

Coriolis Coupled Dynamics of the $\text{H}(^2\text{S}) + \text{CH}^+(\text{X}^1\Sigma^+)$ Reaction: A Full-Dimensional Quantum Wavepacket Study

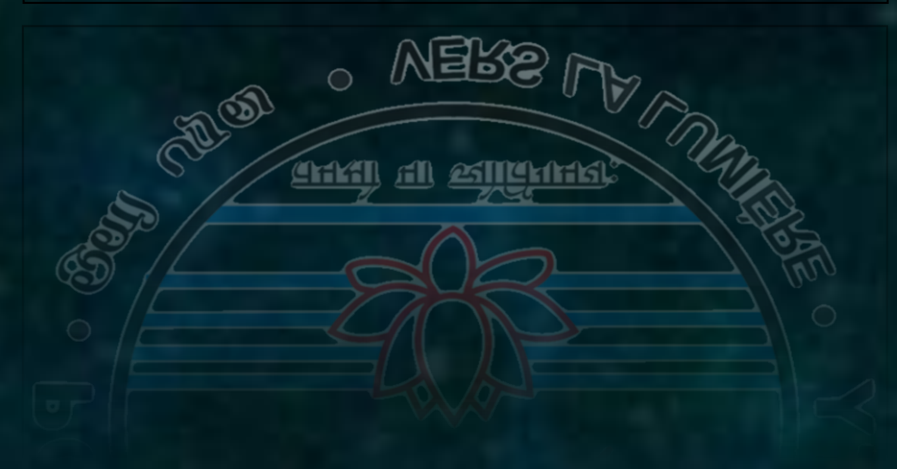
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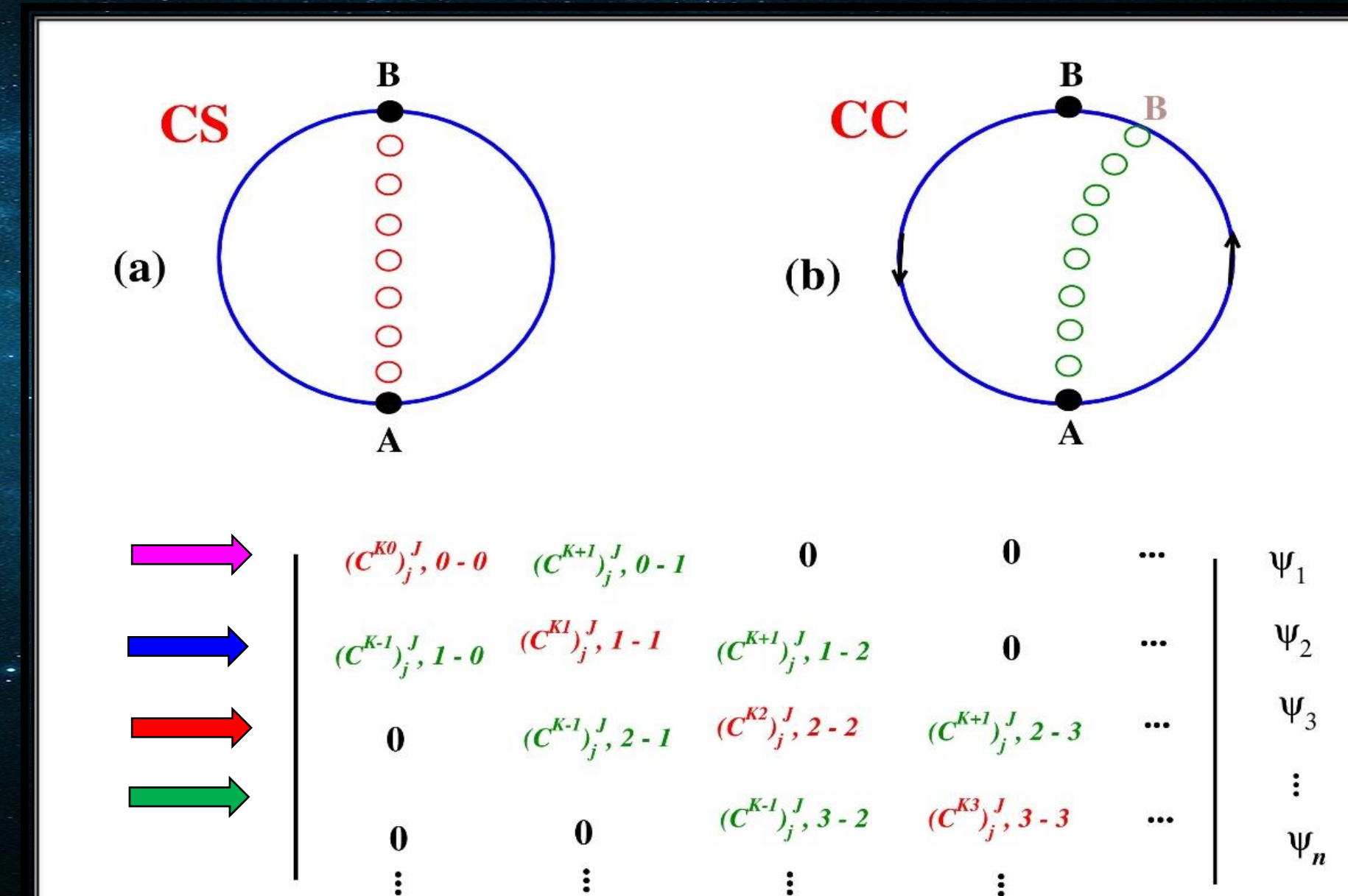
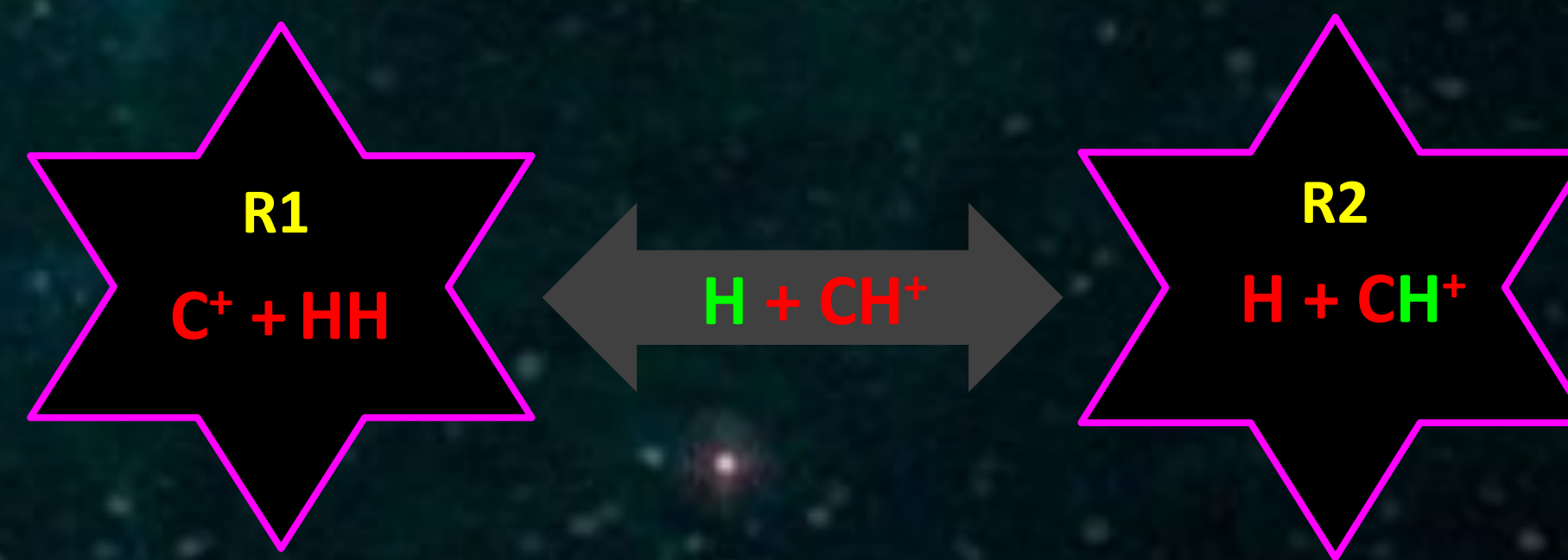
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Introduction

- Reactions between the atoms and molecular ions are known to play a significant role in the chemistry of diffuse interstellar and circumstellar regions, planetary ionospheres, and high-energy physics.
- The neutral CH and ionic CH^+ species was extensively studied in past few decades.
- CH^+ typical molecular ion and most important in Interstellar medium (ISM).
- It was the first molecular ion identified in the ISM.



- Theoretical Frame Work^(2,3,4)
- Time-dependent wavepacket approach.
 - Mass scaled body-fixed Jacobi coordinate system.
 - Second Order Split-Operator Method.
 - Centrifugal Sudden (CS) approximation.
 - Coriolis Coupling method

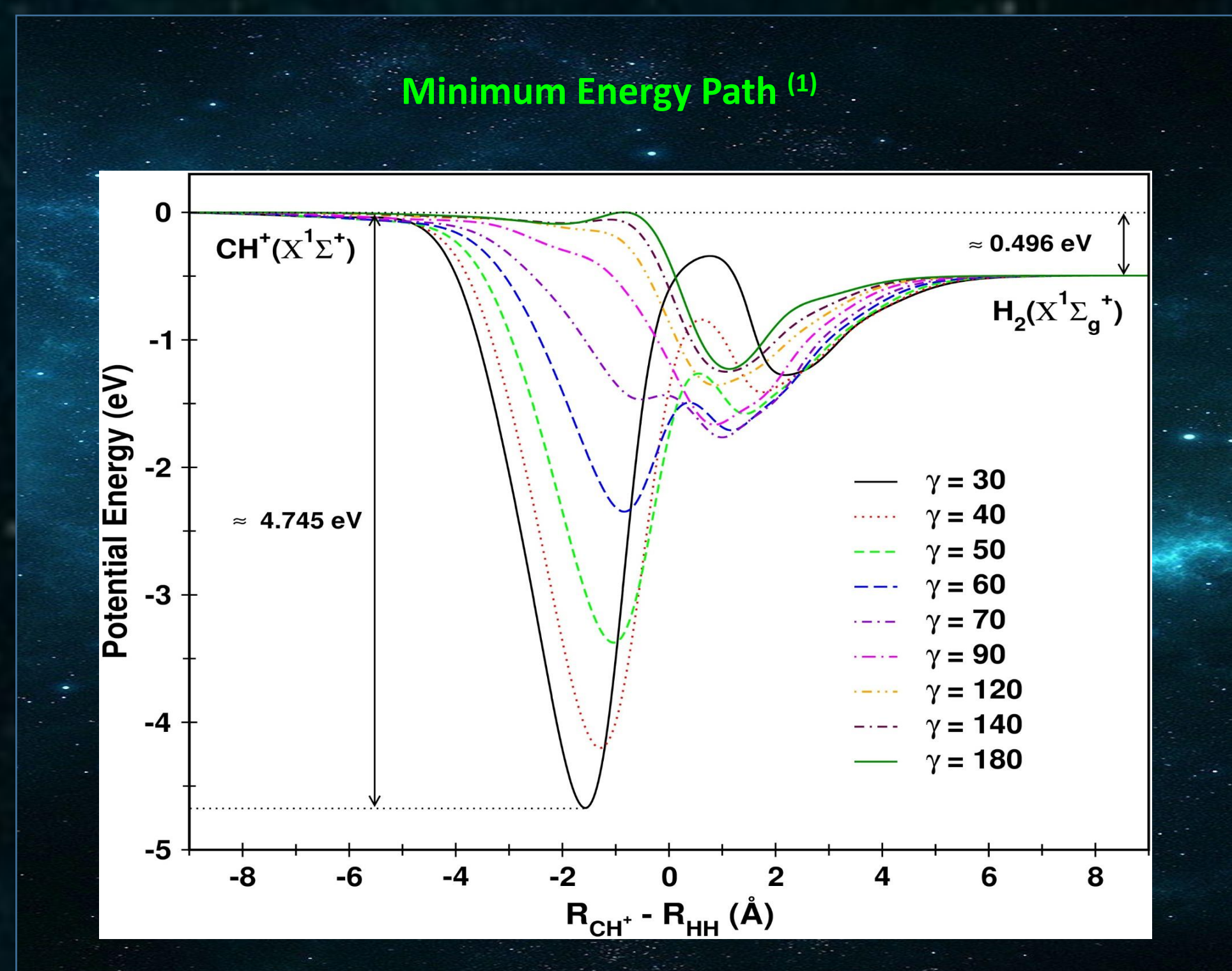
Hamiltonian: $\hat{H} = -\frac{\hbar^2}{2\mu} \left[\frac{\partial^2}{\partial R^2} + \frac{\partial^2}{\partial r^2} \right] + \frac{\hat{j}^2}{2\mu r^2} + \frac{\hat{p}^2}{2\mu R^2} + V(R, r, \gamma)$

$\hat{p}^2 \equiv (\hat{J} - \hat{j})^2 = \hat{J}^2 + \hat{j}^2 - 2\hat{J}_z\hat{j}_z - \hat{J}_+\hat{j}_- - \hat{J}_-\hat{j}_+$ (Coriolis coupling terms)

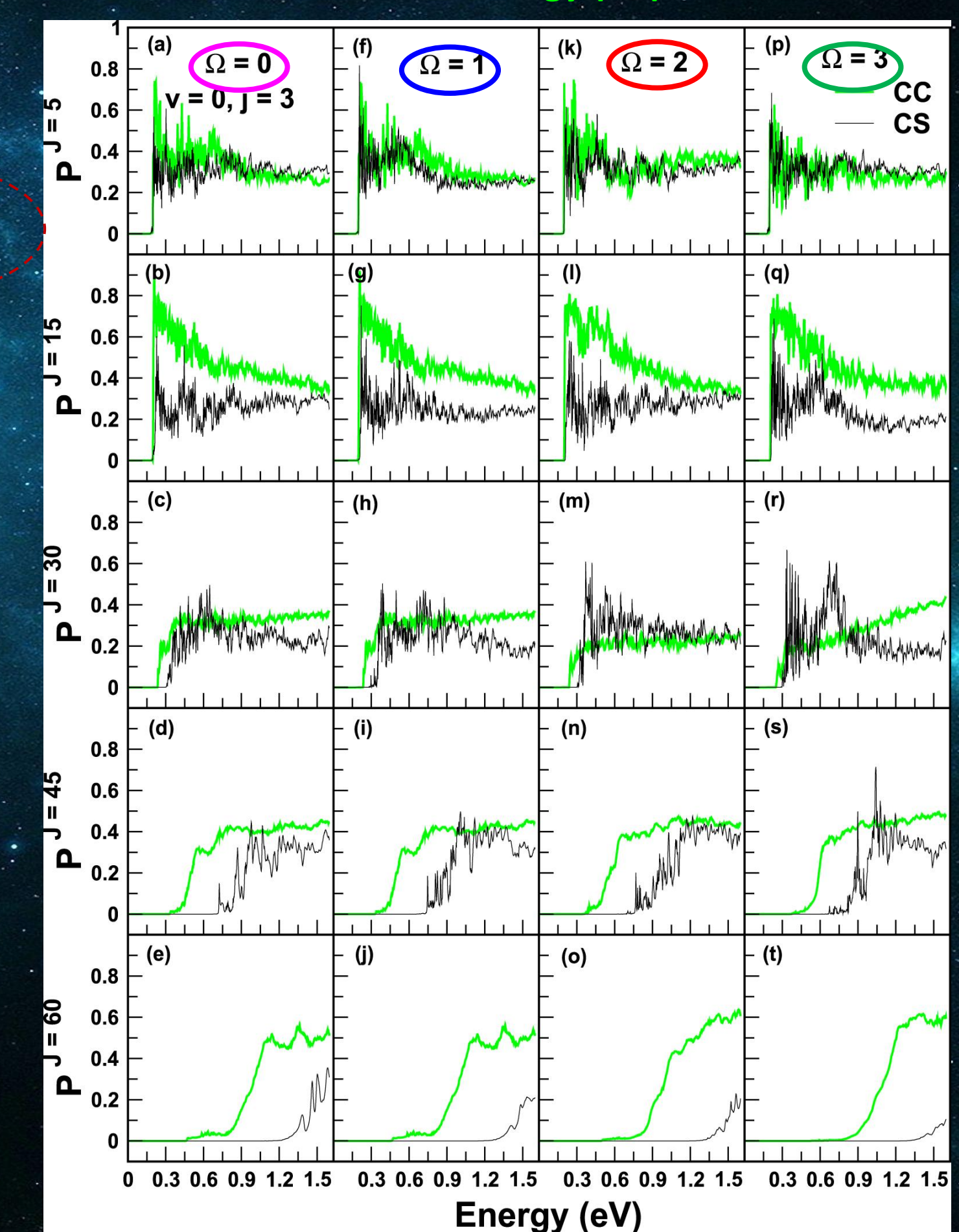
Initial wave function: $|\Psi_{KM}^j(R, r, \gamma, \omega, t)\rangle = \frac{1}{Rr} \sum_{K=-j}^j F_{KM}^j(\omega) |\Psi_K^j(R, r, \gamma, t)\rangle$

$F_{KM}^j(\omega) = [2(1 + \delta_{K0})]^{-1/2} \sqrt{\frac{2J+1}{8\pi^2}} [D_{KM}^J(\omega) + (-1)^{J+K+p} D_{-K, -M}^J(\omega)]$ (Wigner-rotation matrix for M=0)

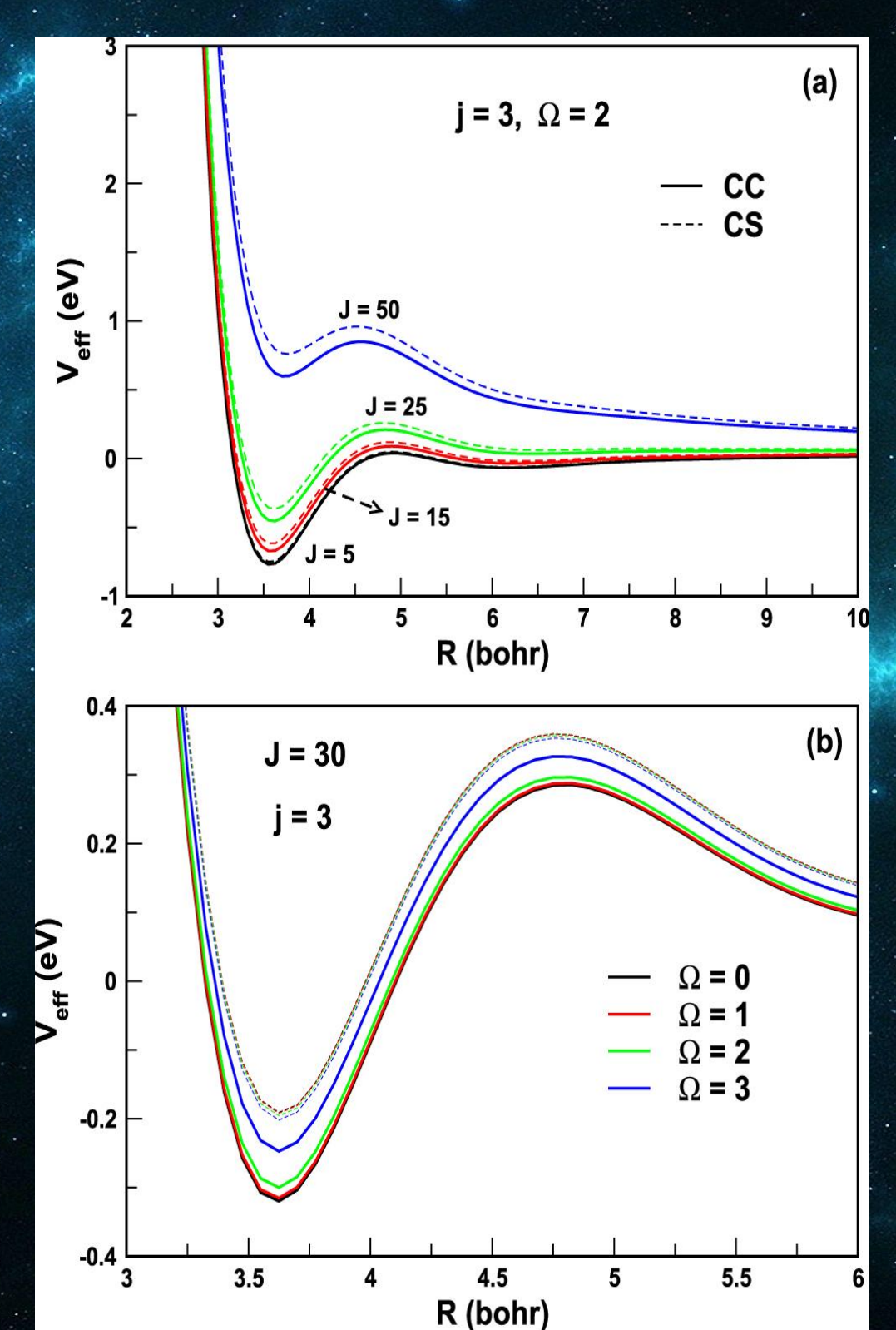
$|\Psi_K^j(R, r, \gamma, t = 0)\rangle = |\Psi_{lmn}\rangle = \sqrt{w_n} F(R_l) \phi_{vj}(r_m) \tilde{P}_l^K(\cos \gamma_n)$



J-dependent CS and CC reaction probabilities as a function of energy (eV)



Effective potential of the $\text{H} + \text{CH}^+ (v=0, j=3)$ system along the Jacobi coordinate R for different J and Omega values



Final Analysis

$\hat{F} = -\frac{i\hbar}{2\mu} \left[\frac{\partial}{\partial r} \delta(r - r_d) + \delta(r - r_d) \frac{\partial}{\partial r} \right]$ (Wave packet Flux)

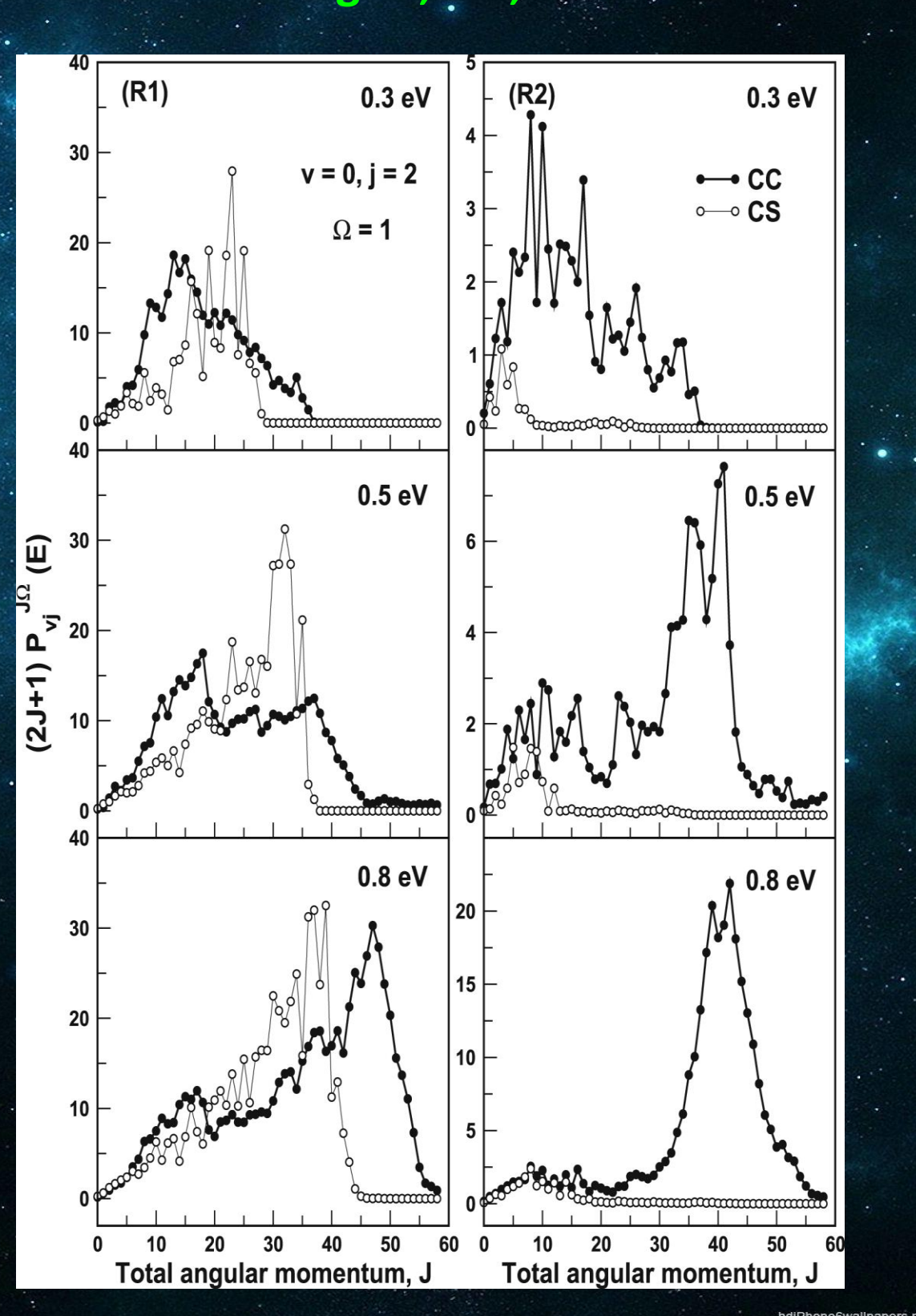
$P_i^{JK}(E) = \sum_f |S_{fi}^{JK}|^2 = \langle \Phi(R, r, \gamma, E) | \hat{F} | \Phi(R, r, \gamma, E) \rangle_{r=r_d}$ (Reaction Probability)

$N_{vj}(E) = \frac{1}{2j+1} \sum_{K=0}^{K_{max}} \sum_{J \geq K}^{J_{max}} (2J+1) P_i^{JK}(E)$ (Cumulative Reaction Probability, $J_{max} = 60$)

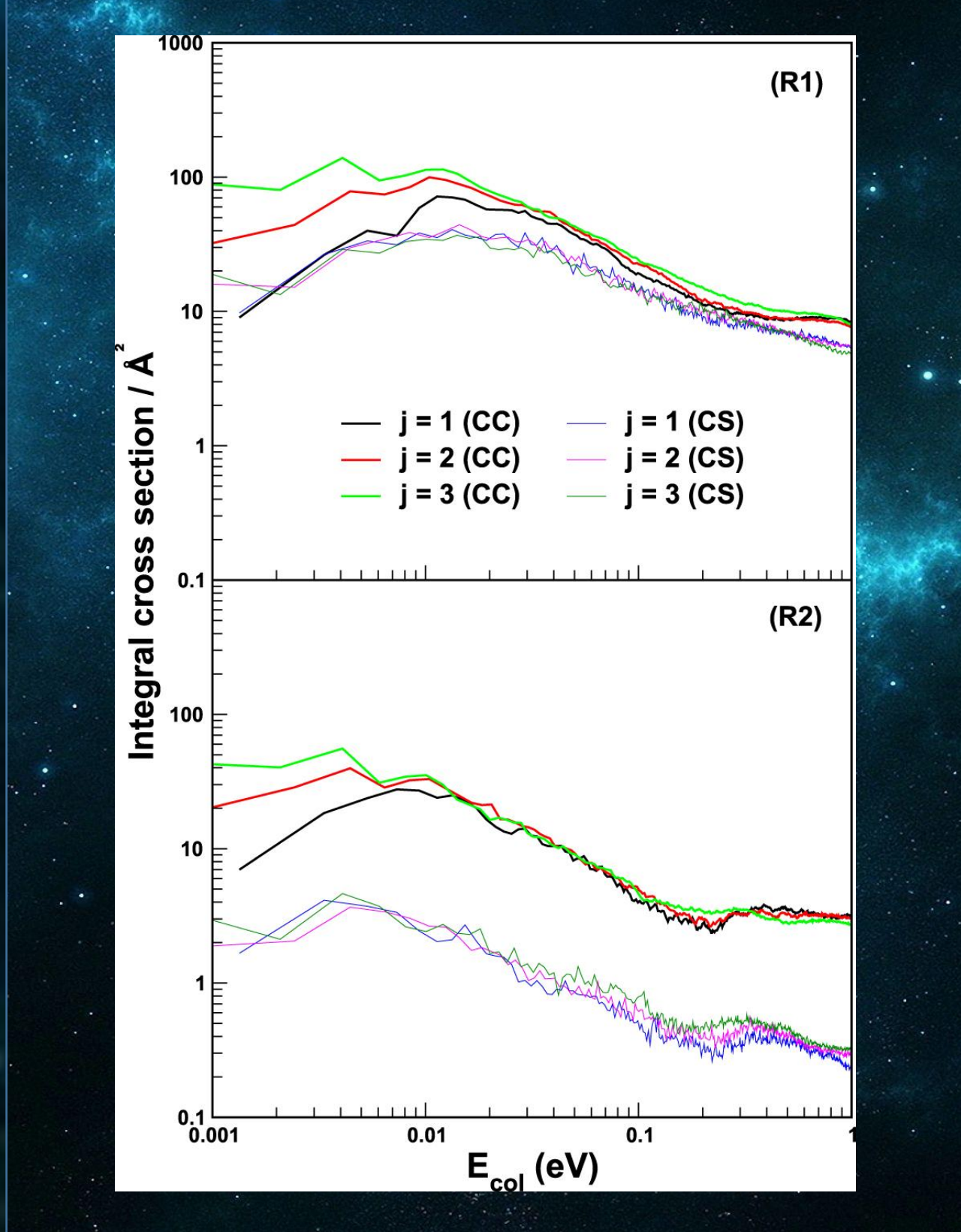
$\sigma_{vj}(E) = \frac{\pi}{k_{vj}^2} N_{vj}(E)$ (Integral reaction cross section)

$k(T) = (2\pi\hbar Q_R(T))^{-1} \int_{-\infty}^{+\infty} dE e^{-E/k_B T} N_{vj}(E)$ (Thermal rate constant)

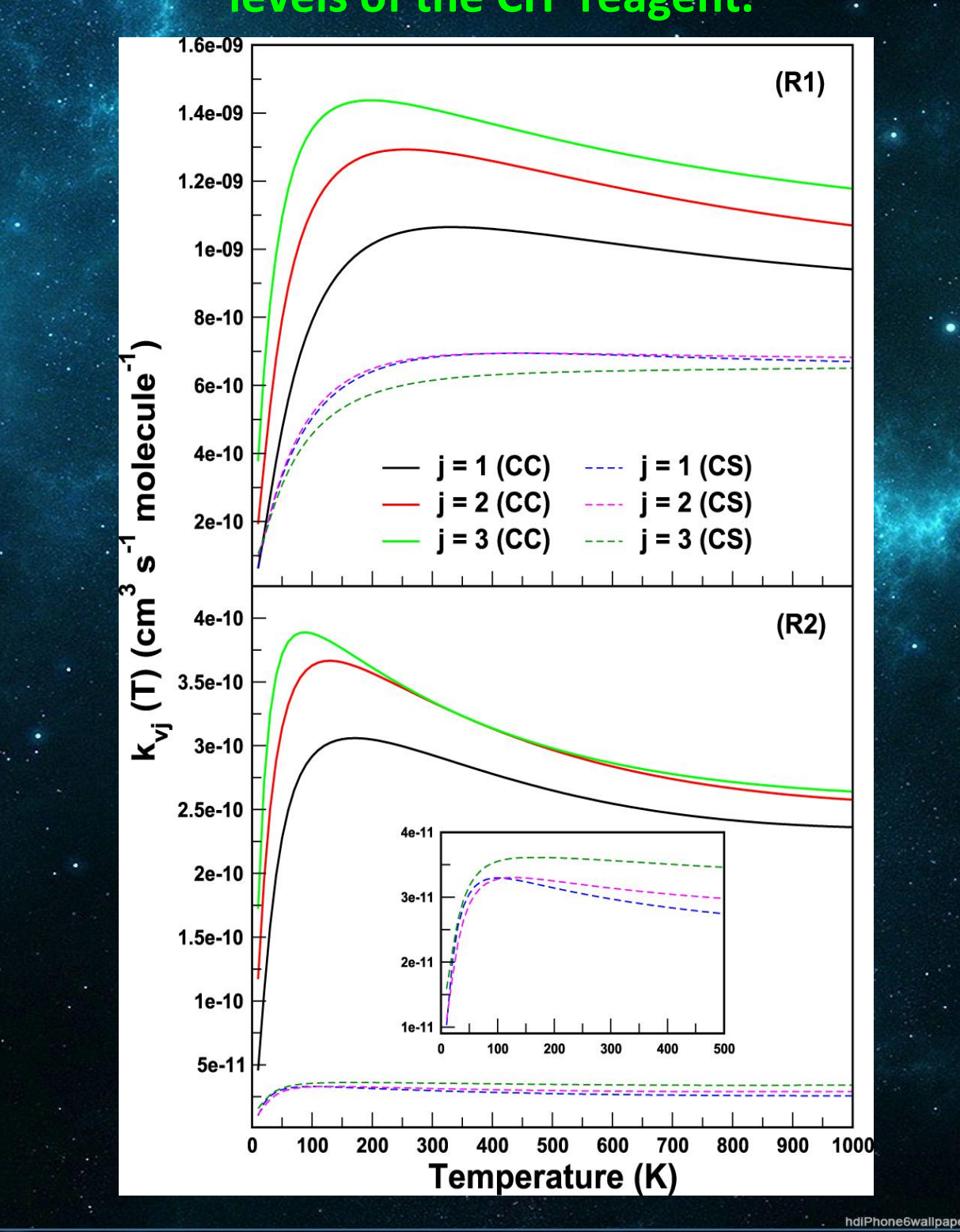
(2J+1) weighted reaction probabilities for both R1 and R2 channels for the selected collision energies, 0.3, 0.5 and 0.8 eV



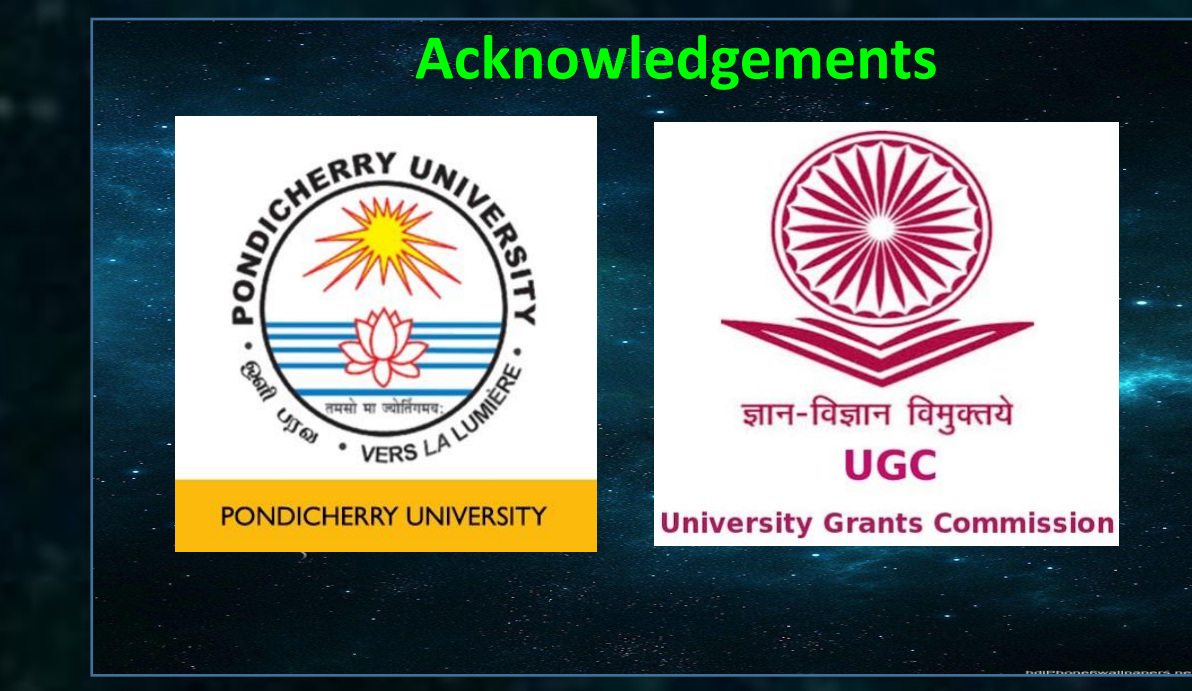
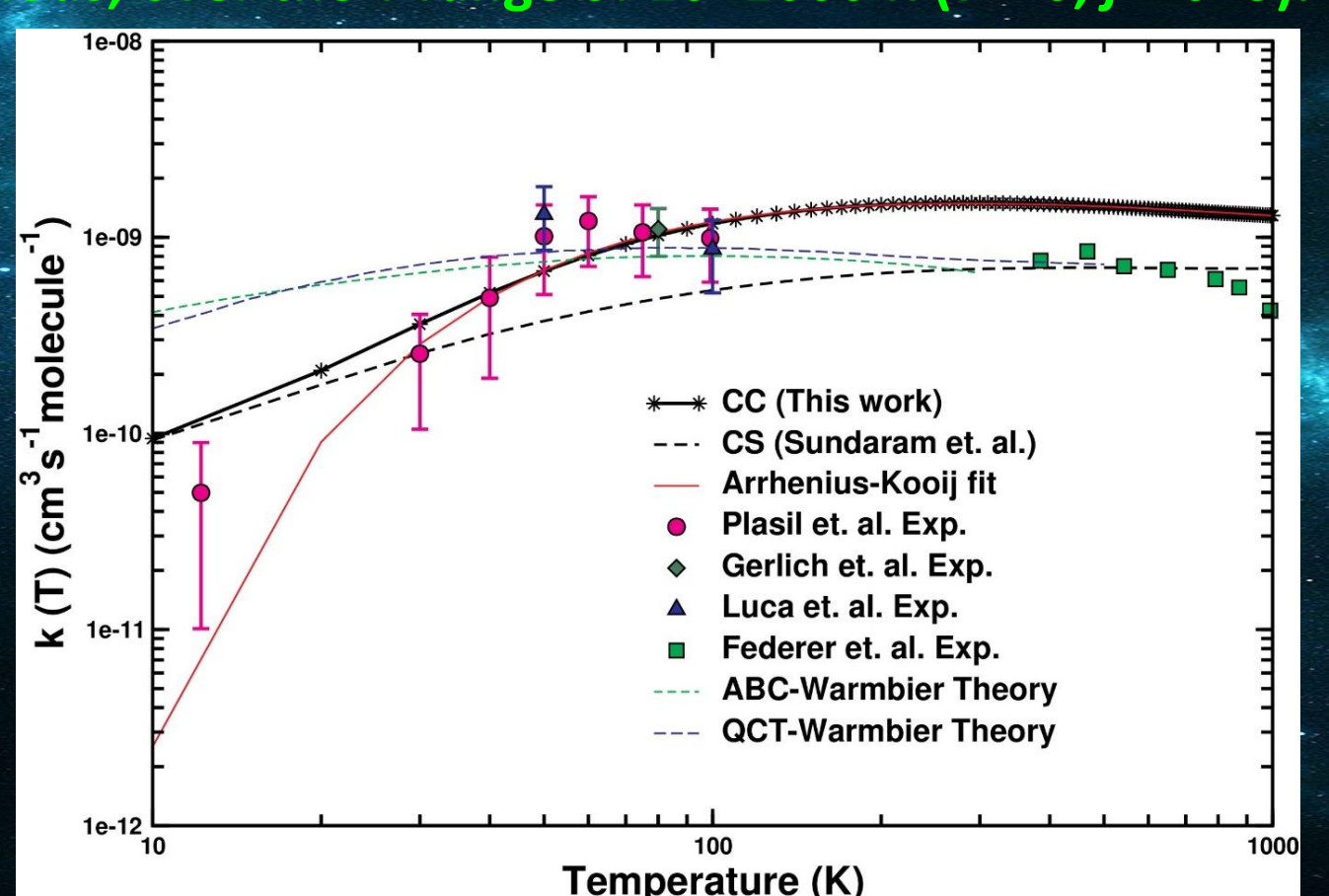
Initial state-selected and energy-resolved integral cross sections for both the R1 and R2 channels as a function of collision energy up to 1.0 eV for different j = 1-3.



Initial state-selected and channel-specific rate constants of the title reaction over the temperature range of 10-1000 K, obtained from the CC (solid line) and CS (dashed line) methods are compared for different j = 1-3 levels of the CH^+ reagent.



The Boltzmann state-averaged thermal rate constant of the title reaction, calculated using the exact (CC, represented by solid line with asterisks) and approximate (CS, represented by dashed line) methods, over the T range of 10-1000 K (v=0, j=0-3).



Conclusion

- In order to predict the accurate rate constants, the Coriolis coupled dynamical calculations are carried out for the $\text{H} + \text{CH}^+$ reaction. Using this exact approach, the dynamical quantities are calculated and compared with the CS results.
- We predicted that the CS approximation is underestimating the results for the R1 and R2 channels compared to the exact (CC) method in the ground electronic state.
- At the outset, we calculated that the CC predicts the exact rate constants (at 10 - 100 K ultra-cold T), on par with the experimental results, for overall T range (10-1000 K) of astrochemical interests of the complex-forming ion-molecule type reactions⁽⁴⁾.

References

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