

Calculation of Cold Infrared Spectra of Water Dimer

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Background

The spectroscopy of water dimer has been studied for than half a century, and its OH...O hydrogen bond is considered by many to be the archetype of hydrogen bonds. A range of experimental jet-cooled spectra have been published of the water dimer OH-stretching regions (fundamental and first overtone), but a firm assignment of the observed transitions has not yet been possible due to the lack of accurate calculations. The water dimer is a deceptively simple molecule (only six nuclei and 20 electrons) with eight versions of its equilibrium structure connected by low-energy barriers. The light molecular frame and the highly anharmonic potential energy surface results in large amplitude motion, making conventional vibrational models unreliable. We calculate the spectrum of water dimer in the OH-stretching regions with a finite basis representation of an effective Hamiltonian.¹⁻³

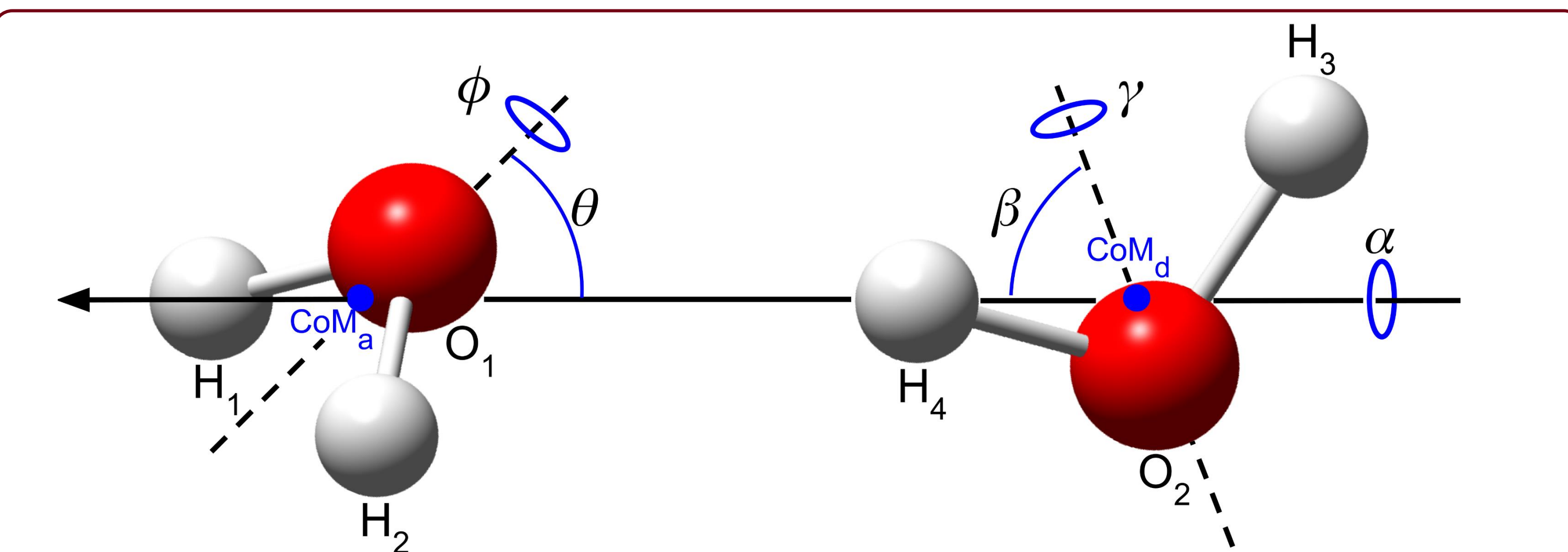


Figure 1: Definition of the intermolecular coordinates of the water dimer and the numbering of the atoms of the two H₂O units. The two centers of mass are used to define the last internal coordinate: $R = |\overline{CoM}_a - \overline{CoM}_d|$.

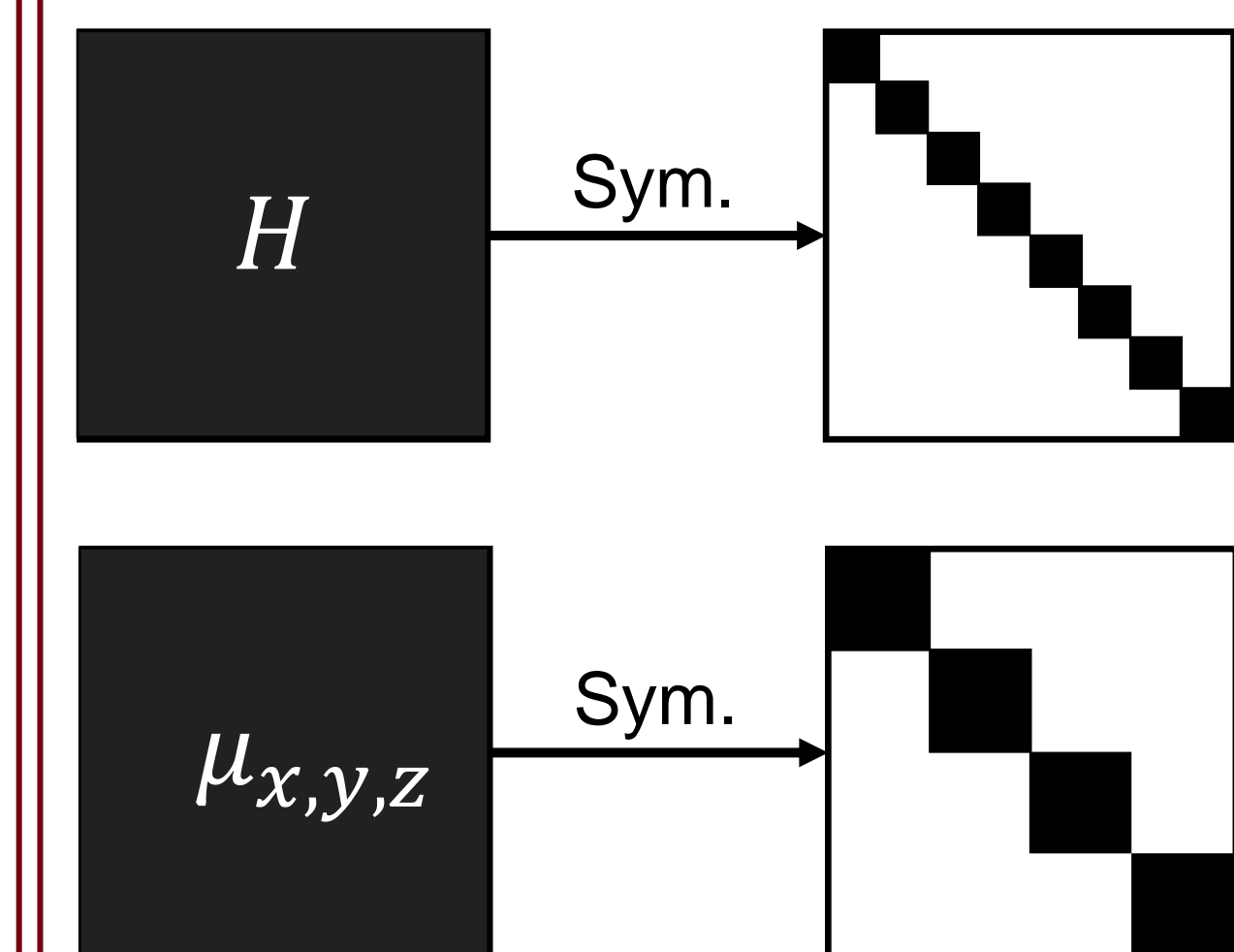
Molecular Symmetry

Table 1: Action of the generators* of the molecular symmetry group G_8 and G_{16} on the internal coordinates defined in Figure 1.

	G_{16}		E^*	P_{da}
	G_8			
E	(12)	(34)	E^*	P_{da}
R	R	R	R	R
β	β	β	β	$\pi - \theta$
θ	θ	θ	θ	$\pi - \beta$
ϕ	$\phi + \pi$	ϕ	$2\pi - \phi$	$\gamma + \pi$
α	α	α	$-\alpha$	α
γ	γ	$\gamma + \pi$	$2\pi - \gamma$	$\phi + \pi$
r_1	r_2	r_1	r_1	r_3
r_2	r_1	r_2	r_2	r_4
t_a	t_a	t_a	t_a	t_d
r_3	r_3	r_4	r_3	r_1
r_4	r_4	r_3	r_4	r_2
t_d	t_d	t_d	t_d	t_a

Generator (12) permutes H₁ and H₂, (34) permutes H₃ and H₄, E^ denotes inversion, and $P_{da} = (O_1 O_2)(13)(24)$ permutes the donor and acceptor nuclei.

Figure 2: The Hamiltonian and the dipole moment matrices are block-diagonalized with the use of the G_8 molecular symmetry group.



The eigenvectors and eigenvalues of the Hamiltonian matrix can be obtained by diagonalizing each submatrix, which significantly reduces the computational cost. Each block of the Hamiltonian contains basis functions that transform as different irreducible representations of the G_8 molecular symmetry group.

The Vibrational Model

Podolsky Hamiltonian with CCSD(T)-F12a/cc-pVTZ-F12 potential energy surface:

$$\hat{H} = \frac{1}{2} \sum_{ij} \tilde{g}^{-\frac{1}{4}} \hat{p}_i^\dagger G_{ij} \tilde{g}^{\frac{1}{2}} \hat{p}_j \tilde{g}^{-\frac{1}{4}} + V, \text{ where } \hat{p}_i = -i\hbar \frac{\partial}{\partial q_i},$$

$$\tilde{g} = \det(\mathbf{g}), \mathbf{g}_{ij} = \sum_{\alpha} m_{\alpha} \frac{\partial x_{\alpha}}{\partial q_i} \frac{\partial x_{\alpha}}{\partial q_j}, G_{ij} = \sum_{\alpha} \frac{1}{m_{\alpha}} \frac{\partial q_i}{\partial x_{\alpha}} \frac{\partial q_j}{\partial x_{\alpha}}.$$

Many-mode expansion of G , V , and $\mu_{x,y,z}$ (the dipole moment function), shown here for V :

$$V(q_1, q_2, \dots, q_{12}) \approx V_0 + \sum_i V_i^{1D}(q_i) + \sum_{i<j} V_{ij}^{2D}(q_i, q_j) + \sum_{i<j<k} V_{ijk}^{3D}(q_i, q_j, q_k)$$

12D basis functions expressed as symmetrized products of 1D eigenfunctions:

$$\Psi(r_1, r_2, t_a, r_3, r_4, t_d, R, \beta, \theta, \phi, \alpha, \gamma) = \psi_{v_1 v_2 \pm}(r_1, r_2) \psi_{v_a}(t_a) \psi_{v_3 v_4 \pm}(r_3, r_4) \psi_{v_d}(t_d) \psi_{v_R}(R) \psi_{v_{\beta}}(\beta) \psi_{v_{\theta}}(\theta) \psi_{v_{\phi}}(\phi) \psi_{v_{\alpha}}(\alpha) \psi_{v_{\gamma}}(\gamma)$$

1D eigenfunctions (at reference value of all other coordinates) are obtained from:

$$\hat{h}(q_i) \psi_{v_q}(q_i) = \epsilon_i \psi_{v_q}(q_i)$$

Energy ceilings and polyad truncations are used to control the size of the 12D basis.¹

OH-stretching Fundamental Region

Table 2: Calculated³ and experimental⁴⁻⁷ transition wavenumbers ($\tilde{\nu}$, in cm⁻¹) and relative oscillator strengths (f , in parentheses) for the OH-stretching fundamental transitions.

Transitions	6D*	12D	Jet	He-droplet	Ne-matrix
ν_{OH_b}	3555.5 (100)	3599.0 (100)	3601	3597.4 (100)	3590.5 (100)
ν_{OH_+}	3651.6 (2.5)	3650.6 (3.4)	3651	3654.3 (3.1)	3660.6 (3.3)
ν_{OH_f}	3726.9 (24)	3726.7 (54)	3730	3730.1 (66)	3733.7 (46)
ν_{OH_-}	3746.0 (22)	3742.6 (33)	3745.5	3748.6 (31)	3756.5 (26)

*The model includes the four OH-stretching modes and the two HOH-bending modes.

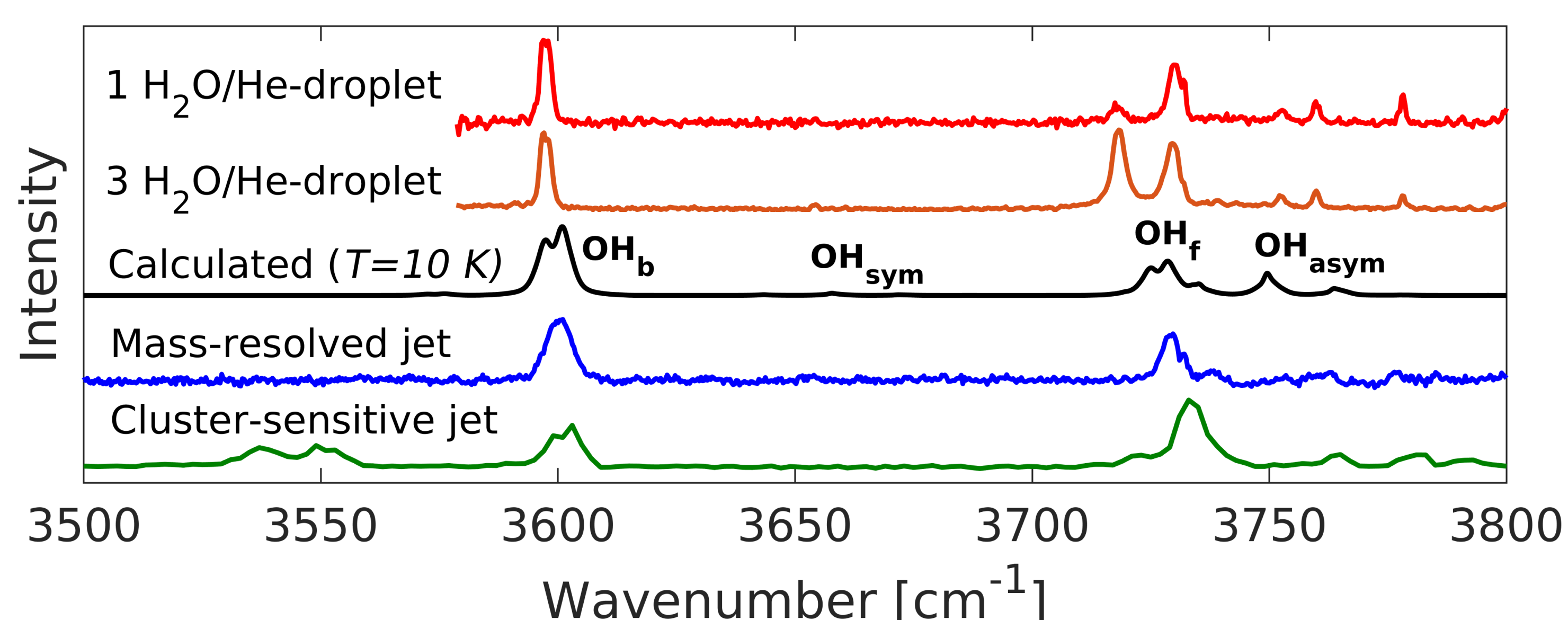


Figure 3: Calculated³ and experimental spectra⁷⁻⁹ in the OH-stretching fundamental region.

OH-stretching First Overtone Region

Table 3: Calculated³ transition wavenumbers ($\tilde{\nu}$), oscillator strengths (f), and rotational band types for selected OH-stretching transitions.

Transition	$\tilde{\nu}$ [cm ⁻¹]	f [$\times 10^{-6}$]	Type
$2\nu_{OH_b}$	7045.9	5.5	A/C
$2\nu_{OH_+}$	7187.6	9.3	A/C
$2\nu_{OH_f}$	7221.2	25	A/C
$2\nu_{OH_-}$	7231.1	44	B

Figure 4: Infrared-ultraviolet vibrationally mediated dissociation spectrum of water dimer.¹⁰ Reprinted from [J. Chem. Phys. 122, 194316 (2005)], with the permission of AIP Publishing.

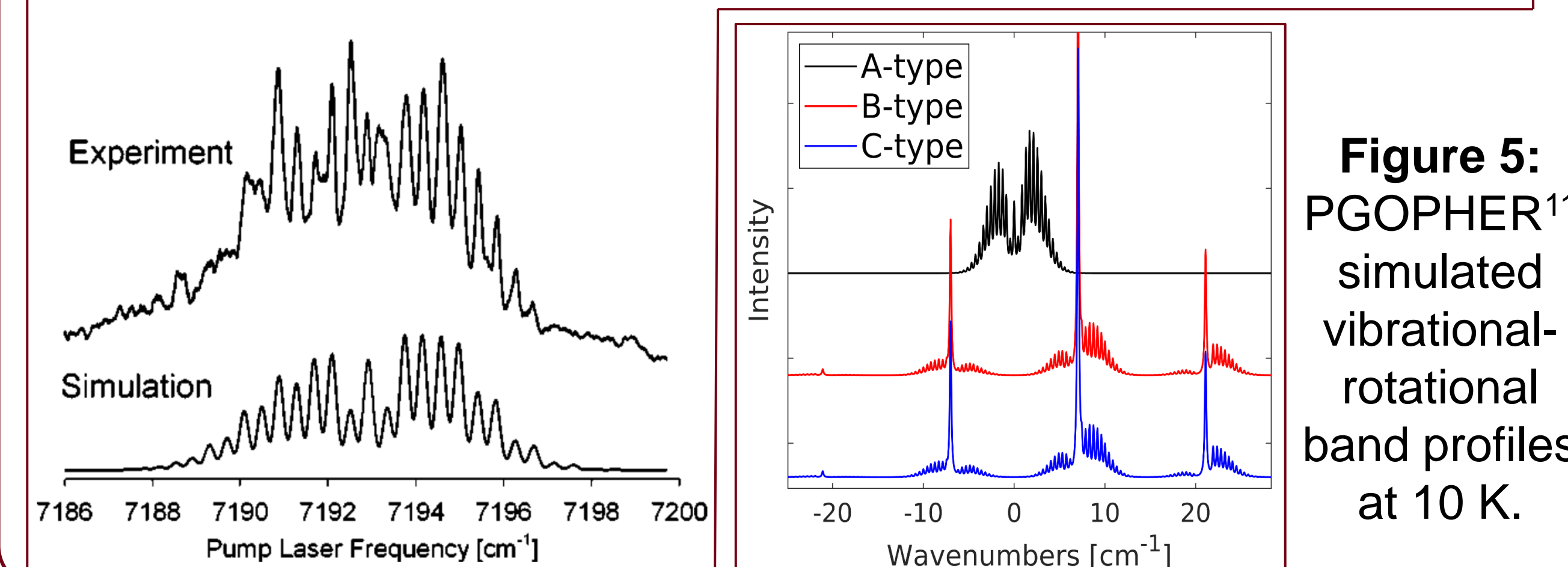
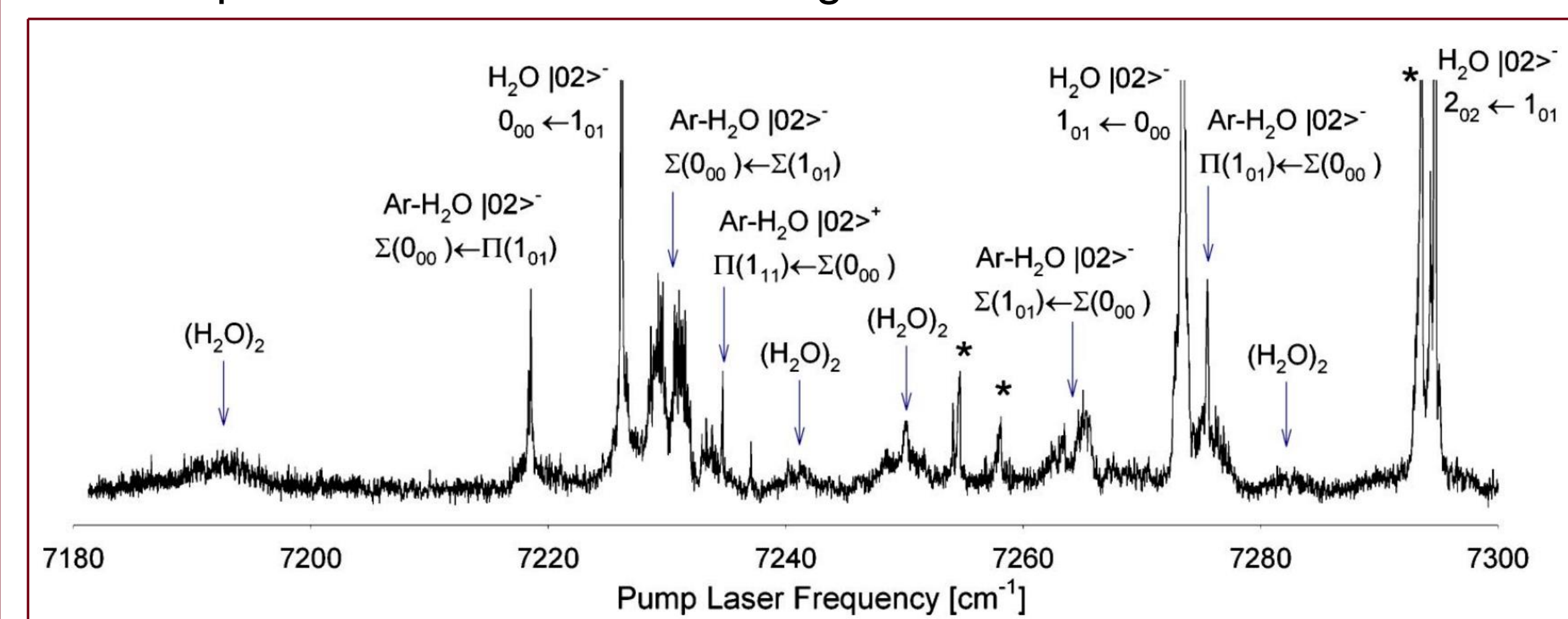


Figure 5: PGOPHER¹¹ simulated vibrational-rotational band profiles at 10 K.

Acknowledgements

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