

**Supporting Material**

**Sub-50 fs excited state dynamics of 6-chloroguanine  
upon deep ultraviolet excitation**

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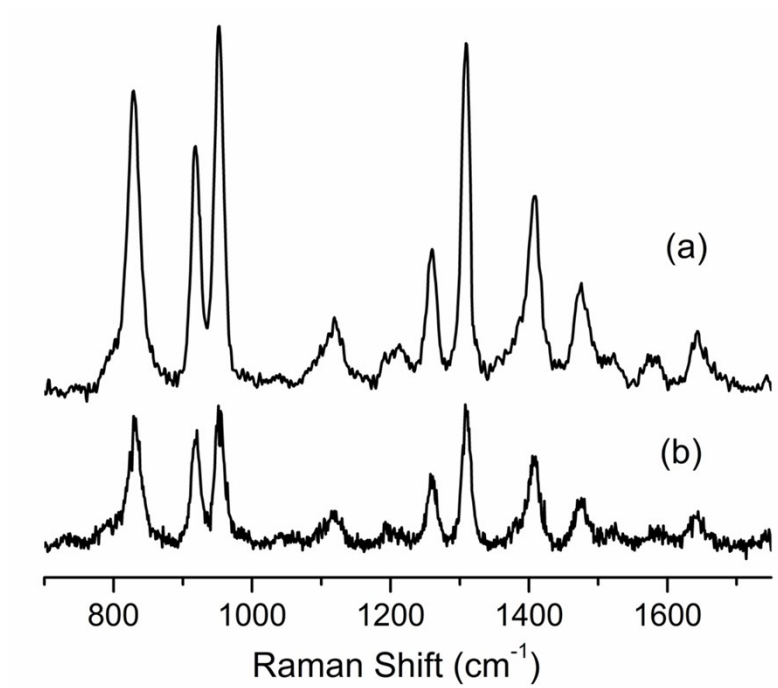
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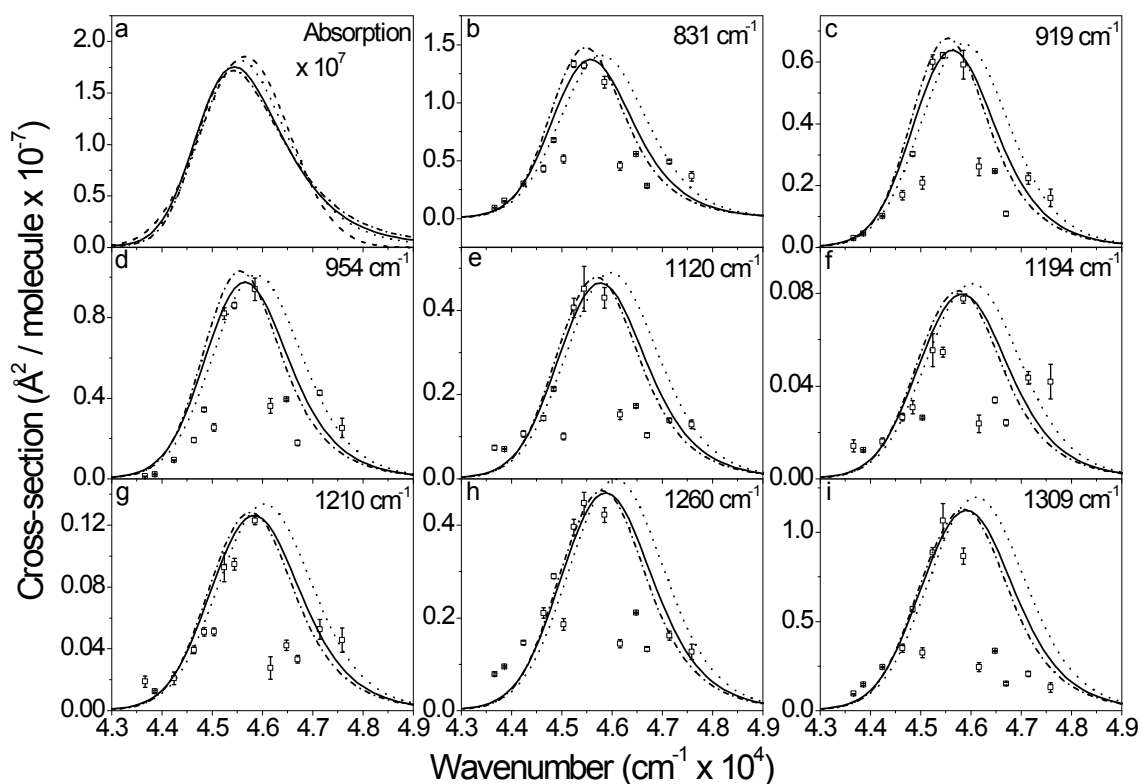
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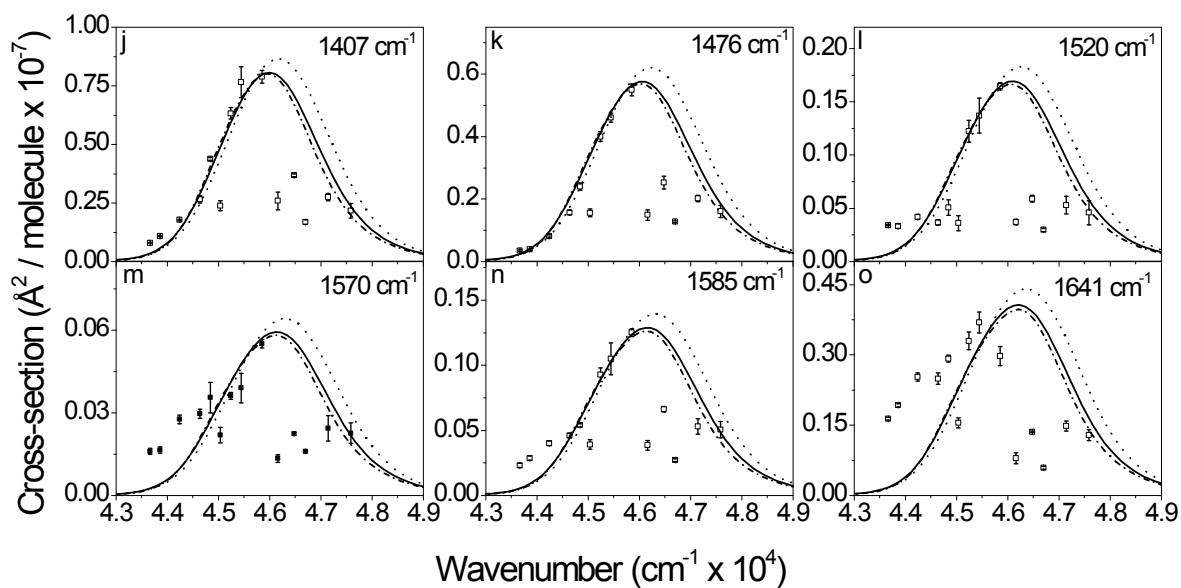
## FIGURES



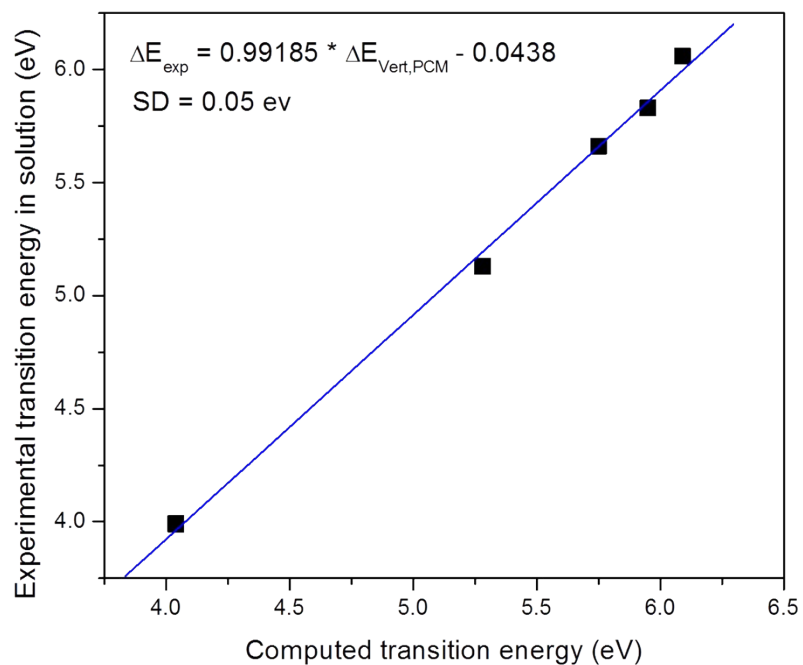
**Fig S1.** (a) parallel polarized and (b) depolarized spectra of 6-CIG with 220 nm laser excitation. Incident laser power on sample was 0.6 mw.



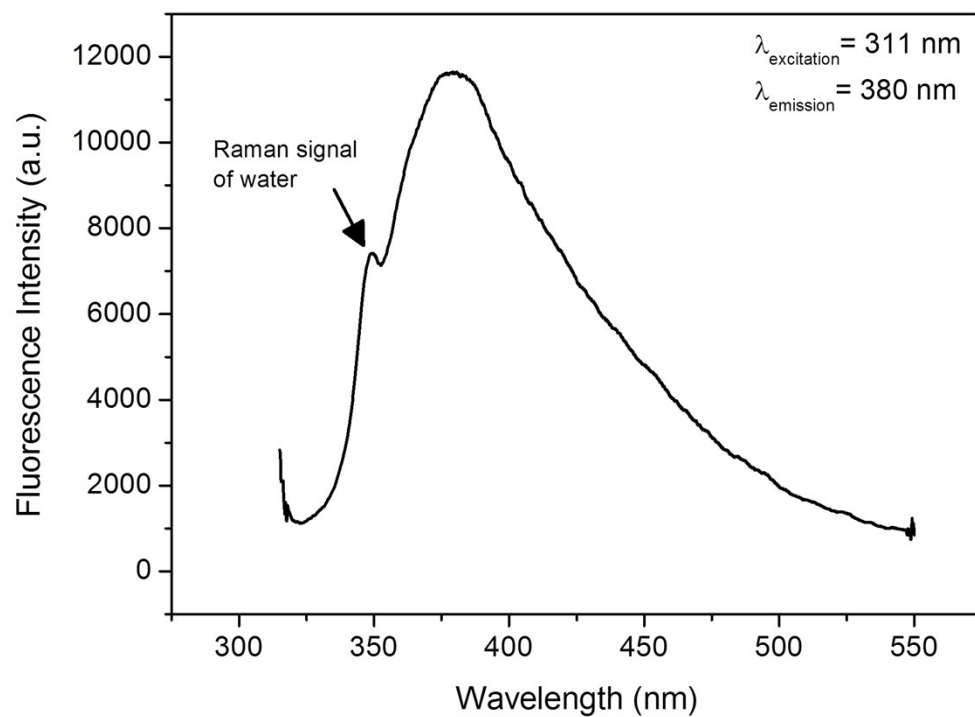
**Fig. S2.** Dependence of the simulated absorption and Raman excitation profiles on inverse of solvent relaxation time,  $\Lambda$ . Panel (a) the experimental (*dashed*) and simulated (*solid*) absorption spectrum. Panel (b-i) The experimental (*open square*) and simulated (*solid*) Raman excitation profiles for eight resonant modes of 6-CIG. The simulated absorption and Raman excitation profiles were obtained by using the best fitted parameters in Table 2 while varying  $\Lambda$  and adjusting  $E_0$ . Set 1 (*dash dot*) and set 2 (*dot*) were obtained with values of  $\Lambda$  of  $550 \text{ cm}^{-1}$  and  $175 \text{ cm}^{-1}$  respectively with adjusted  $E_{00}$  values to  $45820 \text{ cm}^{-1}$  and  $45680 \text{ cm}^{-1}$  respectively while all other parameters remained the same.



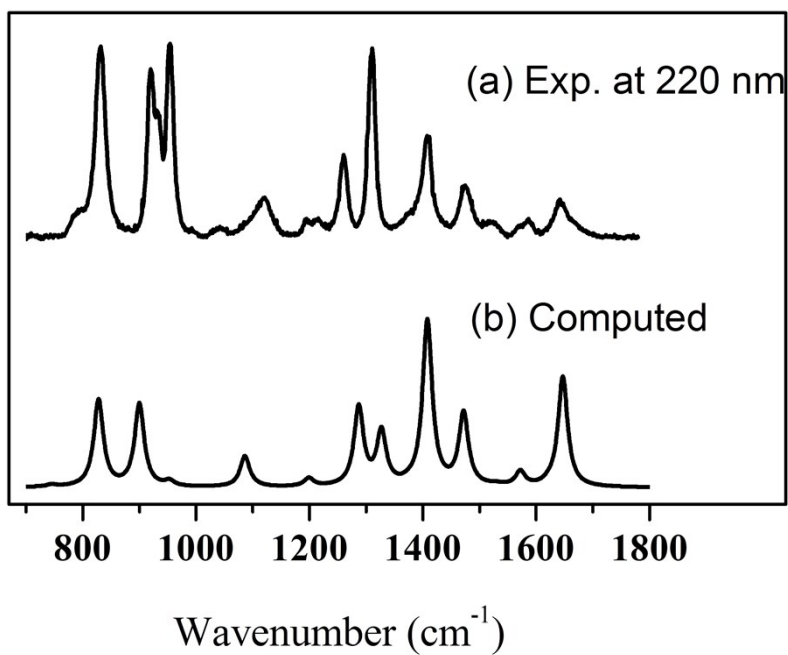
**Fig. S3.** Dependence of the simulated absorption and Raman excitation profiles on the amplitude of homogeneous broadening parameter,  $\Delta$ . Panels (j)-(o): experimental (*open square*) and simulated (*solid*) Raman excitation profiles for five resonant modes of 6-ClG. The absorption and Raman excitation profiles were obtained with the same set of parameters as in Figure S2.



**Fig. S4.** Linear fit to experimental transition energies as a function of computed transition energies of 6-ClG•6H<sub>2</sub>O complex. Computed transition energies were obtained using cluster-continuum model at TD-B3LYP/6-311+G(2d,p)//PCM level of theory and experimental values. Computed and experimental values are taken from Table 1 and converted to eV for plotting.



**Fig. S5.** Steady state fluorescence spectra of 6-CIG (2.5 mM in Phosphate buffer, pH 7.0, 20 mM) with 311 nm excitation wavelength. Emission spectra was recorded with Fluorolog spectrophotometer (FluoroMax 4, Horiba Scientific, USA).



**Fig. S6.** (a) Experimental RR spectrum of 6-CIG at 220 nm and (b) computed spectrum with excited state ( $B_b$ ) gradient computed at TD-B3LYP level of theory. This spectrum is computed using Equation S1 and method described in of ESI<sup>†</sup>.

## TABLES

**Table S1.** Depolarization ratios of Raman bands of solvents at excitation wavelength of 220 nm.  
<sup>a</sup>This Work; <sup>b</sup>Ref 86 of main paper

Solvent	RR Band (cm <sup>-1</sup> )	Depolarization ratio $\lambda_{\text{exc}}=220\text{nm}^{\text{a}}$	Depolarization ratio $\lambda_{\text{exc}}=220\text{nm}^{\text{b}}$
NaNO <sub>3</sub>	1045	0.21	0.19 ± 0.05
NaClO <sub>4</sub>	932	0.018	0.04 ± 0.02
Acetonitrile	919	0.078	0.08 ± 0.02
	1375	0.5	0.45 ± 0.06



**Table S2.** Absorption cross-section of  $B_b$  electronic state of 6-CIG and GMP.

State	6-CIG <sup>a</sup>		Guo <sup>b</sup>	
	$\Delta E_{Exp}$ (nm)	$f_{exp}$	$\Delta E_{Exp}$ (nm)	$f_{exp}$
$B_b$	219.1	0.62	200	0.4

<sup>a</sup>this study; <sup>b</sup>Ref 110 of main paper, guanosine in aqueous solution at pH 6.0, experimental oscillator strength ( $f_{exp}$ ) is evaluated with the formula,  $f_{exp} = 1.13 \times 10^{12} \eta \int \sigma(\tilde{\nu}) d\tilde{\nu}$ , where  $\eta$  is refractive index of the medium and  $\int \sigma(\tilde{\nu}) d\tilde{\nu}$  is integrated absorption cross-section in  $\text{cm}^2 \text{molecule}^{-1}$ .

**Table S3.** Coordinate of the optimized structure of 6-ClG.6H<sub>2</sub>O complex at B3LYP/6-311+G(2d,p)//PCM level described in Fig 1.

N	0.029122000	-1.433469000	0.043728000
C	1.069940000	-0.545825000	0.030316000
N	0.927304000	0.797116000	0.025623000
C	-0.334469000	1.213200000	-0.007139000
C	-1.474145000	0.388454000	-0.011473000
C	-1.201009000	-0.968081000	0.025356000
N	-0.812667000	2.490979000	-0.041554000
C	-2.181160000	2.395031000	-0.068395000
N	-2.621797000	1.161915000	-0.049509000
N	2.313882000	-1.050126000	0.035520000
C	-2.510972000	-2.128306000	0.045568000
H	-2.806183000	3.273707000	-0.102423000
H	-0.250085000	3.355067000	-0.071838000
H	2.474395000	-2.051527000	-0.038853000
H	3.107436000	-0.431519000	-0.115885000
O	0.370307000	-4.317125000	0.260467000
H	-0.177575000	-4.757276000	-0.400361000
H	0.179663000	-3.357326000	0.167768000
O	3.045798000	-3.952457000	-0.220527000
H	2.135861000	-4.277424000	-0.044387000
H	3.588984000	-4.290740000	0.500786000
O	4.707115000	0.736803000	-0.390873000
H	5.014485000	0.846006000	-1.298506000
H	4.261420000	1.575266000	-0.159755000
O	2.911988000	2.708995000	0.521800000
H	2.224280000	2.001946000	0.394418000
H	3.064839000	2.761119000	1.474519000
O	-5.433377000	0.549393000	-0.112575000
H	-5.531012000	-0.375277000	-0.365798000
H	-4.463750000	0.706353000	-0.090691000
O	1.019974000	4.651816000	-0.189506000
H	0.950556000	5.380869000	0.438723000
H	1.812918000	4.141001000	0.078693000

**Table S4.** Experimental, computed wavenumbers and potential energy distributions (PED) of all RR bands of 6-CIG.

Experimental (cm <sup>-1</sup> )	Computed frequency <sup>a</sup> (cm <sup>-1</sup> )	PED (%) <sup>b</sup>
800	807	tors C6N1C2N3 (14) – N1C2N3C4 (21) + C5N7C8N9 (12) – out N2N1N3C2 (10) + N3N9C5C4 (32)
831	828	str N3C4 (10) – be C2N3C4 (10) + N1C2N3 (17) + C4N9C8 (21)
919	900	str N1C2 (13 ) + N2C2 (10 ) – Cl6C6 (23 ) + be C6N1C2 (11 ) + C5N7C8 (12 ) – N9C8N7 (12 )
954	953	– be C5N7C8 (12) + N9C8N7 (47)
1043	1037	str N1C2 (25) – be H2aN2C2 (11) – Cl6C6N1 (11)
1088	1086	str N9C8 (54) – be N9N9C4 (28)
1120	1103	str N3C2 (25) + be H2aN2C2 (48)
1194	1199	str N7C5 (21) – be C5N7C8 (10) + H8C8N7 (24)
1260	1287	str N7C8 (16) – N1C6 (19) + N3C4 (15) + N1C2 (14) + be H8C8N7 (10)
1309	1327	– str N7C8 (15) + N7C5 (14) – be C5N7C8 (11) – H8C8N7 (23) + N9C8N7 (12)
1407	1408	str N1C6 (23) – N3C4 (12) – N2C2 (12) + N9C4 (17)
1476	1472	str N2C2 (20) + be N1C2N3 (15)
1520	1528	str N7C8 (37) – be H8C8N7 (19)
1585	1572	str N3C4 (12) + str N3C2 (19) – be C2N3C4 (11) – C4N9C8 (13)
1602	1622	str N2C2 (10) + be H2aN2H2a (76)
1641	1647	str N1C6 (18) + N3C4 (16) – be N3C4C5 (14)

<sup>a</sup> at B3LYP/6-311+G(2d,p)//PCM; <sup>b</sup>using VEDA 4.0, sign indicates relative phase of movement of internal coordinates.

**Table S5.** Depolarization ratio for Raman bands of 6-ClG obtained at excitation wavelength of 220 nm.

RR Band ( $\text{cm}^{-1}$ )	Depolarization ratio
6-ClG, $\lambda_{\text{exc}}=220$ nm	
831	$0.37 \pm 0.04$
919	$0.38 \pm 0.02$
954	$0.35 \pm 0.05$
1120	$0.40 \pm 0.04$
1260	$0.38 \pm 0.01$
1309	$0.33 \pm 0.04$
1407	$0.37 \pm 0.04$
1476	$0.35 \pm 0.04$
1643	$0.46 \pm 0.16$

**Table S6.** Sign of dimensionless displacements ( $\Delta$ ) on resonant  $B_b$  electronic state obtained with three different functionals at B3LYP optimized geometry on isolated 6-CIG.

Experimental wavenumber ( $\text{cm}^{-1}$ )	Computed wavenumber <sup>a</sup> ( $\text{cm}^{-1}$ )	TD-B3LYP on S6	TD-PBE0 on S7	TD-wB97xD on S6
800	807	-1	-1	-1
831	828	-1	-1	-1
919	900	1	1	1
954	953	-1	-1	-1
1043	1037	-1	-1	-1
1088	1086	-1	-1	-1
1120	1103	-1	-1	-1
1194	1199	-1	-1	-1
1260	1287	-1	-1	-1
1309	1327	-1	-1	-1
1407	1408	-1	-1	-1
1476	1472	1	1	1
1520	1528	1	1	1
1585	1572	-1	-1	-1
1602	1622	-1	-1	-1
1641	1647	1	1	1

<sup>a</sup>at B3LYP/6-311+G(2d,p)//PCM; All calculations are performed with 6-311+G(2d,p) basis set and PCM solvation. All single point TD-DFT calculations are performed on equilibrium geometry of isolated 6-CIG, optimized with B3LYP functional. Signs of  $\Delta$ s (with three functional mentioned) are obtained with ground state normal modes computed with B3LYP functional using Equation S2 and S3.  $B_b$  state of 6-CIG corresponds to the computed 6<sup>th</sup> (S6), 7<sup>th</sup> (S7) and 6<sup>th</sup> (S6) singlet state with B3LYP, PBE0 and wB97xD functional respectively.

### Method of determining sign of dimensionless $\Delta$ s

Within independent mode displaced harmonic oscillator model (IMDHO) and assumption of short-time dynamics,<sup>1-5</sup> the resonance Raman (RR) intensity,  $I_k$  of  $k^{\text{th}}$  fundamental mode can be expressed as,<sup>5-10</sup>

$$I_k \propto \frac{1}{\omega_k^g \mu_k^g} \left( \frac{\partial E^N}{\partial Q_k} \right)_{FC}^2 \quad (S1)$$

where  $\omega_k$  and  $\mu_k$  are the frequency and reduced mass of  $k^{\text{th}}$  mode and  $V_k = (\partial E^N / \partial Q_k)_{FC}$  is the mass-weighted gradient in Frank-Condon (FC) region of the  $N^{\text{th}}$  resonant electronic surface along  $k^{\text{th}}$  normal mode coordinate. The superscript ‘N’ and ‘g’ stand for  $N^{\text{th}}$  electronic excited state and ground electronic state respectively.

In this formalism, the dimensionless displacement,  $\Delta_k$  is expressed as,

$$\Delta_k \propto - \frac{1}{\omega_k^g} \left( \frac{\partial E^N}{\partial Q_k} \right)_{FC} = - \frac{1}{\omega_k} V_k \quad (S2)$$

The gradient,  $V_k$  is evaluated as,<sup>9</sup>

$$V_k = \left( \frac{\partial E^N}{\partial Q_k} \right)_{FC} = L^T \left( \frac{\partial E^N}{\partial \mathbf{x}} \right)_{FC} \quad (S3)$$

where the  $L$  is the orthogonal matrix obtained as solution of ground state normal mode eigenvalue problem.  $L$  is a matrix of  $3N \times (3N-6)$  dimension. Transpose of this matrix,  $L^T$  performs the basis change from cartesian coordinate to normal mode coordinate.  $(\partial E^N / \partial \mathbf{x})_{FC}$  is non-mass weighted cartesian forces (in Hartrees/Bohr) obtained from analytic gradient calculation<sup>11</sup> within TD-DFT formalism. For a molecule having  $N$  atoms both  $(\partial E^N / \partial Q_k)_{FC}$  and  $(\partial E^N / \partial \mathbf{x})_{FC}$  are column vector of  $(3N-6) \times 1$  and  $3N \times 1$  dimensions respectively.

## References

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