Supporting Information

The Physics behind the Barrier to internal rotation of Acetyl Chloride molecule: A combined approach from DFT, Car Parrinello Molecular dynamics and time resolved wavelet transform theory

Bipan Dutta^a, Biplab Bhattacharjee^b, Joydeep Chowdhury^{c*}

^aDepartment of Physics, Sammilani Mahavidyalaya, E.M. Bypass, Baghajatin Station, Kolkata 700094, India

^bDepartment of Chemistry, Jadavpur University, 88, Raja S.C. Mallick Road, Kolkata 700032, India

^cDepartment of Physics, Jadavpur University, 88, Raja S.C. Mallick Road, Kolkata 700032, India

*Corresponding Author

E-mail: joydeep72_c@rediffmail.com

Phone: (033)24138917

1. Fourier transform of the dipole moment autocorrelation function (DMAF):

The DMAF averaged over a period of time t, is expressed as:

$$C(t) = \langle \mu(0)\mu(t) \rangle \tag{1}$$

where $\mu(0)$ and $\mu(t)$ are the dipole moments of the molecule estimated at t=0 and t=t. Within short period of time the dipole moment $\mu(t)$ is strongly correlated with the dipole moment $\mu(0)$. The spectral density of the system is calculated by using the Fourier transform of the correlation function of dipole moment.

The dynamic IR spectrum is represented as:

$$I(\omega) = \frac{h\beta}{(2\pi)^2} \omega^2 \int dt e^{-i\omega t} \langle \mu(0)\mu(t) \rangle$$
⁽²⁾

where I, ω , h, and β represent the IR Intensity, frequency, Planck constant and inverse of the Boltzmann constant respectively. The dipole moment (μ) of the molecule at successive time steps ~ 0.096 fs has been obtained from CPMD simulation studies¹.

References:

(1) a) Gaigeot, M. P.; Sprik, M. Ab Initio Molecular Dynamics Computation of the Infrared Spectrum of Aqueous Uracil. *J. Phys. Chem. B* 2003, *107*, 10344 - 10358, b) Gaigeot, M. P.; Vuilleumier, R.; Sprik, M. D.; Borgis, J. Infrared Spectroscopy of *N*-Methylacetamide Revisited by ab Initio Molecular Dynamics Simulations. *Chem. Theory Comput.* 2005, *1*, 772 - 789.



Figure S1: Potential energy curve as a function of torsion angle (τ) about the C_{methyl} – C₁ bond of the – CH₃ group of the AC molecule as obtained from (a) B3LYP/6-31G(d,p) and (b) MP2/6-21G(d) level of theories.

Table S1: Relevant Structural Parameters (bond length in Å, bond angles in degrees) of "E" and "S" forms of AC molecule calculated at MP2/6-21G(d), B3LYP/6-31G(d,p) and CPMD level of theories. Figures in the parenthesis represent the standard deviation of the estimated value.

	MP2/6-21G(d)		B3LYP/6- 31G(d,p)		CPMD
	Ε	S	E	S	
$C_{methyl} - C_1$	1.502	1.507	1.495	1.511	1.501 (±0.014)
$C_{methyl}-H_4$	1.091	1.094	1.093	1.098	1.107 (±0.013)
$C_1 - Cl_3$	1.835	1.834	1.835	1.834	1.872 (±0.0027)
$C_{methyl} - H_5$	1.093	1.092	1.102	1.098	1.109 (±0.009)
$C_{methyl} - H_6$	1.093	1.094	1.091	1.093	1.109 (±0.008)
$C_1 - C_{methyl} - H_4$	108.61	108.05	109.32	108.54	106.56 (±1.86)
$H_4 - C_{methyl} - H_6$	110.61	107.84	110.55	107.55	109.98 ((±1.21)

Table S2: Theoretically fitted "V₃" and "V₆ "coefficients for methyl rotational barrier of AC molecule using B3LYP/6-31G(d,p) [MP2/6-21G(d)] level of theory.

	Methyl Rotation				
Conditions imposed	V ₃	V ₆			
ac molecule	(Kcal / mol)	(Kcal / mol)			
Fully relaxed	1.31 [1.32]	-0.019 [-0.21]			
$C_{methyl} - C_1$ and in plane $C_{methyl} - H_4$ is freezed	1.26 [1.28]	0.059 [0.68]			



Figure S2: Variation of the (a) $C_1 - C_{methyl} - H_4$, (b) $C_1 - C_{methyl} - H_4$, (c) $C_1 - C_{methyl} - H_6$, and (d) $C_{methyl} - C_1 - C_{l_3}$ angles of AC molecule with torsion angle (τ) as obtained from B3LYP/ 6-31G(d,p) level of theory.



Figure S3: Rotational dependence of the ΔV_{nn} , ΔV_{ee} and ΔV_{ne} of the (a, A) out-plane $C_{methyl} - H_5$, and (b, B) out-plane $C_{methyl} - H_6$ skeletal flexing of AC molecule.