

Supporting Information for
Ultrafast Nonradiative Decay of a Dipolar Plasmon-like State in Naphthalene

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Table S1. Optimized coordinates of naphthalene at the B3LYP/6-31G(d,p) level of theory

H	-1.245080	0.000000	3.377170
C	-0.708340	0.000000	2.433020
H	-2.489500	0.000000	1.242170
C	-1.402480	0.000000	1.244600
C	1.402480	0.000000	1.244600
C	-0.716870	0.000000	0.000000
C	0.708340	0.000000	2.433020
C	0.716870	0.000000	0.000000
C	-1.402480	0.000000	-1.244600
H	1.245080	0.000000	3.377170
H	2.489500	0.000000	-1.242170
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C	-0.708340	0.000000	-2.433020
H	-2.489500	0.000000	-1.242170
H	-1.245080	0.000000	-3.377170
C	0.708340	0.000000	-2.433020
H	1.245080	0.000000	-3.377170
C	1.402480	0.000000	-1.244600

Table S2. MO transitions responsible for the α peak, β peak, three p-band peaks and the 6th excited state for the equilibrium geometry of naphthalene at the B3LYP/6-31G(d,p) level of theory.

Classification	Energy (eV)	Wavelength (nm)	Oscillator strength	Transitions	Weight
p-band 1	4.46	278.18	0.0603	HOMO – 1 \rightarrow LUMO + 1	0.157
				HOMO \rightarrow LUMO	0.685
α peak	4.52	274.27	0.0002	HOMO – 1 \rightarrow LUMO	0.505
				HOMO \rightarrow LUMO + 1	-0.493
β peak	6.10	203.20	1.2078	HOMO – 1 \rightarrow LUMO	0.493
				HOMO \rightarrow LUMO + 1	0.506
p-band 2	6.26	197.94	0.1821	HOMO – 2 \rightarrow LUMO + 2	0.161
				HOMO – 1 \rightarrow LUMO + 1	0.673
				HOMO \rightarrow LUMO	-0.139
6 th Excited State	6.37	194.71	0.0000	HOMO – 3 \rightarrow LUMO	0.125
				HOMO – 2 \rightarrow LUMO + 1	0.498
				HOMO – 1 \rightarrow LUMO + 2	-0.480
p-band 3	8.22	150.74	0.4716	HOMO – 2 \rightarrow LUMO + 2	0.679
				HOMO – 1 \rightarrow LUMO + 1	-0.138
				HOMO \rightarrow LUMO	0.113

Table S3. Normal modes of naphthalene, their symmetry representations, and their energies

Mode	Symmetry	Energy		Mode	Symmetry	Energy	
		(cm ⁻¹)	(eV)			(cm ⁻¹)	(eV)
1	B_{2u}	176.57	0.022	25	B_{3u}	1154.58	0.143
2	A_u	189.61	0.024	26	B_{2g}	1177.30	0.146
3	B_{3u}	364.09	0.045	27	B_{1u}	1178.05	0.146
4	B_{3g}	397.05	0.049	28	A_g	1189.20	0.147
5	B_{1g}	481.18	0.060	29	B_{1u}	1240.97	0.154
6	B_{2u}	491.96	0.061	30	B_{2g}	1272.80	0.158
7	B_{2g}	517.83	0.064	31	B_{3u}	1291.69	0.160
8	A_g	520.51	0.065	32	B_{1u}	1407.82	0.175
9	A_u	633.74	0.079	33	A_g	1415.74	0.176
10	B_{1u}	634.99	0.079	34	B_{3u}	1424.94	0.177
11	B_{3g}	734.91	0.091	35	B_{2g}	1501.48	0.186
12	A_g	776.04	0.096	36	A_g	1502.53	0.186
13	B_{1g}	784.42	0.097	37	B_{1u}	1562.44	0.194
14	B_{2u}	803.36	0.100	38	A_g	1628.24	0.202
15	B_{3u}	807.57	0.100	39	B_{3u}	1655.90	0.205
16	A_u	853.64	0.106	40	B_{2g}	1686.24	0.209
17	B_{1g}	899.19	0.111	41	B_{2g}	3173.11	0.393
18	B_{2g}	947.96	0.118	42	B_{3u}	3174.91	0.394
19	B_{3g}	951.78	0.118	43	B_{1u}	3176.77	0.394
20	B_{2u}	968.40	0.120	44	A_g	3180.25	0.394
21	A_u	989.08	0.123	45	B_{2g}	3191.63	0.396
22	B_{1g}	997.04	0.124	46	B_{3u}	3192.82	0.396
23	B_{1u}	1042.85	0.129	47	B_{1u}	3204.69	0.397
24	A_g	1053.49	0.131	48	A_g	3205.87	0.397

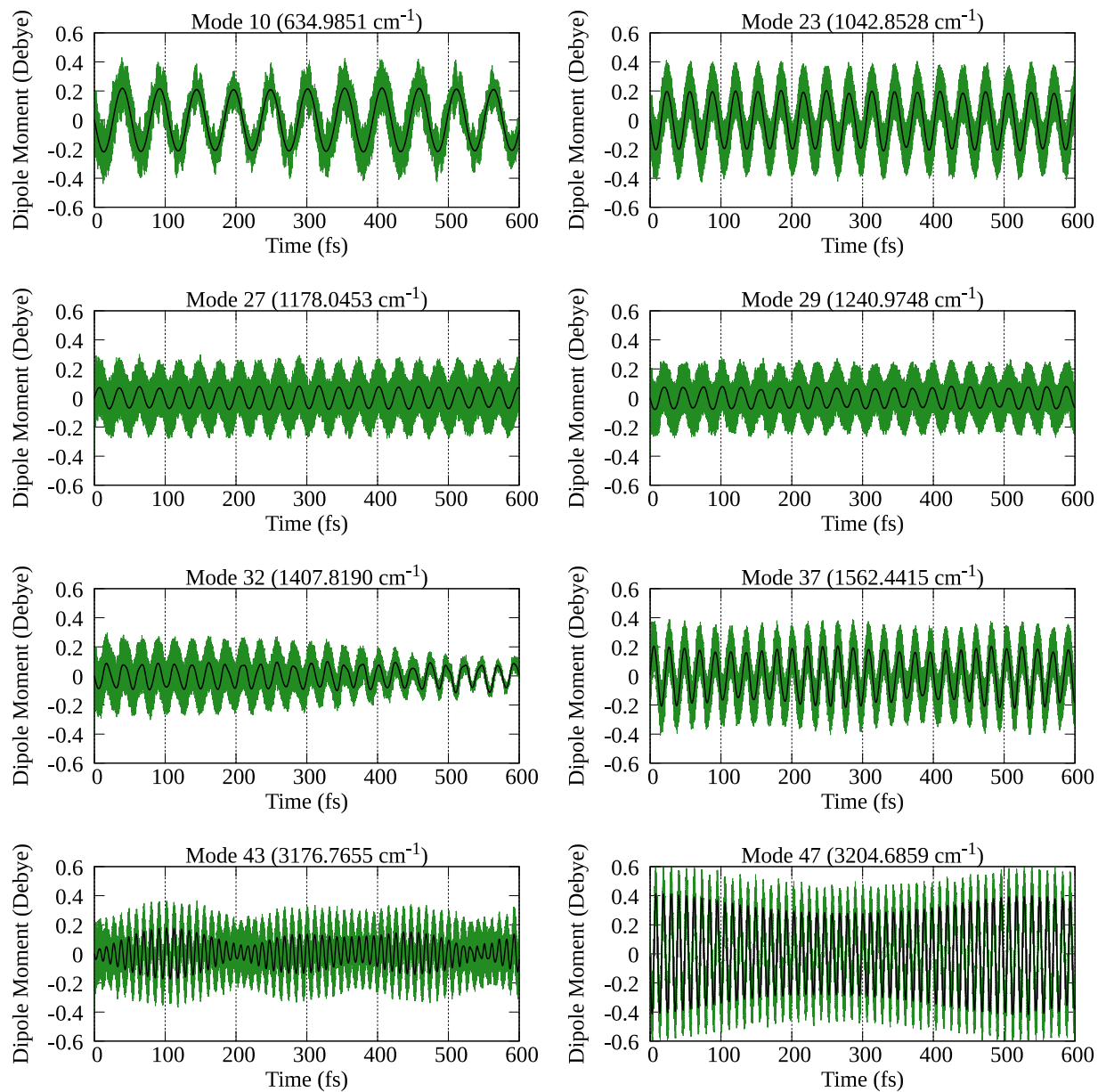


Figure S1. Variation of the z -component of the dipole moment for B_{1u} normal modes of naphthalene. Green: Average dipole moment during an Ehrenfest dynamics with electrons excited along the z direction and black: Born-Oppenheimer molecular dynamics (BOMD) in the ground electronic state.

Symmetry-adapted selection rules for pure electronic transitions and vibronic transitions¹

The intensity of a transition from state i to state j is given by eq S1 where $\hat{\mu}$ is the transition dipole moment operator and ψ_i and ψ_j are the initial and final electronic wave functions respectively. Note that to a first approximation, the total wavefunction Ψ for a molecule can be written as a product of an electronic wavefunction ψ_e , a vibrational wavefunction ψ_v , and a rotational wave function ψ_r ($\Psi = \psi_e \cdot \psi_v \cdot \psi_r$). Assuming that the three wavefunctions are independent from each other, the wave equation can be simplified into three different equations. Under this assumption, for an electronic transition to be allowed, the integral $\int \psi_i \hat{\mu} \psi_j d\tau$ should be nonzero for the initial and final electronic states and the dipole polarization direction x , y or z . According to the symmetry-adapted selection rules, this integral will be nonzero if the direct product of the point group representations of the initial and final electronic wavefunctions and the transition dipole moment operator contains the totally symmetric representation. Since the initial electronic state is totally symmetric, the electric dipole transition will be allowed with x , y or z polarization if the final state shares the same representation as the x , y or z linear functions, respectively. For instance, in the D_{2h} point group, the totally symmetric initial state belongs to the A_g representation and the x , y and z linear functions independently belong to the B_{3u} , B_{2u} and B_{1u} representations respectively. When the β peak is excited, which belongs to the B_{1u} representation, dipole response only along the z axis can be expected from the above selection rules.

$$I \propto \int \psi_i \hat{\mu} \psi_j d\tau \quad \#(S1)$$

If the initial and final states account for coupling of the electronic (e) and vibrational (v) wavefunctions, the integral would now look like eq S2. Since both the ground electronic and vibrational wavefunctions are totally symmetric, the symmetries of both the excited electronic and vibrational states must be considered.

$$\int (\psi_i^e \psi_i^v) \hat{\mu} (\psi_j^e \psi_j^v) d\tau \quad \#(S2)$$

In the case where the electrons are excited along the z axis with excitation of normal mode 35, the representations of the final electronic and vibrational states can be identified as B_{1u} and B_{2g} respectively. The direct product of these representations ($B_{1u} \otimes B_{2g}$) then gives rise to a B_{3u} representation, meaning that the coupling between these electronic and vibrational states yields a dipole response along the x cartesian direction. Therefore, activation of the x -component of the dipole moment is allowed via vibronic coupling when the B_{2g} vibrational mode is activated along with excitation of a B_{1u} electronic state. Likewise, B_{3g} vibrational modes coupled with the B_{1u} electronic state can give rise to B_{2u} electronic states that are polarized along the y direction.

When the electronic and vibrational excited states belong to B_{1u} (in the case of mode 32), the direct product representation becomes A_g . However, this totally symmetric excitation is dipole-forbidden in a molecule with D_{2h} symmetry like naphthalene.

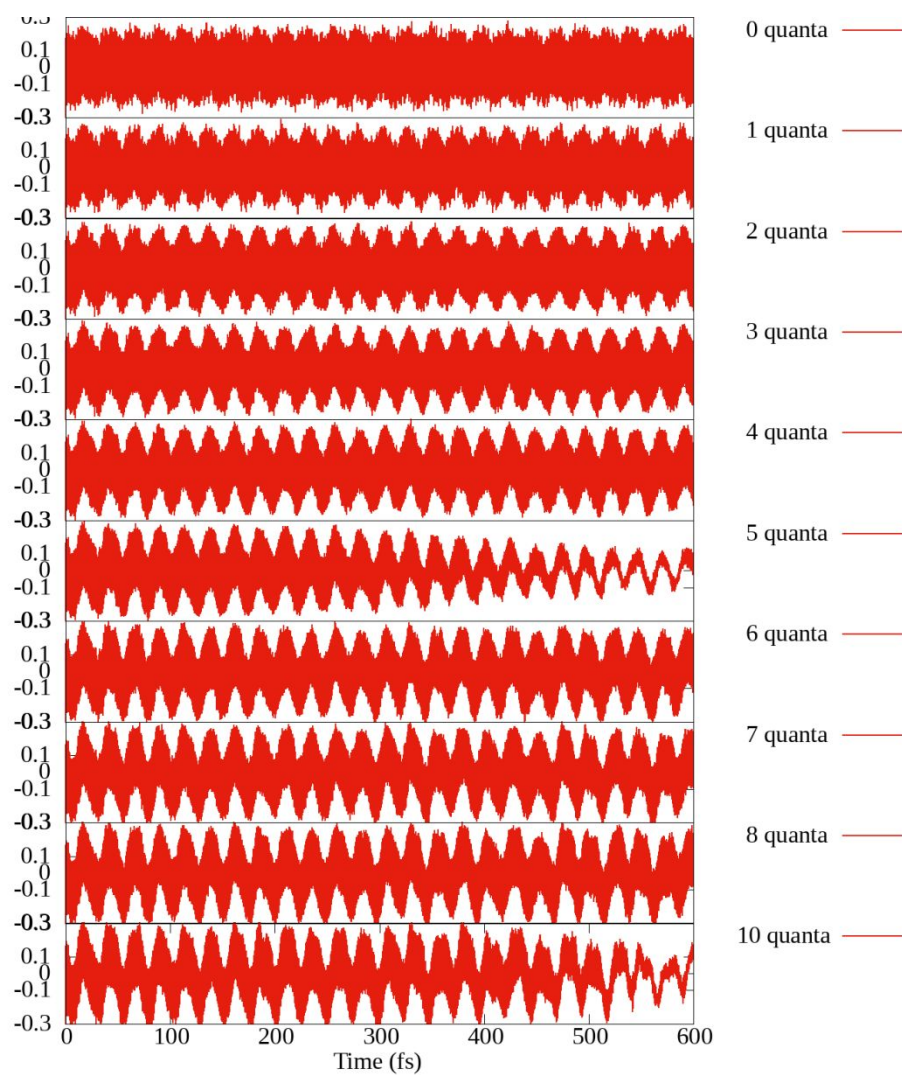


Figure S2. z -component of the dipole moment when mode 32 (B_{1u}) is activated with different number of quanta.

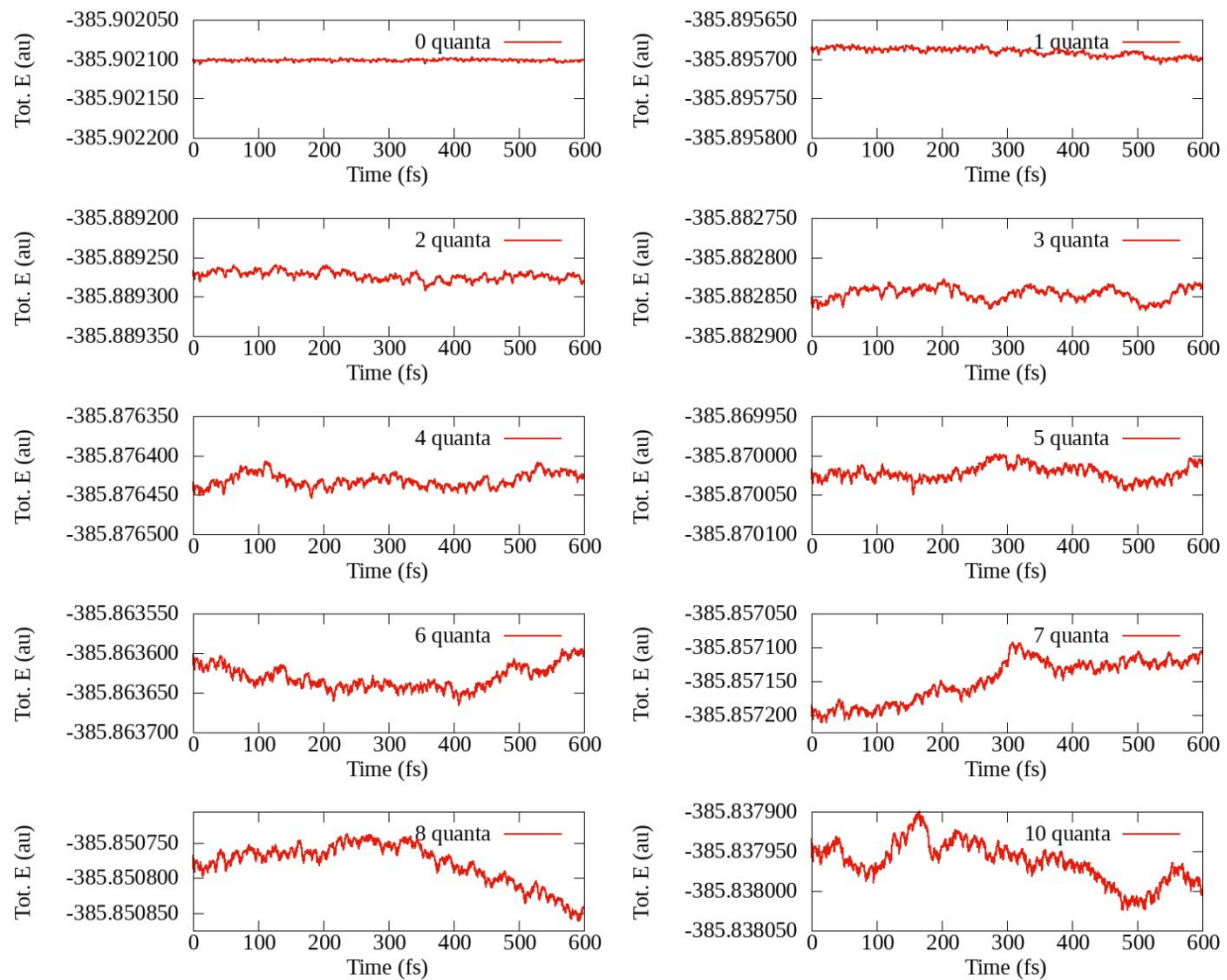


Figure S3. Total energy conservation during an Ehrenfest molecular dynamics simulation when mode 32 (B_{1u}) is activated with different numbers of quanta.

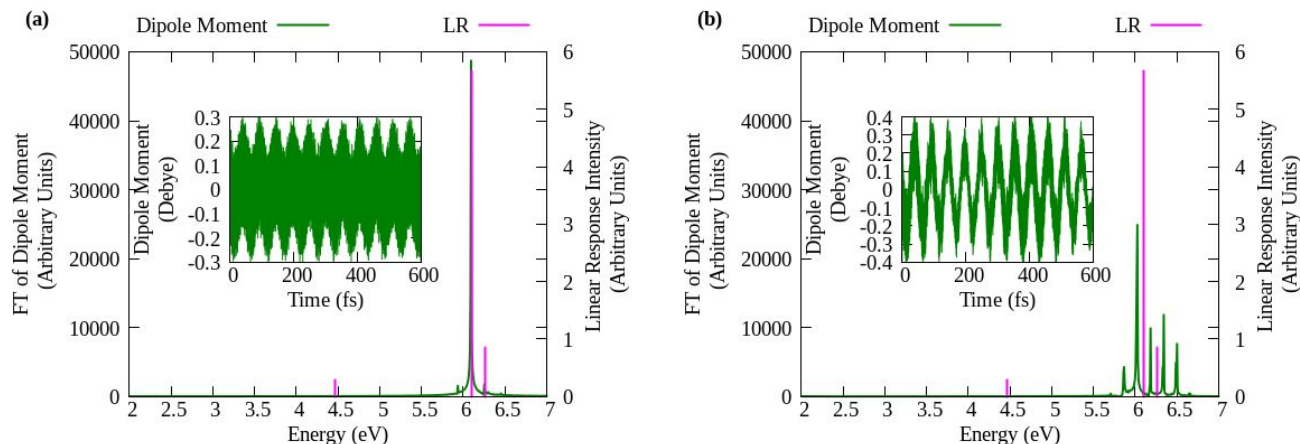


Figure S4. Fourier transform of the z-component of the dipole moment (green) when mode 10 (B_{1u}) is activated with (a) 0 quanta and (b) 5 quanta compared with the LR-TDDFT stick spectrum (pink). The insets show the time variation of the dipole moment.

Table S4. B3LYP/6-31G(d,p) MO transitions responsible for the peaks at 5.96 eV and 6.46 eV for the most distorted geometry of naphthalene during activation of normal mode 10 (geometry at 40.0 fs). Note that the transitions with A_g irreducible representation in D_{2h} point group symmetry are forbidden, but they become allowed when the structural symmetry is lowered to C_{2v} because the transitions with A_1 representation are allowed in C_{2v} point group symmetry.

Energy (eV)	Wavelength (nm)	Oscillator strength	Transitions	Symmetry of Transitions		Weight
				D_{2h}	C_{2v}	
5.96	207.92	0.8781	HOMO – 2 \rightarrow LUMO + 1	A_g	A_1	0.174
			HOMO – 1 \rightarrow LUMO	B_{1u}	A_1	-0.452
			HOMO – 1 \rightarrow LUMO + 2	A_g	A_1	-0.216
			HOMO \rightarrow LUMO + 1	B_{1u}	A_1	0.465
6.46	192.05	0.3060	HOMO – 3 \rightarrow LUMO	A_g	A_1	-0.135
			HOMO – 2 \rightarrow LUMO + 1	A_g	A_1	0.466
			HOMO – 1 \rightarrow LUMO	B_{1u}	A_1	0.190
			HOMO – 1 \rightarrow LUMO + 2	A_g	A_1	-0.428
			HOMO \rightarrow LUMO + 1	B_{1u}	A_1	-0.199

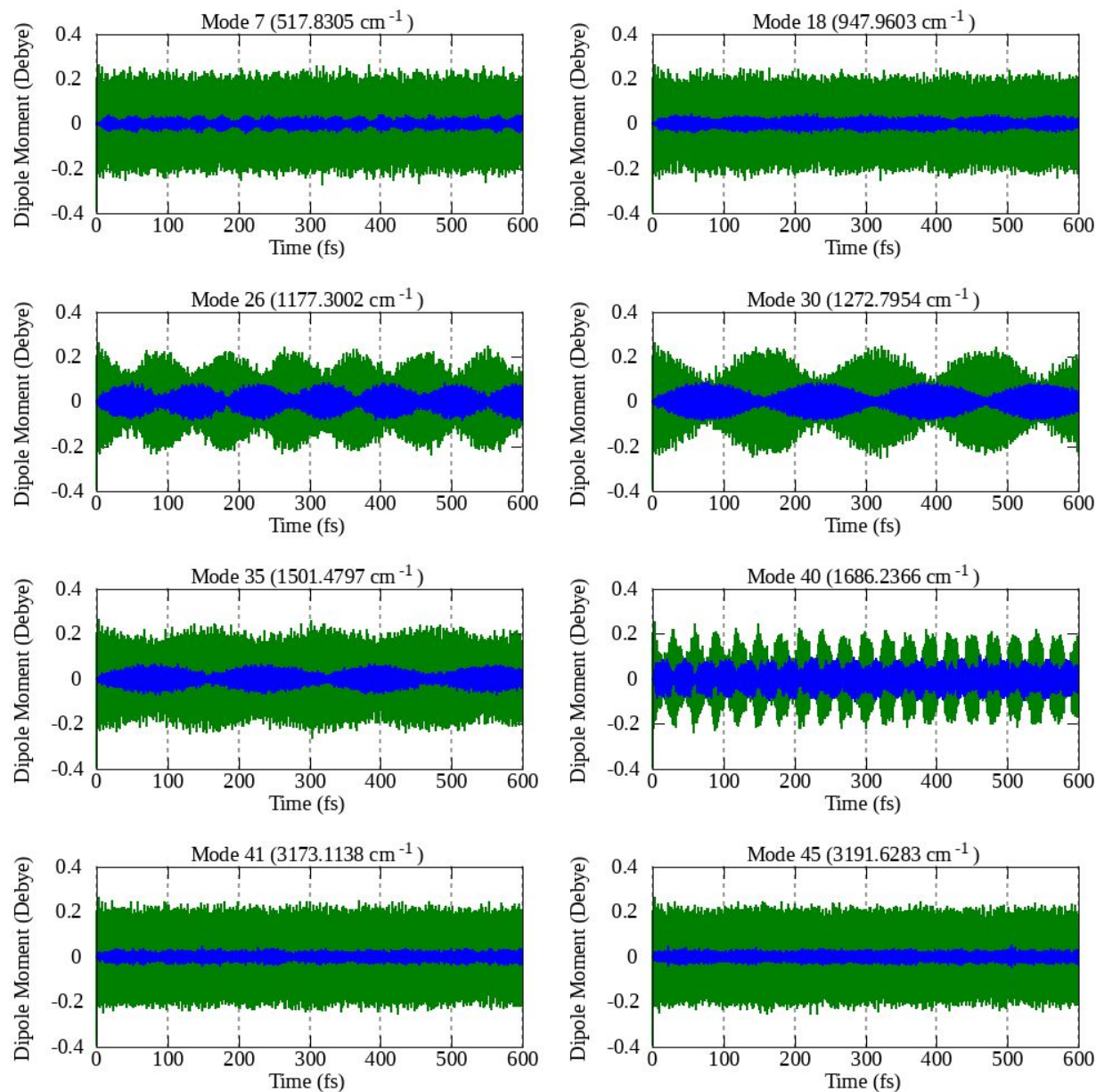


Figure S5. Variation of dipole moment during an Ehrenfest dynamics with electrons excited along the z direction and B_{2g} normal modes of naphthalene are activated with zero quanta. green: z -component; blue: x -component of the dipole moment.

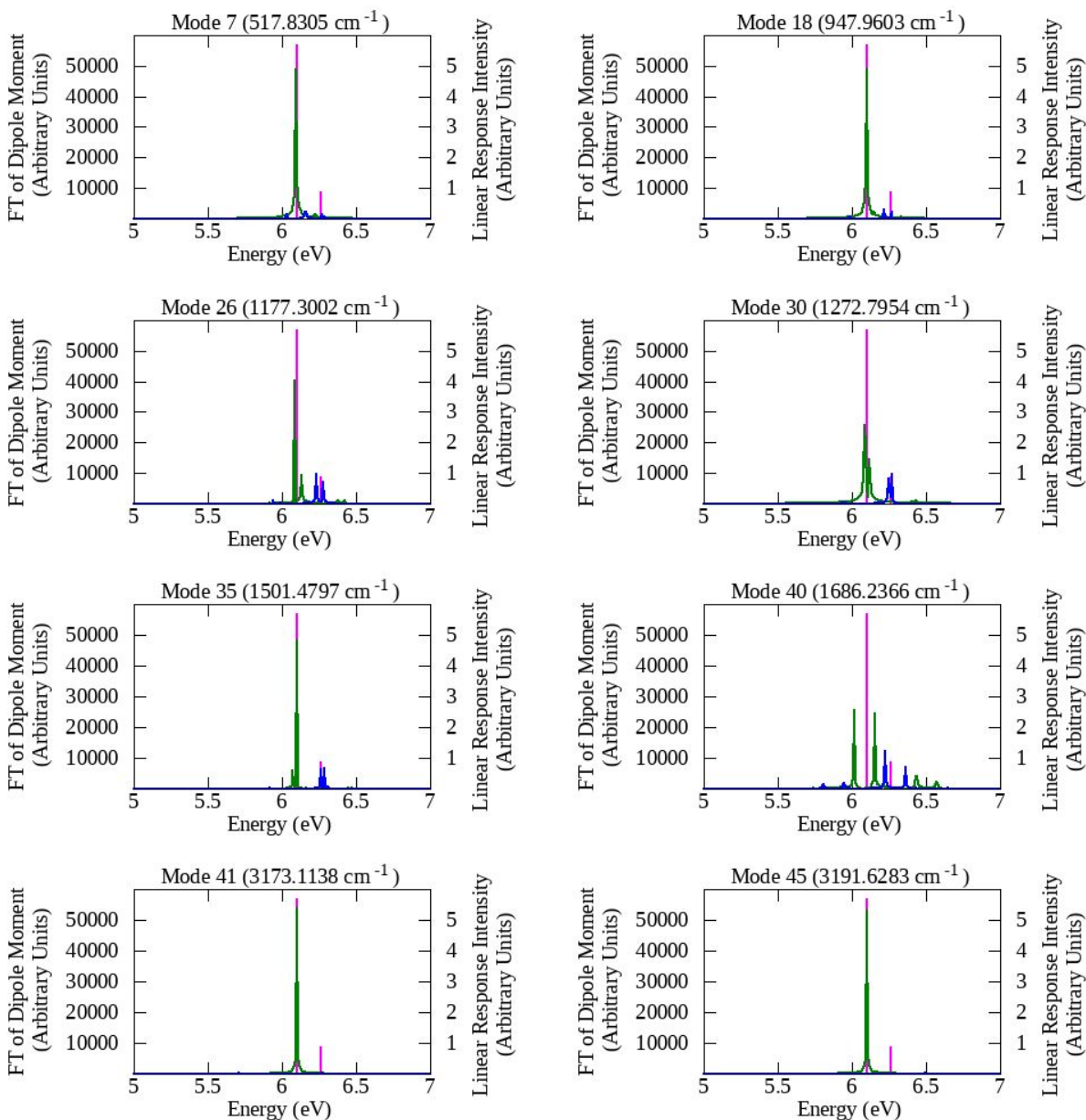


Figure S6. Fourier transforms of dipole moment components during an Ehrenfest dynamics with electrons excited along the z direction and B_{2g} normal modes of naphthalene are activated with zero quanta. Peak positions are compared with the LR-TDDFT excitation energy positions. green: z -component; blue: x -component of the dipole moment; pink: LR-TDDFT stick spectrum.

Reference

- (1) Cotton, F. A., *Chemical Applications of Group Theory*. 3rd ed.; Wiley: New York, 1990.