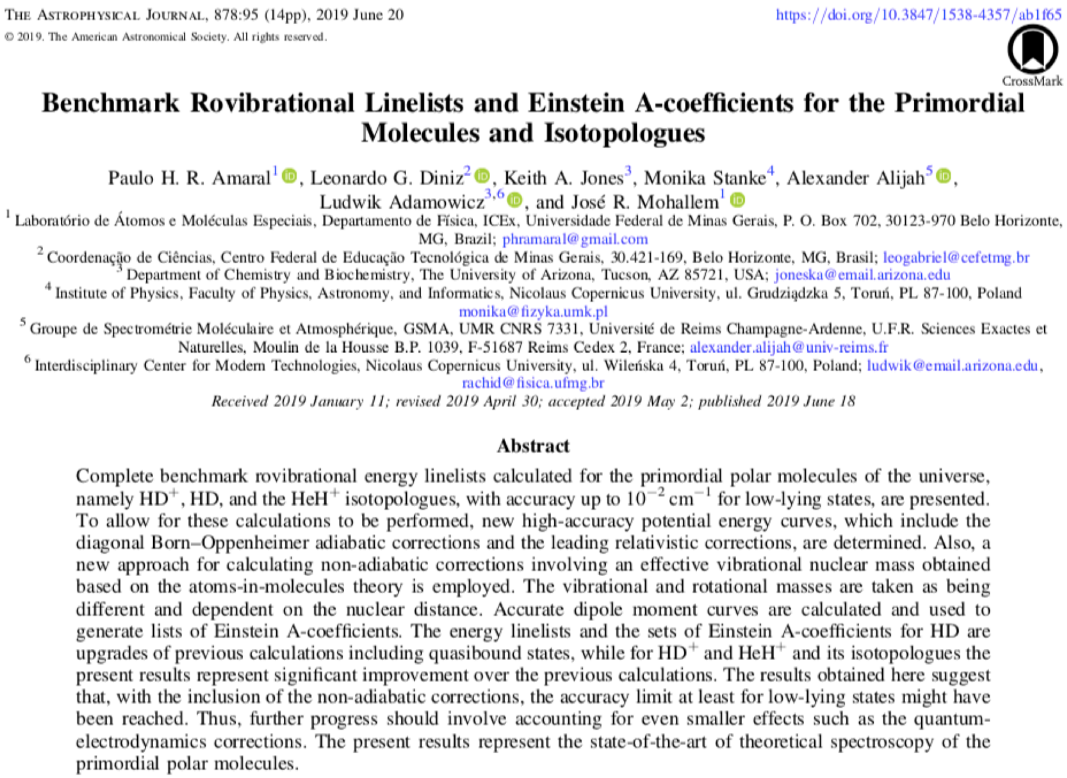
Linelists and radiative cooling functions in the local thermodynamic equilibrium limit have been computed for the six most important isotopologues of lithium hydride, ^{7}LiH, ^{6}LiH, ^{7}LiD, ^{6}LiD, ^{7}LiT, and ^{6}LiT. The data are based on the most accurate dipole moment and potential energy curves presently available, the latter including adiabatic and leading relativistic corrections. Distance-dependent reduced vibrational masses are used to account for non-adiabatic corrections of the rovibrational energy levels. Even for ^{7}LiH, for which linelists have been reported previously, the present linelist is more accurate. Among all isotopologues, ^{7}LiH and ^{6}LiH are the best coolants, as shown by the radiative cooling functions.

Key words: astrochemistry – molecular data – molecular processes – radiation mechanisms: thermal

LiH and isotopologues

With the linelists in hand, we calculate
Einstein coefficients and, in consequence,
cooling functions and other properties

HD^{+}, HD, HeH^{+} and isotopologues



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Benchmark Rovibrational Linelists and Einstein A-coefficients for the Primordial Molecules and Isotopologues

Paulo H. R. Amaral[1], Leonardo G. Diniz[2], Keith A. Jones[3], Monika Stanke[4], Alexander Alijah[5],
Ludwik Adamowicz[3,6], and José R. Mohallem[1]
[1] Laboratório de Átomos e Moléculas Especiais, Departamento de Física, ICEx, Universidade Federal de Minas Gerais, P. O. Box 702, 30123-970 Belo Horizonte, MG, Brazil; phramaral@gmail.com
[2] Coordenação de Ciências, Centro Federal de Educação Tecnológica de Minas Gerais, 30.421-169, Belo Horizonte, MG, Brasil; leogabriel@cefetmg.br
[3] Department of Chemistry and Biochemistry, The University of Arizona, Tucson, AZ 85721, USA; joneska@email.arizona.edu
[4] Institute of Physics, Faculty of Physics, Astronomy, and Informatics, Nicolaus Copernicus University, ul. Grudziądzka 5, Toruń, PL 87-100, Poland monika@fizyka.umk.pl
[5] Groupe de Spectrométrie Moléculaire et Atmosphérique, GSMA, UMR CNRS 7331, Université de Reims Champagne-Ardenne, U.F.R. Sciences Exactes et Naturelles, Moulin de la Housse B.P. 1039, F-51687 Reims Cedex 2, France; alexander.alijah@univ-reims.fr
[6] Interdisciplinary Center for Modern Technologies, Nicolaus Copernicus University, ul. Wileńska 4, Toruń, PL 87-100, Poland; ludwik@email.arizona.edu, rachid@fisica.ufmg.br

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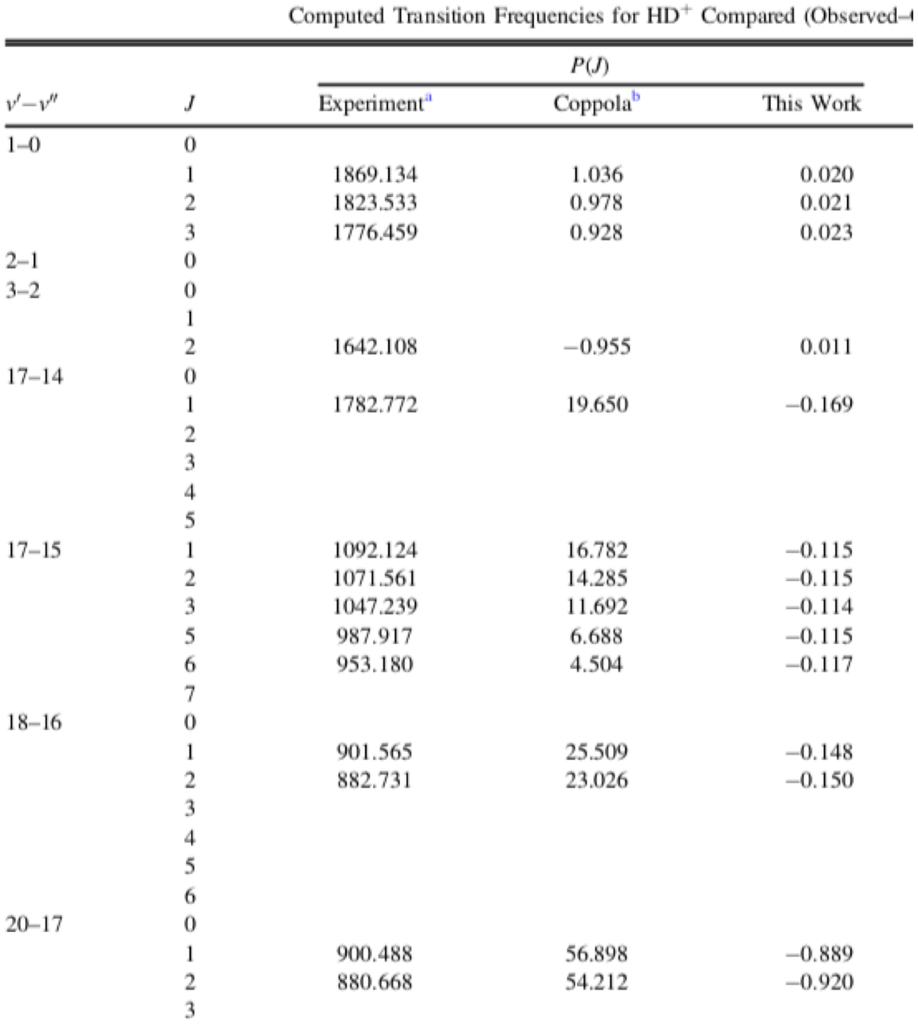
Abstract

Complete benchmark rovibrational energy linelists calculated for the primordial polar molecules of the universe, namely HD^{+}, HD, and the HeH^{+} isotopologues, with accuracy up to 10^{-2} cm^{-1} for low-lying states, are presented. To allow for these calculations to be performed, new high-accuracy potential energy curves, which include the diagonal Born–Oppenheimer adiabatic corrections and the leading relativistic corrections, are determined. Also, a new approach for calculating non-adiabatic corrections involving an effective vibrational nuclear mass obtained based on the atoms-in-molecules theory is employed. The vibrational and rotational masses are taken as being different and dependent on the nuclear distance. Accurate dipole moment curves are calculated and used to generate lists of Einstein A-coefficients. The energy linelists and the sets of Einstein A-coefficients for HD are upgrades of previous calculations including quasibound states, while for HD^{+} and HeH^{+} and its isotopologues the present results represent significant improvement over the previous calculations. The results obtained here suggest that, with the inclusion of the non-adiabatic corrections, the accuracy limit at least for low-lying states might have been reached. Thus, further progress should involve accounting for even smaller effects such as the quantum-electrodynamics corrections. The present results represent the state-of-the-art of theoretical spectroscopy of the primordial polar molecules.

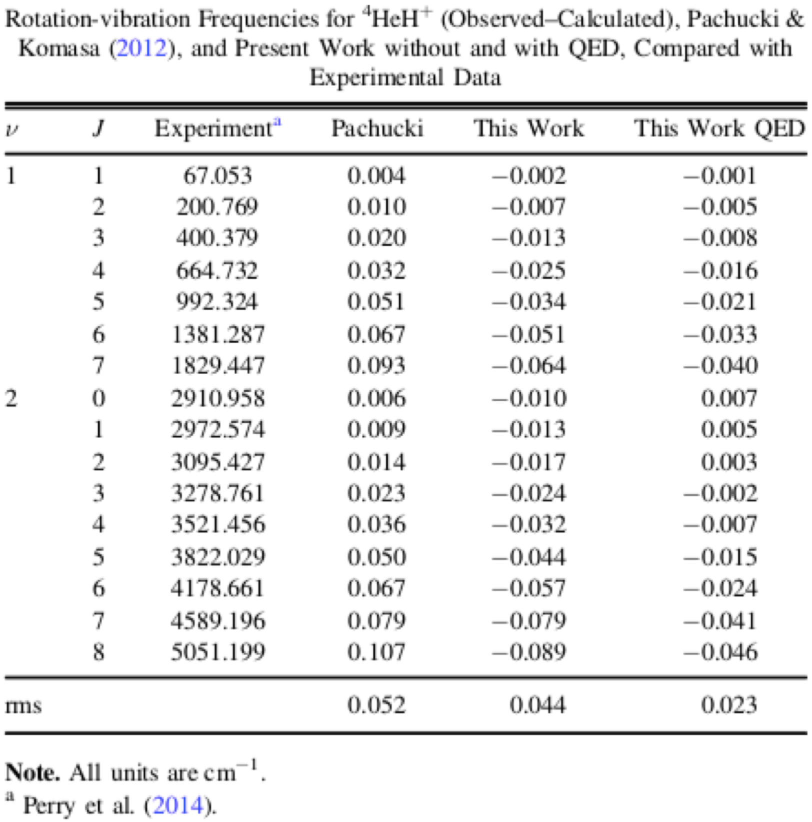
→ Exomol.com

Selected results



Computed Transition Frequencies for HD$^+$ Compared (Observed–

$v'-v''$	J	$P(J)$ Experiment[a]	Coppola[b]	This Work
1–0	0			
	1	1869.134	1.036	0.020
	2	1823.533	0.978	0.021
	3	1776.459	0.928	0.023
2–1	0			
3–2	0			
	1			
	2	1642.108	−0.955	0.011
17–14	0			
	1	1782.772	19.650	−0.169
	2			
	3			
	4			
	5			
17–15	1	1092.124	16.782	−0.115
	2	1071.561	14.285	−0.115
	3	1047.239	11.692	−0.114
	5	987.917	6.688	−0.115
	6	953.180	4.504	−0.117
	7			
18–16	0			
	1	901.565	25.509	−0.148
	2	882.731	23.026	−0.150
	3			
	4			
	5			
	6			
20–17	0			
	1	900.488	56.898	−0.889
	2	880.668	54.212	−0.920
	3			



Rotation-vibration Frequencies for ^{4}HeH$^+$ (Observed–Calculated), Pachucki & Komasa (2012), and Present Work without and with QED, Compared with Experimental Data

ν	J	Experiment[a]	Pachucki	This Work	This Work QED
1	1	67.053	0.004	−0.002	−0.001
	2	200.769	0.010	−0.007	−0.005
	3	400.379	0.020	−0.013	−0.008
	4	664.732	0.032	−0.025	−0.016
	5	992.324	0.051	−0.034	−0.021
	6	1381.287	0.067	−0.051	−0.033
	7	1829.447	0.093	−0.064	−0.040
2	0	2910.958	0.006	−0.010	0.007
	1	2972.574	0.009	−0.013	0.005
	2	3095.427	0.014	−0.017	0.003
	3	3278.761	0.023	−0.024	−0.002
	4	3521.456	0.036	−0.032	−0.007
	5	3822.029	0.050	−0.044	−0.015
	6	4178.661	0.067	−0.057	−0.024
	7	4589.196	0.079	−0.079	−0.041
	8	5051.199	0.107	−0.089	−0.046
rms			0.052	0.044	0.023

Note. All units are cm^{-1}.

[a] Perry et al. (2014).

Quantities of interest

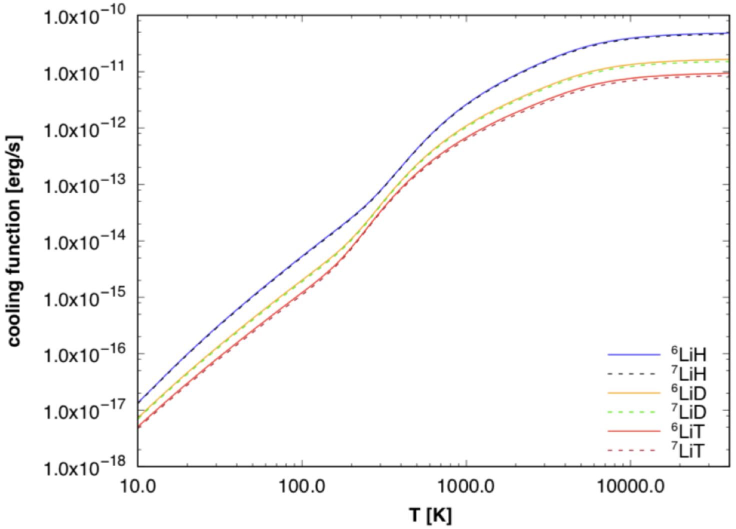
- Cooling functions, opacity functions

- The partition function

$$Z(T) = \sum_i (2J_i + 1)\, g_i\, e^{-E_i/(k_B T)}.$$

- The cooling function

$$W(T) = \frac{1}{Z(T)} \sum_{\mathrm{u,l}} A_{\mathrm{ul}}(E_{\mathrm{u}} - E_{\mathrm{l}})(2J_{\mathrm{u}} - 1) g_{\mathrm{u}} n_{\mathrm{u}},$$



What is there beyond 10^{-1}-10^{-2} cm^{-1} ?

- The AIM masses work well for vibrations, but best rotational masses are still fully empirical

  There is no appropriate physical model for rotations yet

- Masses dependent on ν, J

- Further corrections (finite nuclear volume,...)

Further challenge: Excited electronic states

People

PEC (PES points), DBOC, RELAT., QED:
L. Adamowicz, N. Kirnosov, K. A. Jones (Arizona), M. Stanke, E. Palikot (Poland)

SOLUTION OF “NUCLEAR” EQUATION WITH VARIABLE MASSES, PES:
A. Alijah (Reims), L. G. Diniz (Cefet-MG), P. H. Amaral (UFMG)

NON-ADIABATIC CORRECTIONS:
L. G. Diniz, P. H. Amaral

Projeto atual: → H_2O !!!

Thanks for your attention, obrigado, شكرا جزيلا

Other lines of research in our group

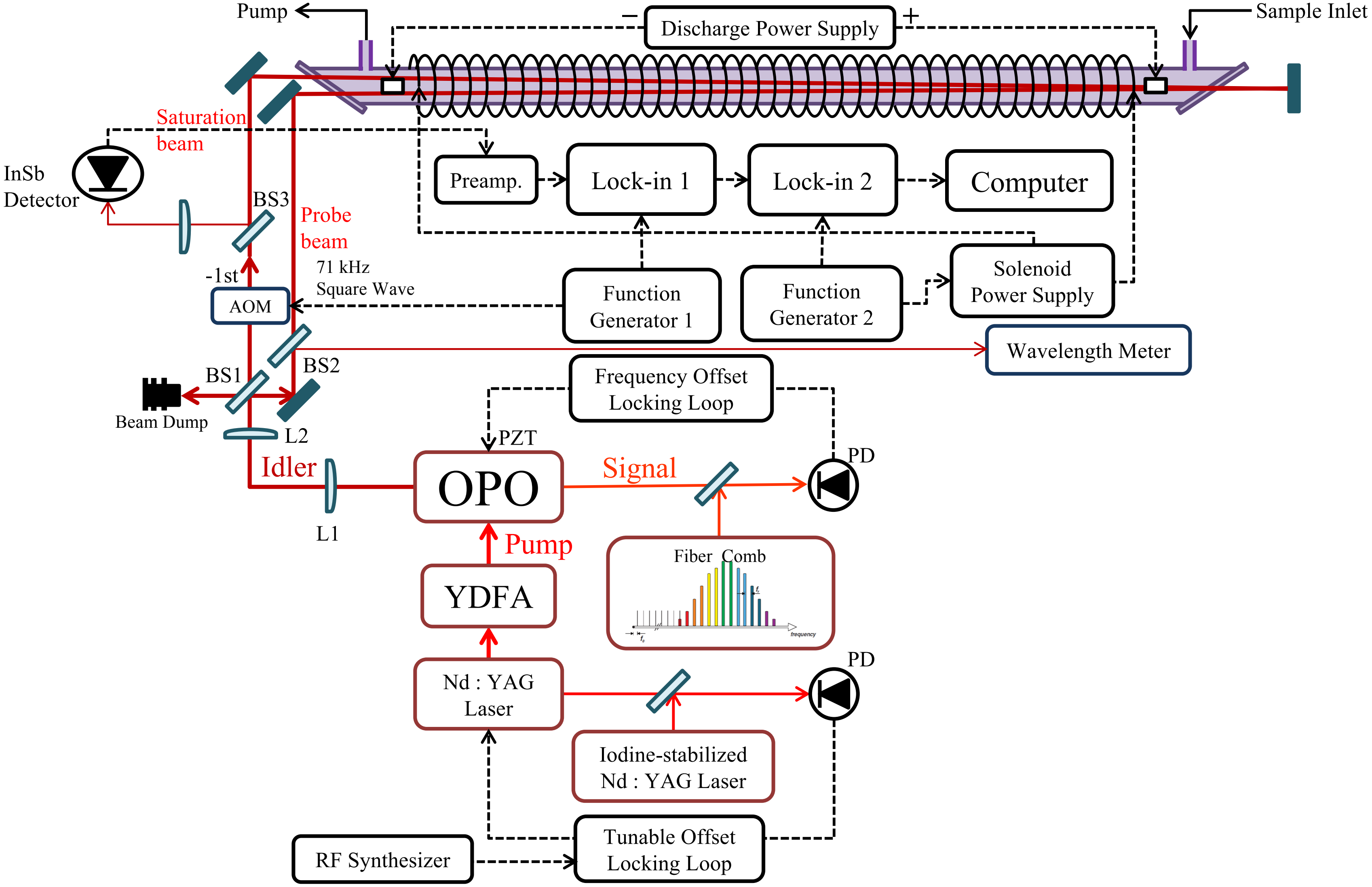
- Positron scattering from atoms and molecules; bound states
- Isotopic effects and isotopic dipole moments of molecules
- Investigating molecular environments with an isotopic probe

Thanks to CNPq, UFMG, GSMA - Université de Reims, CNRS

THANKS FOR YOUR ATTENTION!

Contact: rachid@física.ufmg.br

Experimental Setup



Pump

Discharge Power Supply

−

+

Sample Inlet

Saturation beam

InSb Detector

BS3

Probe beam

-1st

71 kHz Square Wave

AOM

Preamp.

Lock-in 1

Lock-in 2

Computer

Function Generator 1

Function Generator 2

Solenoid Power Supply

Wavelength Meter

BS2

BS1

Beam Dump

L2

Frequency Offset Locking Loop

PZT

Idler

OPO

Signal

PD

L1

Pump

YDFA

Fiber Comb

frequency

Nd : YAG Laser

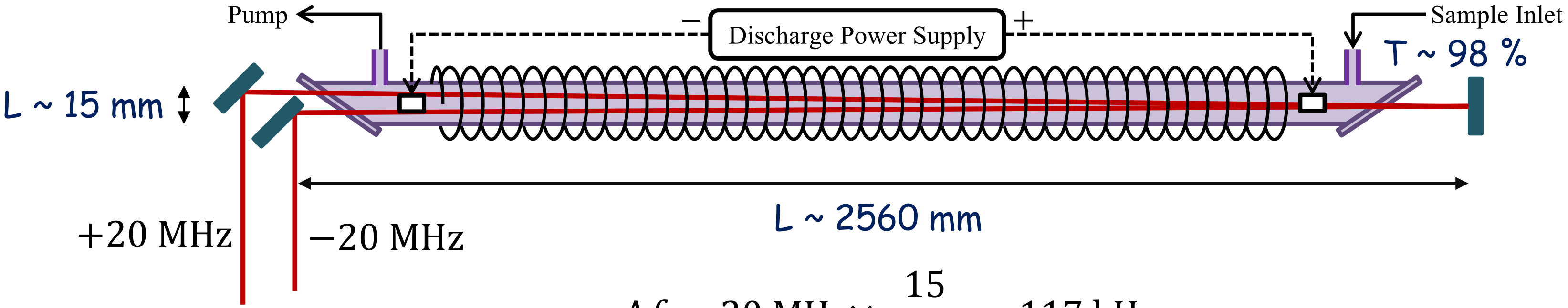
PD

Iodine-stabilized Nd : YAG Laser

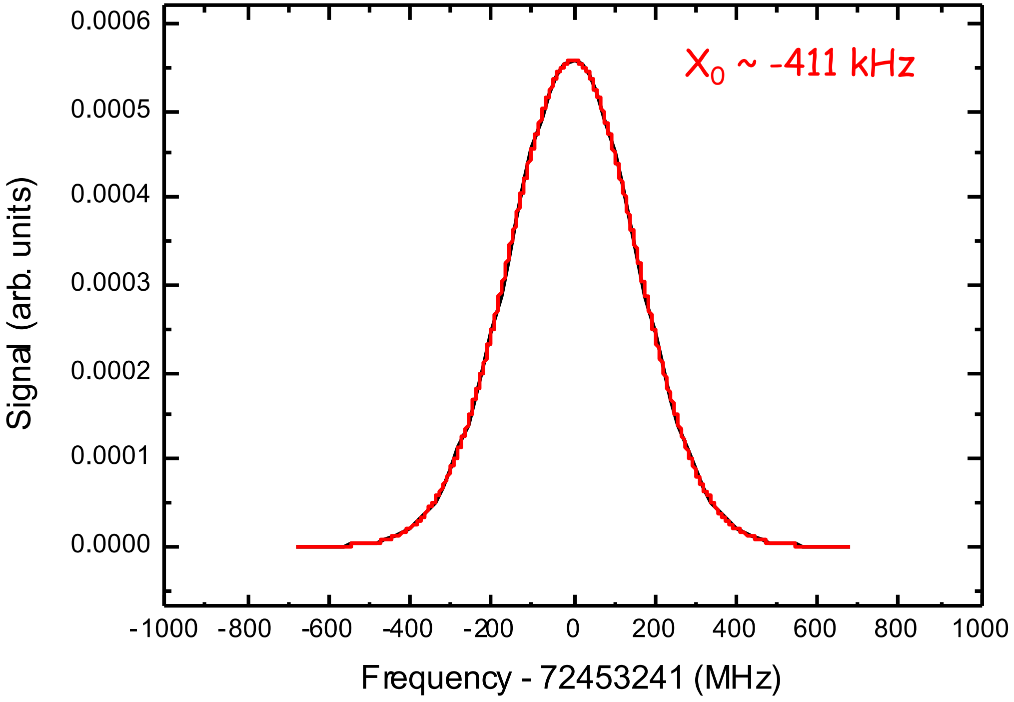
RF Synthesizer

Tunable Offset Locking Loop

Experimental Setup



$$\Delta f = 20\ \mathrm{MHz} \times \frac{15}{2560} = 117\ \mathrm{kHz}$$



Experimental Setup