Supporting Information

Rationalization of Experimental Photoelectron Spectra of Cyanocyclopentadienide Anion ($CpCN^-$) via Vibronic Coupling Theory

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Table S1. **Harmonic vibrational frequencies associated with asymmetric modes [in cm^{-1}] of $CpCN^-$.**

Vibrational Mode(Asymmetry)	Anion Frequency(ω_i)
$\boldsymbol{a_2}$	
ν_{11} (a_2)	627.1699
ν_{12} (a_2)	692.0269
ν_{13} (a_2)	867.1485
$\boldsymbol{b_1}$	
ν_{14} (b_1)	163.0324
ν_{15} (b_1)	549.3511
ν_{16} (b_1)	652.9423
ν_{17} (b_1)	714.5966
ν_{18} (b_1)	829.3983
$\boldsymbol{b_2}$	
ν_{19} (b_2)	178.9352
ν_{20} (b_2)	594.9532
ν_{21} (b_2)	862.2656
ν_{22} (b_2)	1059.4758
ν_{23} (b_2)	1236.0649
ν_{24} (b_2)	1380.6294
ν_{25} (b_2)	1488.8446
ν_{26} (b_2)	3197.6679
ν_{27} (b_2)	3232.3531

Table S2. **higher order coupling terms for symmetric states**

Mode	C	D	C	D
	$\widetilde{B}$		$\widetilde{C}$	
ν_1				
ν_2	0.00081	-0.00001		
ν_3	-0.0010			
ν_4				
ν_5	0.0031			
ν_6			-0.00040	
ν_7				
ν_8			-0.00089	0.00041
ν_9				
ν_{10}	-0.00021			

Table S3. **Hamiltonian parameters of $CpCN^-$ for asymmetric modes.**

Mode	γ	D	γ	D
	$\widetilde{X}$		$\widetilde{A}$	
$\nu_{11}(a_2)$	-0.01804		-0.01571	
$\nu_{12}(a_2)$	0.13705		0.03734	
$\nu_{13}(a_2)$	0.01880		0.17994	
$\nu_{14}(b_1)$	0.01650		-0.00897	
$\nu_{15}(b_1)$	-0.01659		-0.00821	
$\nu_{16}(b_1)$	0.00313		-0.01667	
$\nu_{17}(b_1)$	0.01796		0.00793	
$\nu_{18}(b_1)$	0.02434		0.01269	
$\nu_{19}(b_2)$	0.00297		0.00561	
$\nu_{20}(b_2)$	-0.00651		0.00235	
$\nu_{21}(b_2)$	-0.04142	0.00032	0.04188	-0.00031
$\nu_{22}(b_2)$	-0.01993	0.00017	0.03355	-0.00018
$\nu_{23}(b_2)$	-0.16114	0.00014	0.03096	-0.00015
$\nu_{24}(b_2)$	-0.09341	0.00088	0.11106	-0.00091
$\nu_{25}(b_2)$	-0.04452	0.00037	0.04991	-0.00037
$\nu_{26}(b_2)$	0.00755		0.00825	
$\nu_{27}(b_2)$	0.00509		0.00636	
	$\widetilde{B}$		$\widetilde{C}$	
$\nu_{11}(a_2)$	-0.02247	0.00015	0.01457	-0.00032
$\nu_{12}(a_2)$	-0.06185		0.00393	
$\nu_{13}(a_2)$	-0.06670	0.00048	0.06647	-0.00085
$\nu_{14}(b_1)$	-0.01576		-0.02469	
$\nu_{15}(b_1)$	-0.01481		-0.01865	
$\nu_{16}(b_1)$	-0.00961		-0.01285	
$\nu_{17}(b_1)$	0.00577	-0.00016	-0.02370	
$\nu_{18}(b_1)$	0.00402	-0.00007	-0.04142	
$\nu_{19}(b_2)$	-0.04102		-0.02587	
$\nu_{20}(b_2)$	-0.02490		-0.01001	
$\nu_{21}(b_2)$	0.00726	-0.00078	0.00317	
$\nu_{22}(b_2)$	-0.00156	-0.00005	0.01013	
$\nu_{23}(b_2)$	-0.01635		0.00711	
$\nu_{24}(b_2)$	-0.07642		0.00581	0.00038
$\nu_{25}(b_2)$	-0.08195		0.01932	
$\nu_{26}(b_2)$	-0.00105	-0.00010	0.00770	
$\nu_{27}(b_2)$	0.000059	-0.00004	0.00547	

Table S4. **Combination of Normal Modes, Size of the Primitive Basis, and the Single-Particle Function (SPF) for Uncoupled TD and TI Calculations of $CpCN^-$ utilizing the MCTDH Method.**

Combination of normal modes	Primitive basis	SPF
ν_6	18	[14,14,14,14]
ν_4	17	[12,12,12,12]
ν_1, ν_2, ν_3	16, 16, 16	[10,10,10,10]
ν_5, ν_7	15, 15	[8,8,8,8]
ν_8	14	[4,4,4,4]
ν_1,ν_6	10,10	
ν_1, ν_2, ν_3	8, 8, 8	
ν_5, ν_7	5, 5	
ν_8	3	

Table S5. **Combination of Normal Modes, Size of the Primitive Basis, and the SPF for Coupled TD Calculations of $CpCN^-$ utilizing the MCTDH Method.**

Electronic states	Normal modes	Primitive basis	SPF basis
Coupled $\tilde{X}-\tilde{C}$ electronic states	ν_{12}, ν_{13}, ν_{14}, ν_{19}	(14,14,14,14)	[6,6,6,6]
	ν_6, ν_{15}, ν_{16}, ν_{17}, ν_{18}, ν_{20}, ν_{21}, ν_{22}, ν_{24}	(12,12,12,12,12,12,12,12,12)	[4,4,4,4]
	ν_1, ν_2, ν_3, ν_4, ν_{11}, ν_{25}	(10,10,10,10,10,10)	[2,2,2,2]
	ν_5, ν_7	(8,8)	[2,2,2,2]

Table S6. **Vibronic level assignments in symmetric modes (in cm^{-1}) for $\tilde{X}$ and $\tilde{A}$ states.**

$\tilde{X}$ State		$\tilde{A}$ State	
Vibronic Energy	Assignments	Vibronic Energy	Assignments
0	0_0^0	0	0_0^0
551	ν_{10}^1	569	ν_{10}^1
1081	ν_{20}^1	1069	ν_{20}^1
1102	ν_{30}^1	1093	ν_{30}^1
1108	ν_{10}^2	1138	ν_{10}^2
1481	ν_{60}^1	1507	ν_{60}^1
1514	ν_{70}^1	1539	ν_{70}^1
1632	$\nu_{10}^1+\nu_{20}^1$	1638	$\nu_{10}^1+\nu_{20}^1$
1654	$\nu_{10}^1+\nu_{30}^1$	1662	$\nu_{10}^1+\nu_{30}^1$
1926	ν_{50}^1	1904	ν_{50}^1
2019	ν_{40}^1	2007	ν_{40}^1
2032	ν_{10}^3	2031	ν_{10}^3
2044	$\nu_{10}^1+\nu_{60}^1$	2076	$\nu_{10}^1+\nu_{60}^1$
2065	$\nu_{10}^1+\nu_{70}^1$	2108	$\nu_{10}^1+\nu_{70}^1$
2162	$\nu_{20}^1+\nu_{40}^1$	2137	ν_{20}^2
2184	$\nu_{20}^1+\nu_{30}^1$	2162	$\nu_{20}^1+\nu_{30}^1$
2189	$\nu_{10}^2+\nu_{20}^1$	2186	ν_{30}^2
2209	ν_{30}^2	2207	$\nu_{10}^2+\nu_{20}^1$
2477	$\nu_{10}^1+\nu_{50}^1$	2476	$\nu_{10}^1+\nu_{50}^1$
2562	$\nu_{20}^1+\nu_{60}^1$	2576	$\nu_{20}^1+\nu_{60}^1$

Table S7. **Vibronic level assignments in symmetric modes (in cm^{-1}) for $\tilde{B}$ and $\tilde{C}$ states.**

$\tilde{B}$ State		$\tilde{C}$ State	
Vibronic Energy	Assignments	Vibronic Energy	Assignments
0	0_0^0	0	0_0^0
501	ν_{10}^1	545	ν_{10}^1
902	ν_{20}^1	964	ν_{20}^1
994	ν_{30}^1	1082	ν_{30}^1
1005	ν_{10}^2	1091	ν_{10}^2
1046	ν_{40}^1	1108	ν_{40}^1
1123	ν_{60}^1	1281	ν_{50}^1
1264	ν_{50}^1	1423	ν_{60}^1
1404	$\nu_{10}^1+\nu_{20}^1$	1510	$\nu_{10}^1+\nu_{20}^1$
1496	$\nu_{10}^1+\nu_{30}^1$	1579	ν_{70}^1
1523	ν_{10}^3	1628	$\nu_{10}^1+\nu_{30}^1$
1548	$\nu_{10}^2+\nu_{40}^1$	1638	ν_{10}^3
1766	$\nu_{10}^1+\nu_{50}^1$	1654	$\nu_{10}^1+\nu_{40}^1$
1800	ν_{20}^2	1827	$\nu_{10}^1+\nu_{50}^1$
1897	$\nu_{20}^1+\nu_{30}^1$	1929	ν_{20}^2
1908	$\nu_{10}^2+\nu_{20}^1$	1969	$\nu_{10}^1+\nu_{60}^1$
1948	$\nu_{20}^1+\nu_{40}^1$	2047	$\nu_{20}^1+\nu_{30}^1$
1989	ν_{10}^3	2056	$\nu_{10}^2+\nu_{20}^1$
2000	ν_{10}^4	2072	$\nu_{20}^2+\nu_{40}^1$
		2125	$\nu_{10}^1+\nu_{70}^1$

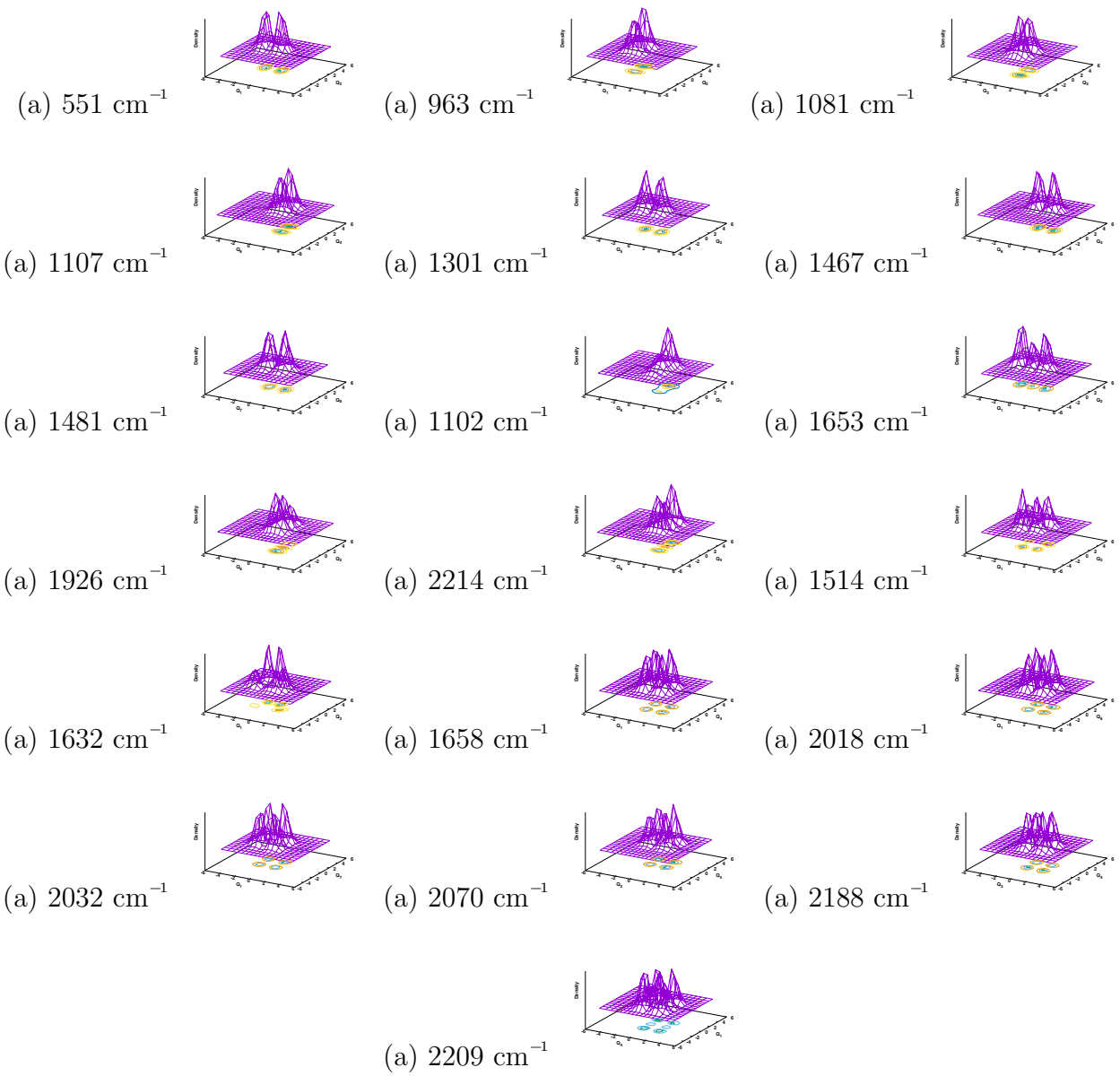

Figure S1. **Wavepacket density plots for the $\tilde{X}$ state including only totally symmetric vibrational modes. The snapshots illustrate Franck–Condon fundamentals, overtones, and combination bands in the absence of interstate vibronic coupling; the coupling parameter λ is therefore inactive in these calculations.**

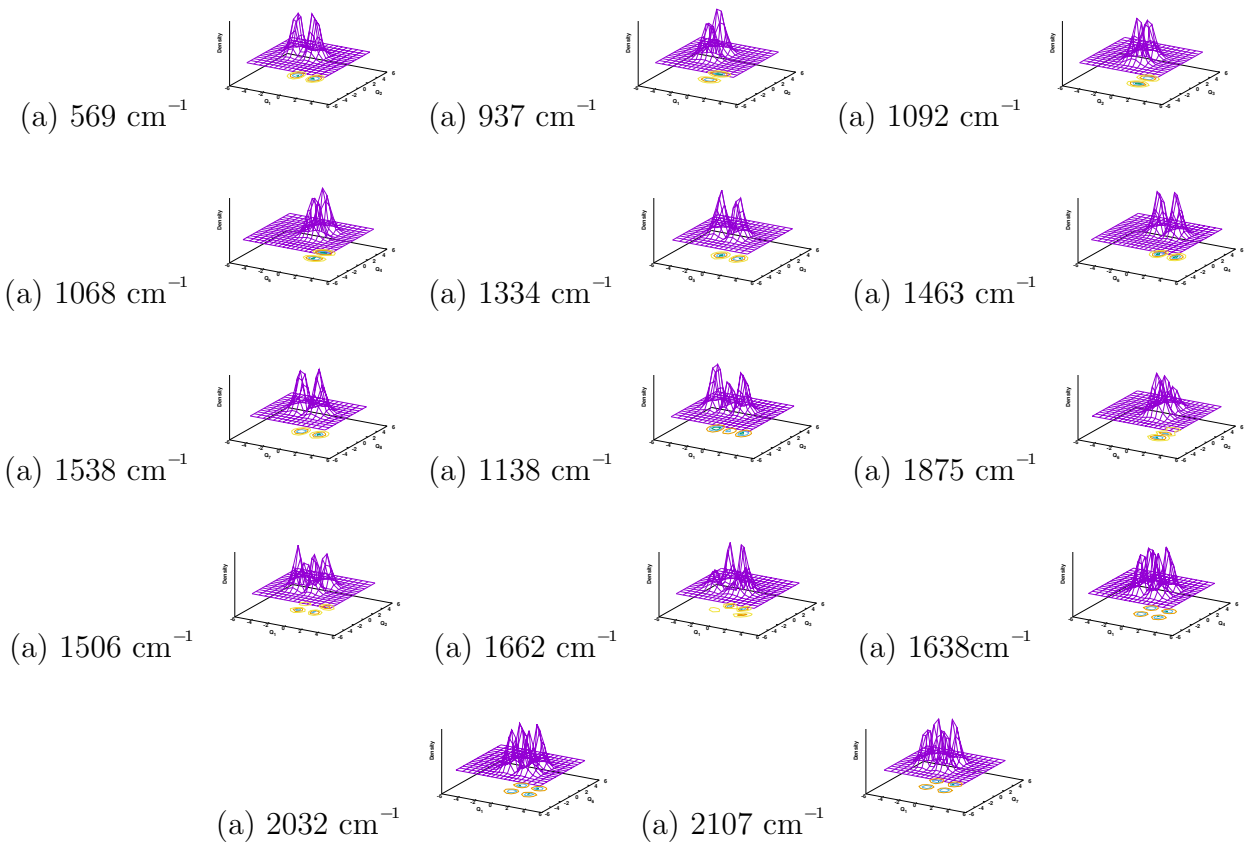

Figure S2. **Wavepacket density plots for the $\tilde{A}$ state including only totally symmetric vibrational modes. The snapshots illustrate Franck–Condon fundamentals, overtones, and combination bands in the absence of interstate vibronic coupling; the coupling parameter λ is therefore inactive in these calculations.**

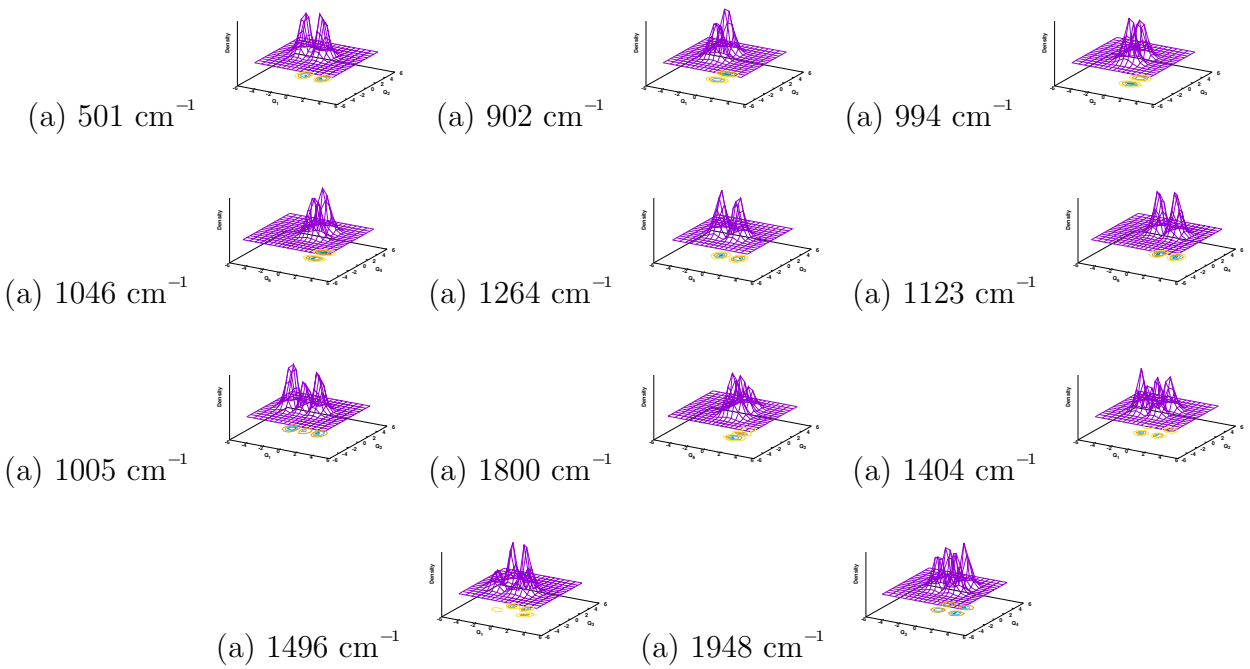

Figure S3. **Wavepacket density plots for the $\tilde{B}$ state including only totally symmetric vibrational modes. The snapshots illustrate Franck–Condon fundamentals, overtones, and combination bands in the absence of interstate vibronic coupling; the coupling parameter λ is therefore inactive in these calculations.**

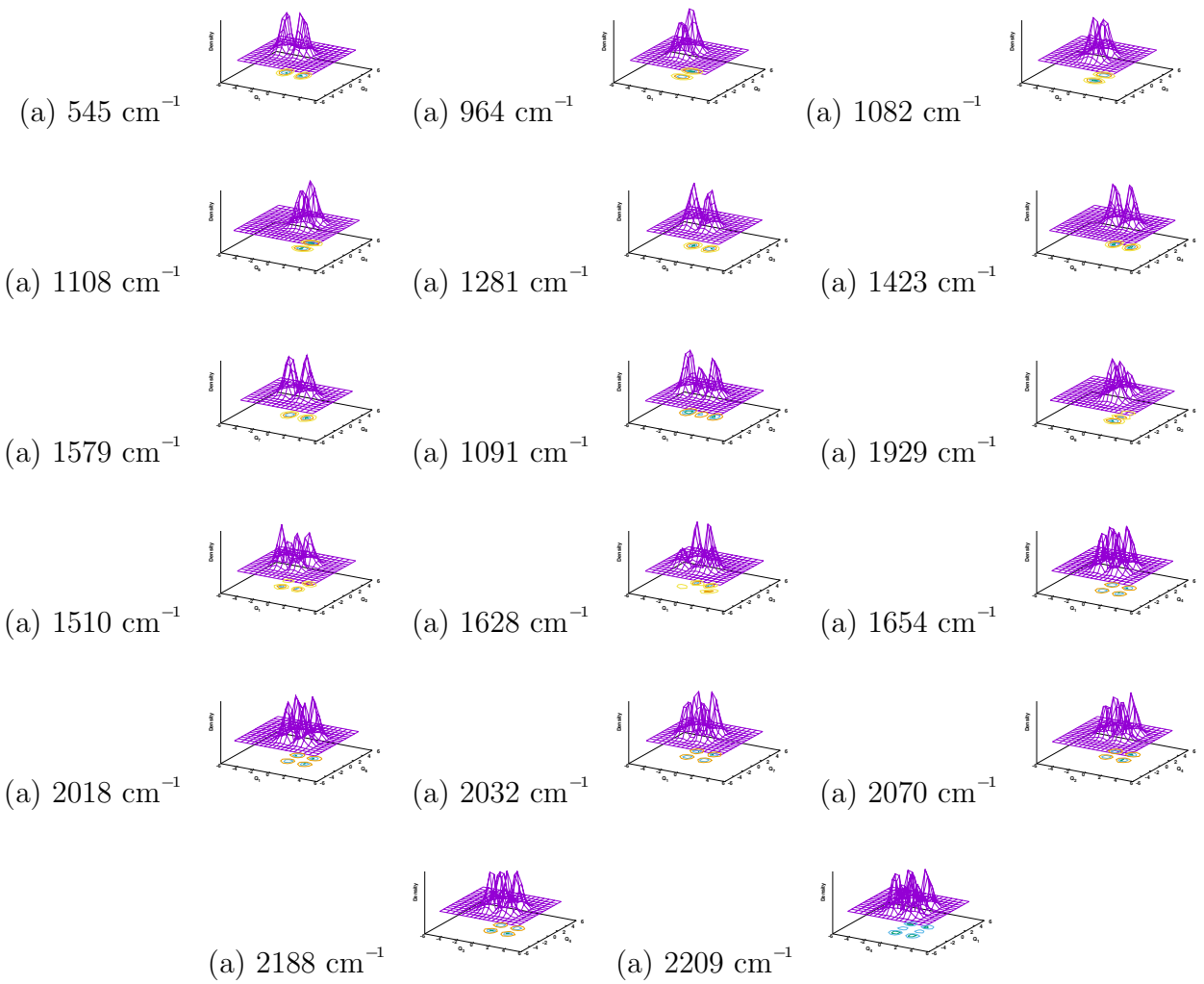

Figure S4. **Wavepacket density plots for the $\tilde{C}$ state including only totally symmetric vibrational modes. The snapshots illustrate Franck–Condon fundamentals, overtones, and combination bands in the absence of interstate vibronic coupling; the coupling parameter λ is therefore inactive in these calculations.**

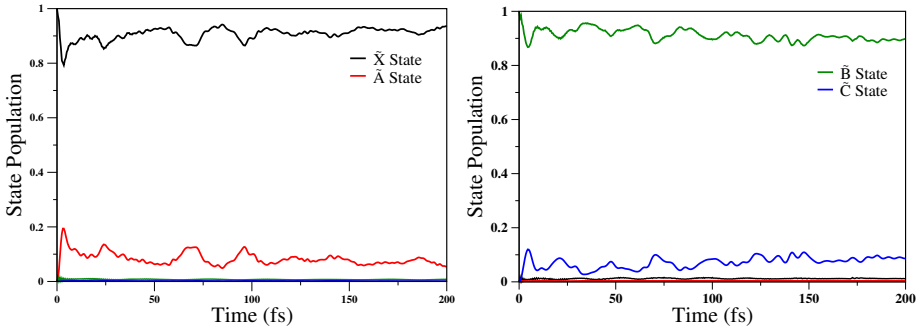

Figure S5. **Electronic population plot showing initiation of WPs in $\tilde{X}$ and $\tilde{B}$ states respectively.**