Suggesting the radio-observation of astrophysical ices' secondary ions: Experimental and computational approaches

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- Water ice: key component of astrochemical reactions & most abundant in the ISM
- Constant sputtering by ionising agents

Molecule	W33A high	NGC7538 IRS9/high	Elias29 low	Elias16 field	Orion hot core	Comet Halley	Comet Hyakutake	Comet Hale-Bopp
H_2O	100	100	100	100	>100	100	100	100
CO	9	16	5.6	25	1000	15	6–30	20
CO_2	14	20	22	15	2–10	3	2–4	6–20
CH_4	2	2	<1.6	—	—	0.2–1.2	0.7	0.6
CH_3OH	22	5	<4	<3.4	2	1–1.7	2	2
H_2CO	1.7–7	5	—	—	0.1–1	0–5	0.2–1	1
OCS	0.3	0.05	<0.08	—	0.5	—	0.1	0.5
NH_3	15	13	<9.2	<6	8	0.1–2	0.5	0.7–1.8
C_2H_6	—	<0.4	—	—	—	—	0.4	0.3
HCOOH	0.4–2	3	—	—	0.008	—	—	0.06
OCN^-	3	1	<0.24	<0.4	—	—	—	—
HCN	<3	—	—	—	4	0.1	0.1	0.25
HNC	—	—	—	—	0.02	—	0.01	0.04

Ehrenfreund et al. (2000)

- Water ice: key component of astrochemical reactions & most abundant in the ISM
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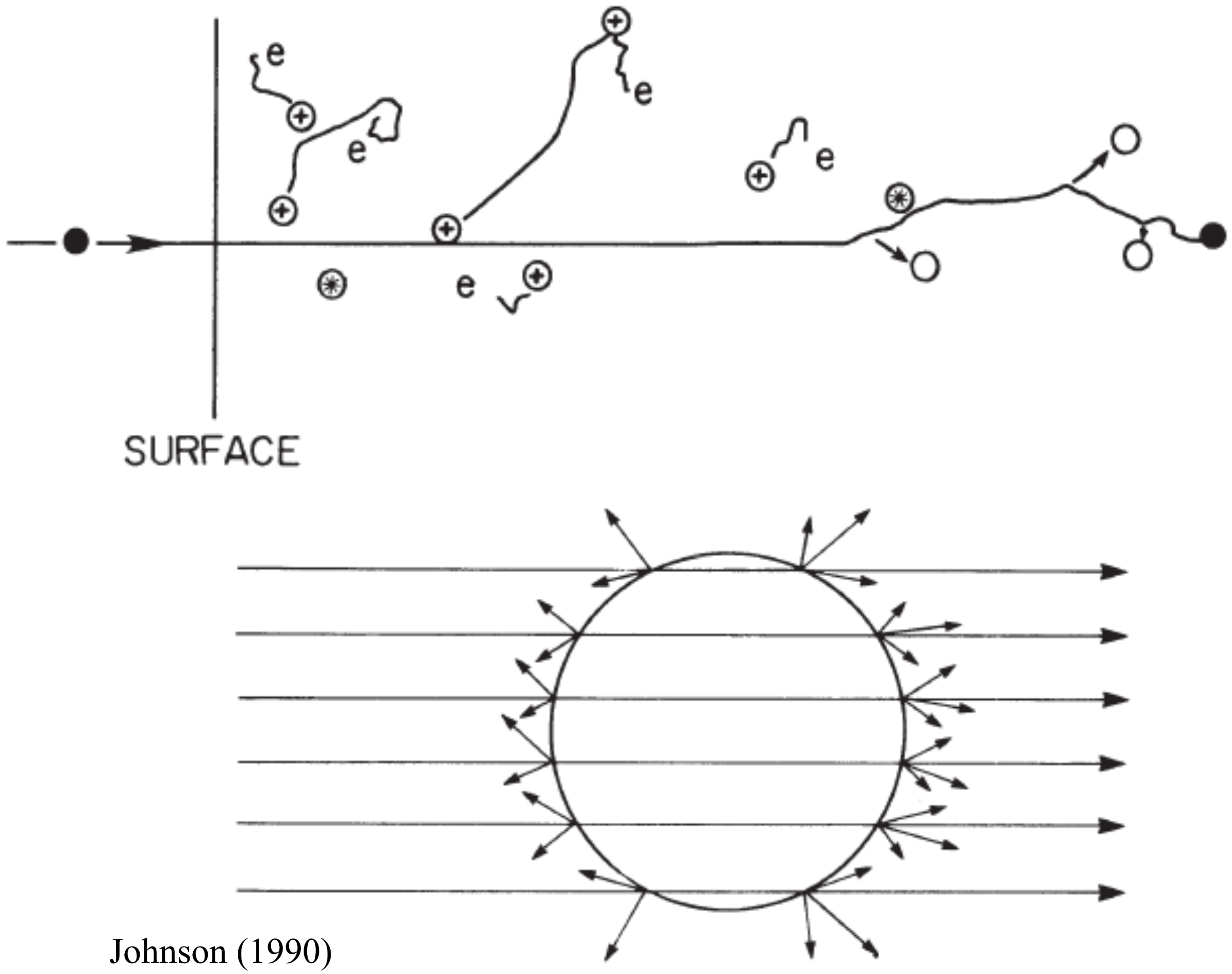
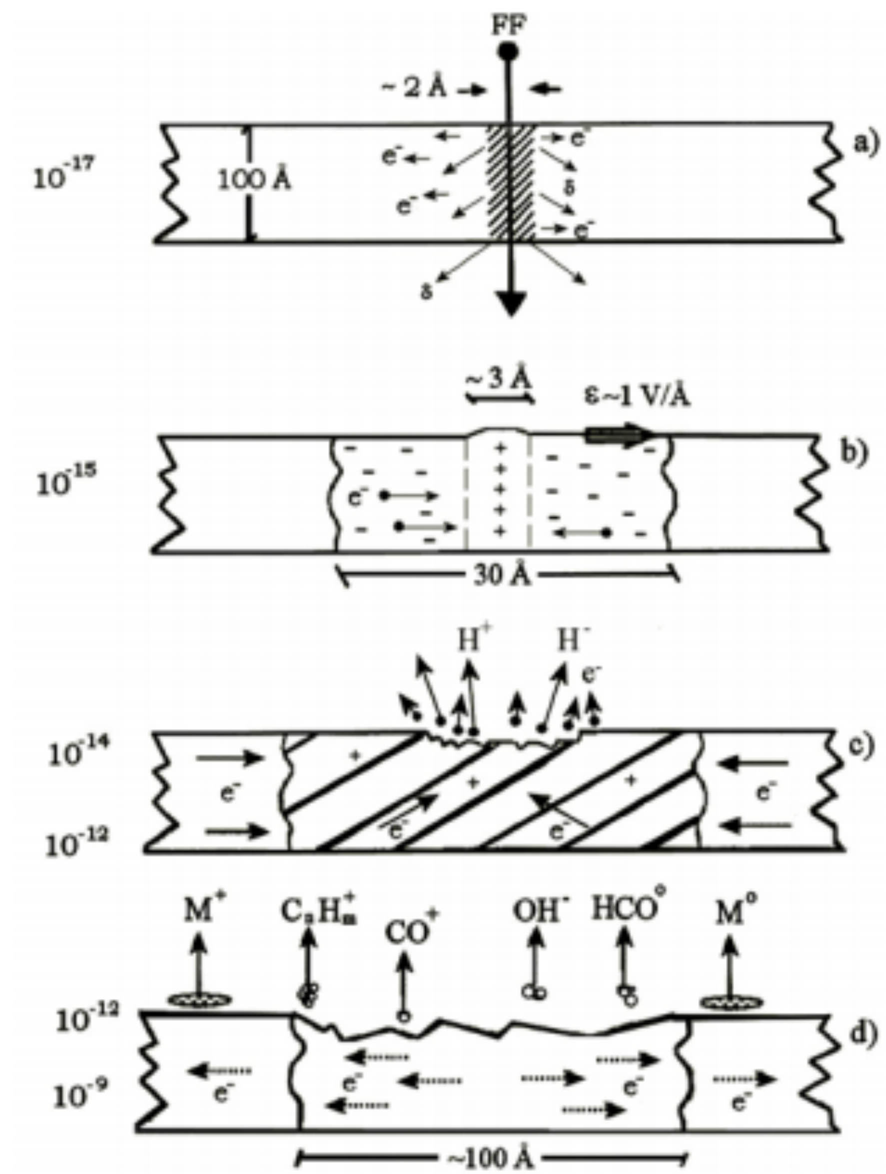


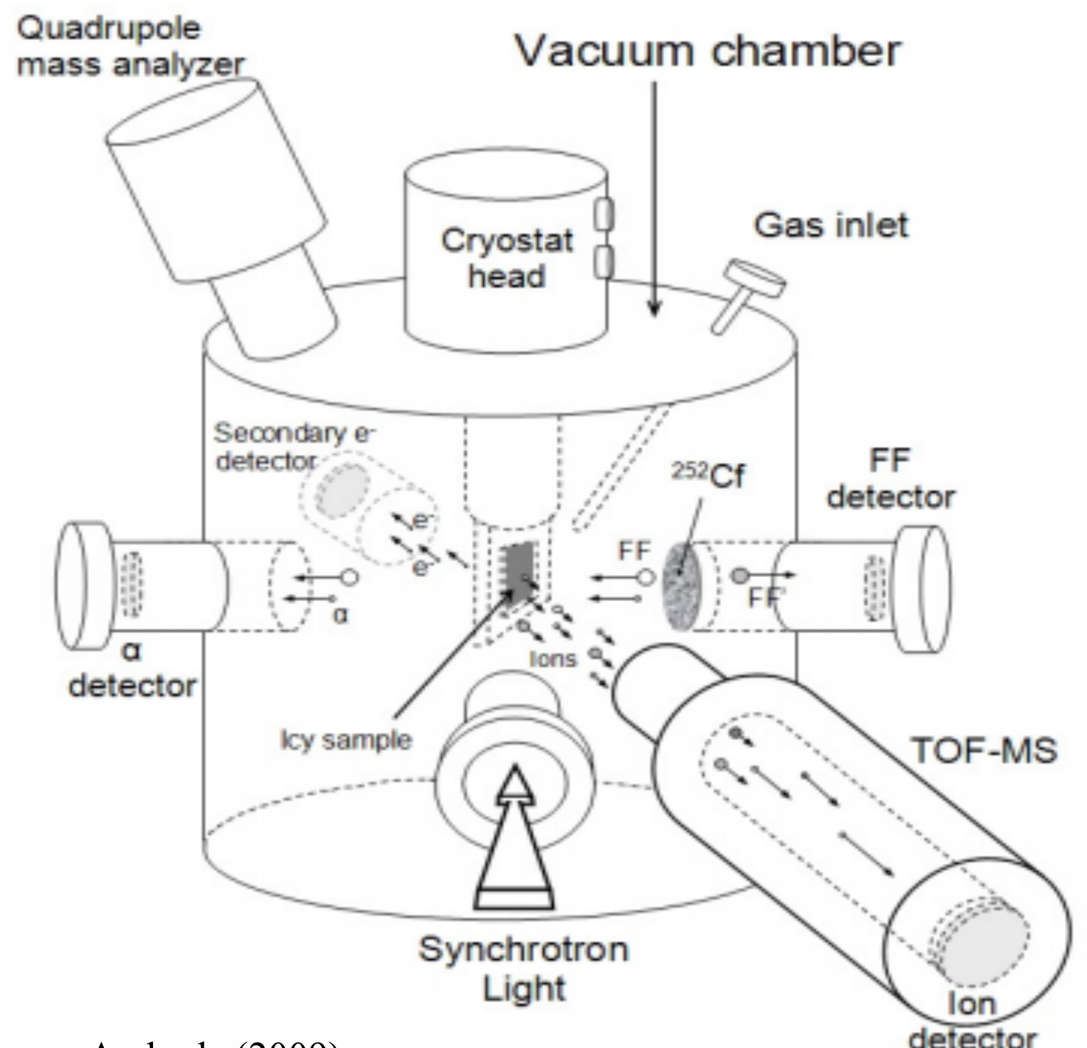
Johnson (1990)



Andrade (2009)

- Simulation of ice sputtering using TOF-PDMS

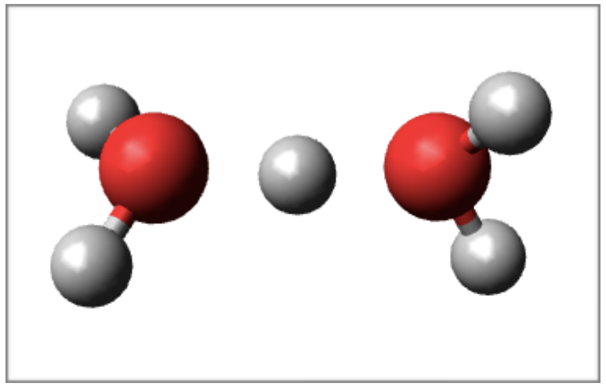
- 65 MeV ^{252}Cf fission fragments → ≈ 0.52 Mev/u
- Ultra-high vacuum
- *In situ* condensation



Andrade (2009)

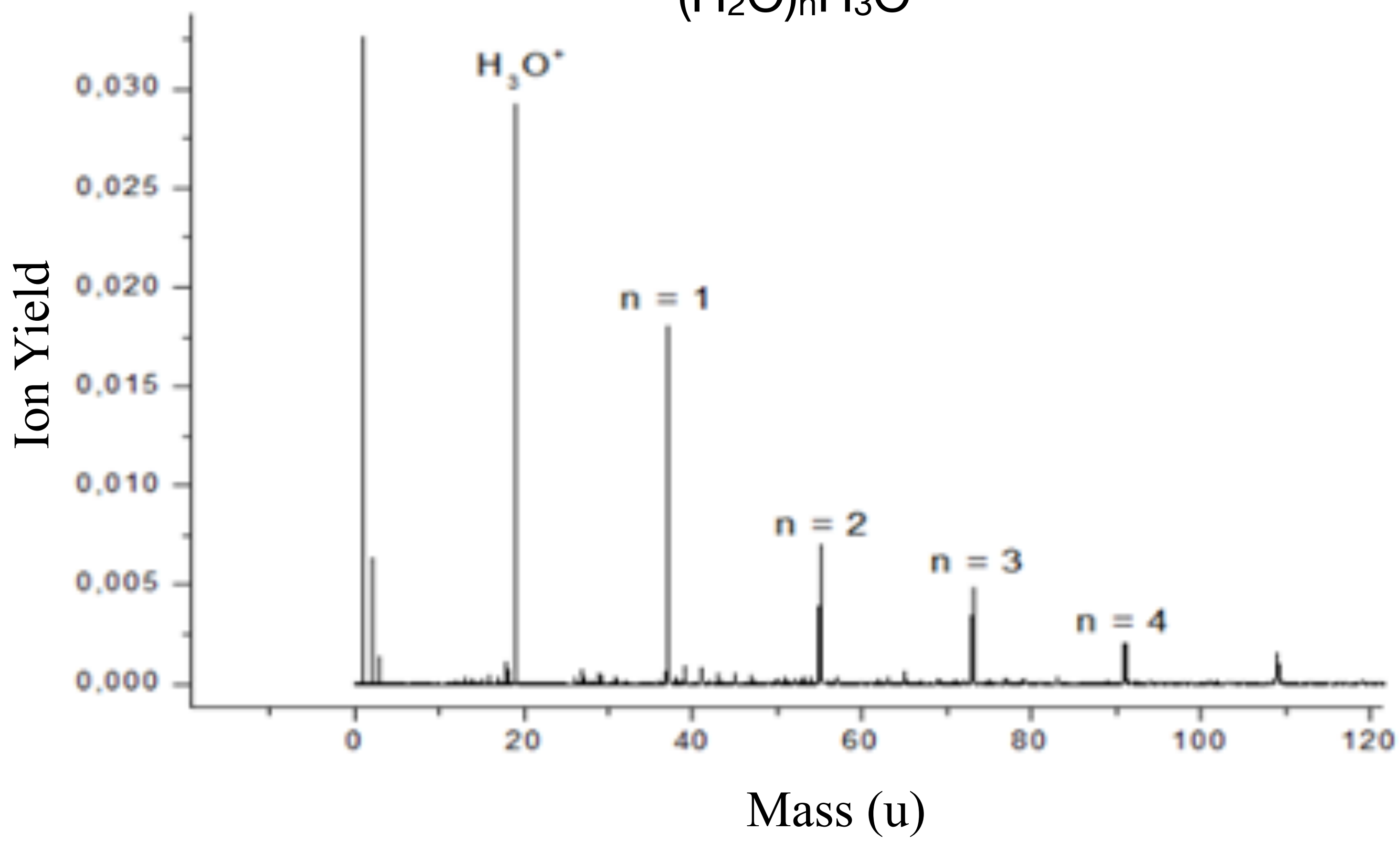
- Simulation of ice sputtering using TOF-PDMS

- Dominant pattern: $(H_2O)_nH_3O^+$ with $1 \leq n \leq 10$



$(H_2O)H_3O^+$

$(H_2O)_nH_3O^+$



- Rigid rotor: 14 candidate bands

$J^n \longrightarrow J^{n+1}$	Frequency (GHz)
n = 0	18.47[1][2]
n = 3	69.51[3], 71.00[3] and 74.40[3]
n = 4	83.02[3][4][5], 84.97[3][4][5], 85.26[3][4], 86.82[3][4][5] and 88.47[3][4]
n = 5	102.48[3][4][6], 104.96[3][4][6], 106.25[4][6] and 107.17[4][6]
n = 7	142.47[5][7]

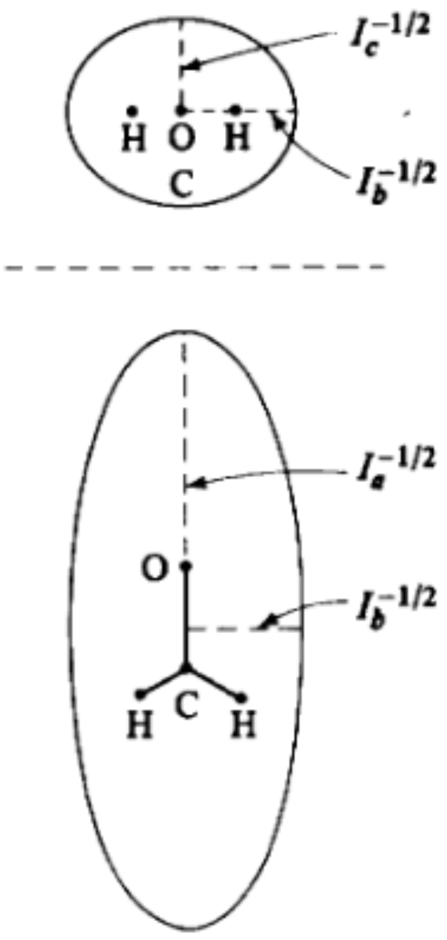
1 – Gong (2014) 2 – Watanabe (2015) 3 – Belloche (2013) 4 – Watanabe (2014) 5 – Gerner (2014) 6 – Muller (2014) 7 – López (2014)

- Computational simulation of rotational spectra

- Asymmetric rotors: $I_a \neq I_b \neq I_c$

$$det\,[\,\langle \varphi_m |\hat{H}| \varphi_n \rangle - E_i \delta_{mn}\,] = 0$$

$$\psi_{i,rot} = \sum_{K'=-J}^{J} c_{i,J,M,K'} \varphi_{i,J,M,K'}$$



Levine, I. N. (1975)

- Computational simulation of rotational spectra

- Complete Hamiltonian

$$\frac{\hat{H}_{rot}}{hc} = \sum_{\alpha} B_v^{(\alpha)} J_\alpha^2 + 1/4 \sum_{\alpha,\beta} (\tau'_{\alpha\alpha\beta\beta})_v J_\alpha^2 J_\beta^2 + \sum_{\alpha} \Phi_{\alpha\alpha\alpha} J_\alpha^6 + \sum_{\alpha\neq\beta} \Phi_{\alpha\alpha\beta}(J_\alpha^4 J_\beta^2 + J_\beta^2 J_\alpha^4) + \ldots$$

- Vib-Rot coupling
- Centrifugal distortion
- Vibrational anharmonicity

- Computational simulation of rotational spectra

- S-type Watson Hamiltonian

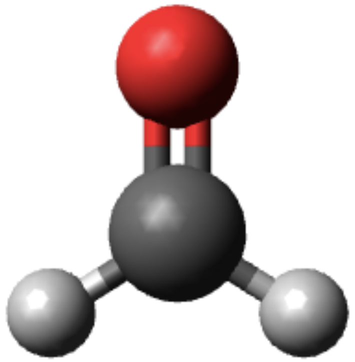
$$\frac{\tilde{H}^S_{rot}}{hc} = \sum_\alpha \tilde{B}^{(\alpha)}_v J^2_\alpha - D_J J^4 - D_{JK} J^2 J^2_z - D_K J^4_z + d_1 J^2 (J^2_+ + J^2_-) + d_2 (J^4_+ + J^4_-) + H_J J^6$$

$$+ H_{JK} J^4 J^2_z + H_{KJ} J^2 J^4_z + H_K J^6_z + h_1 J^4 (J^2_+ + J^2_-) + h_2 J^2 (J^4_+ + J^4_-) + h_3 (J^6_+ + J^6_-) + \ldots$$

- Computational simulation of rotational spectra

- Benchmark: H_2CO
  - B2PLYP/cc-pVQZ
  - Gaussian 09 A.02

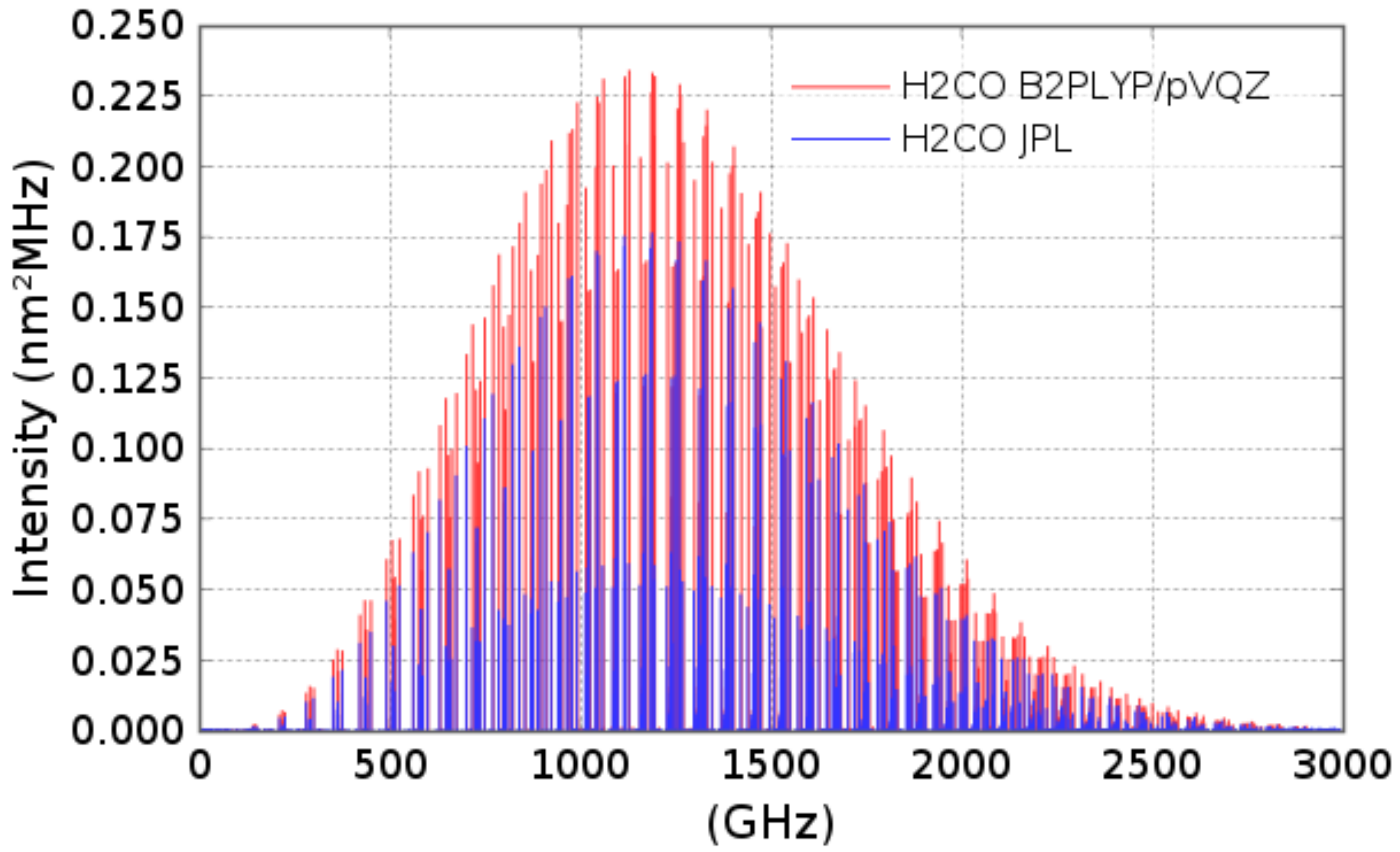
  - Symmetry
  - Good behaviour



	B2PLYP	Experimental
r_e (CO) (Å)	1,2026	1,203 [a]
r_e (CH)	1,1020	1,099 [a]
θ_e (HCH) (deg)	116,1235	116,5 [a]
μ(D)	2,3532	2,331 [b]
A_e (cm^{-1})	9,5629	9,5795 [a]
B_e	1,3019	1,3033 [a]
C_e	1,1459	1,1462 [a]
A'_0	9,4579	9,4055 [c]
B'_0	1,2969	1,2954 [c]
C'_0	1,1360	1,1343 [c]

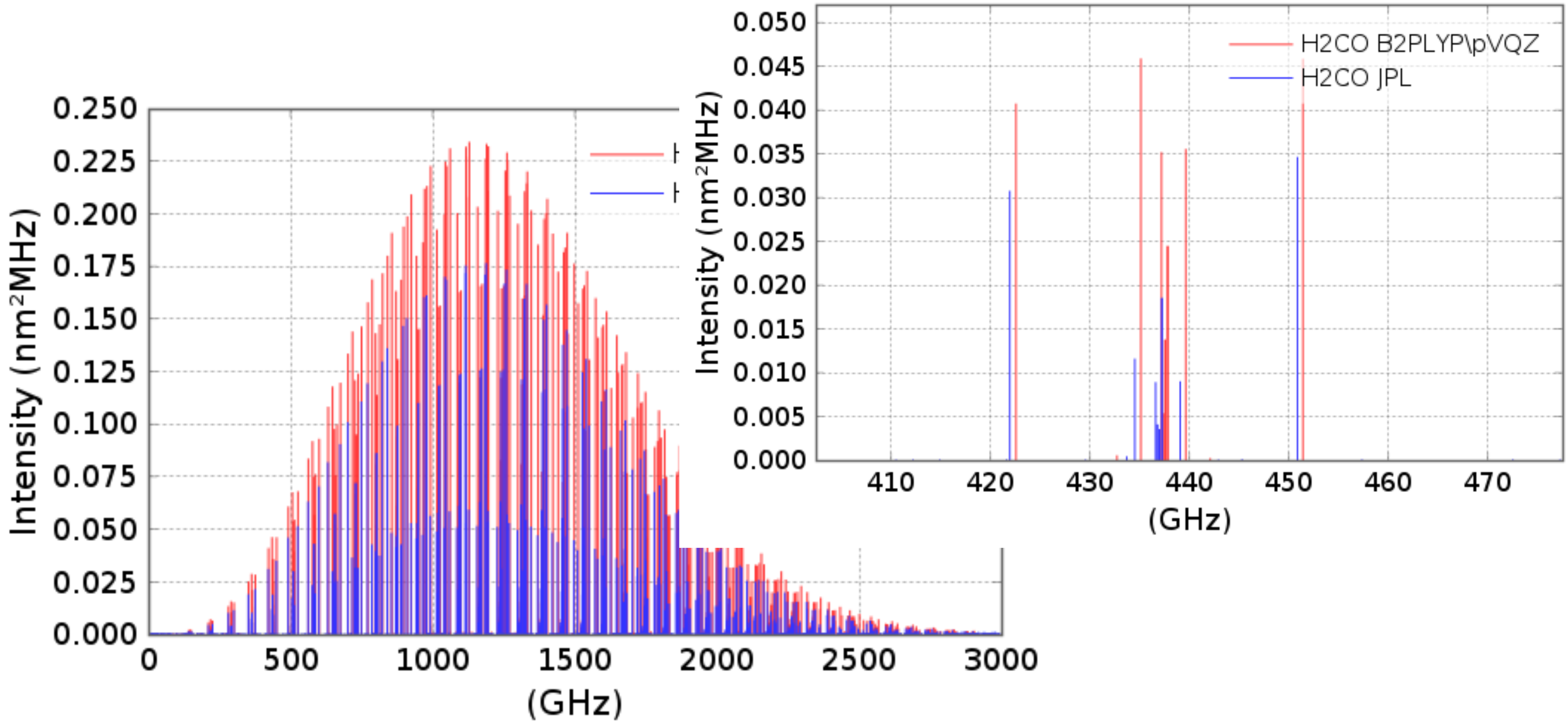
[a] Yamada et al. J. Mol. Spec. 1971; [b] Kondo et al., J. Phys. Soc. Jp. 1960; [c] Johnson et al. J. Phys. Chem Ref. Data 1972

- Computational simulation of rotational spectra



- SPCAT & SPFIT

- Computational simulation of rotational spectra



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- Computational simulation of rotational spectra

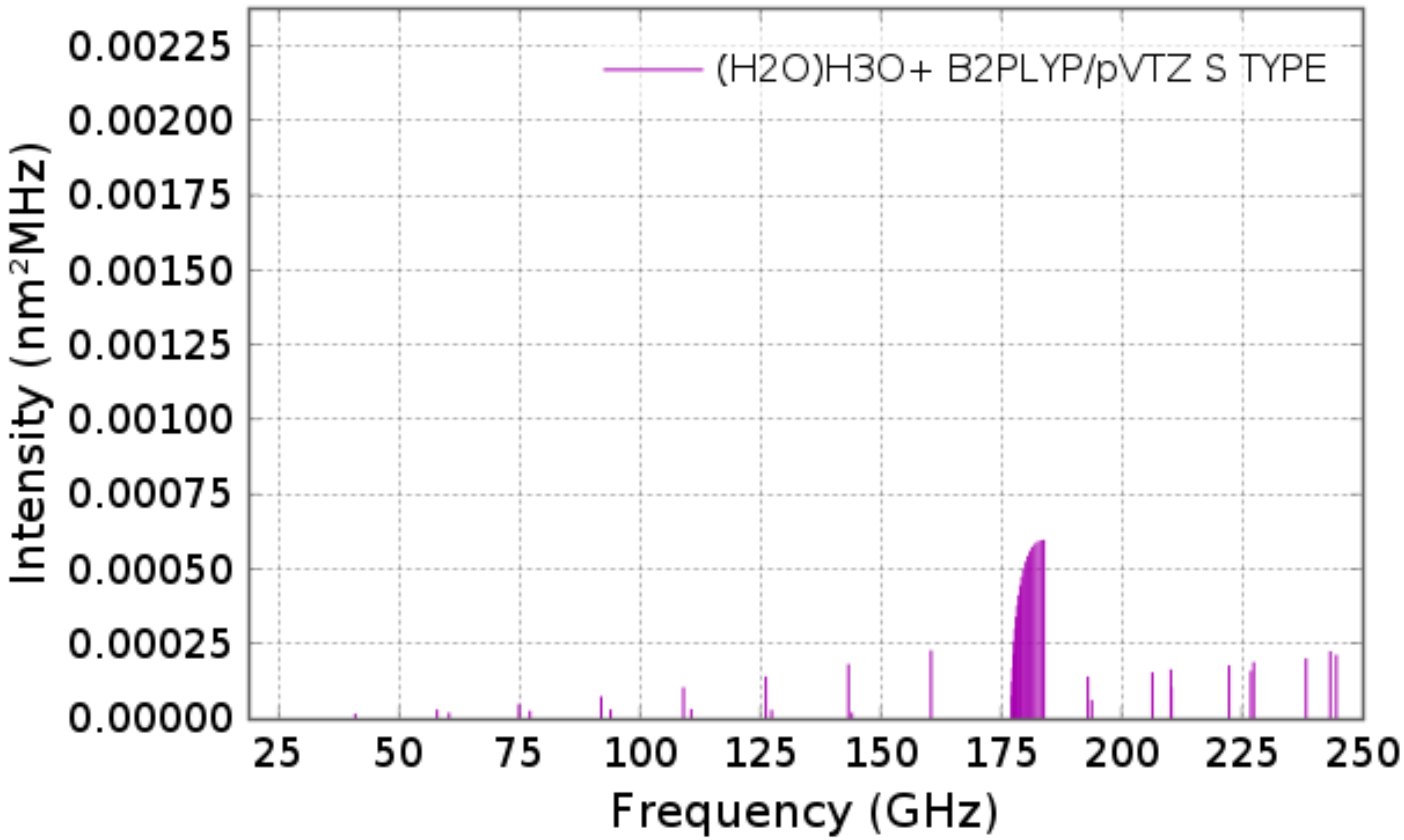
- $(H_2O)H_3O^+$
- B2PLYPD/aug-cc-pVTZ

	B2PLYPD	Experimental [a]
ν_1 (cm^{-1})	3646,589	3684
ν_2	3644,711	3684
ν_3	3572,441	3609
ν_4	3564,719	3609
ν_9	1319,084	1317

[a] Chaban et al. J. Phys. Chem. A. 2000

	B2PLYPD
A'_0	185603,871
B'_0	8344,664
C'_0	8256,968
Δ_J (MHz)	8,1645E-03
Δ_{JK}	2,5198E-01
Δ_K	1,0789E+01
δ_J	1,8672E-05
δ_K	6,1173E+00

- Computational simulation of rotational spectra



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- Conclusion & future perspectives:
  - $(H_2O)_nH_3O^+$ clusters are likely enriching the ISM
  - Preliminary calculations → 14 candidate bands
  - More refined calculations needed → CCSD(T) with larger basis set

Thank you!

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