Electronic Supporting Information for Theoretical Study of Vibronic Interactions in the Photoelectron Spectra of Al_6N^-

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Table S.I. **Bond lengths for Al_6N (in Å unit) obtained using CAM-B3LYP, M06-2X and MP2 level of theories with a 6-311+g(d) basis set.**

Parameter	CAM-B3LYP	M06-2X	MP2
N_1-Al_2	2.3529	2.3402	2.3514
N_1-Al_4	1.9848	1.9869	1.9973
N_1-Al_3	2.3543	2.3416	2.3527
N_1-Al_7	1.9845	1.9865	1.9968
Al_2-Al_3	2.5918	2.5717	2.6057
Al_4-Al_5	2.9704	2.9644	2.9635
Al_4-Al_7	2.5920	2.6055	2.6297
Al_3-Al_6	2.6508	2.6414	2.66243

Table S.II. **Quadratic and higher-order coupling parameters for $\tilde{X}^2B_1$ state. The parameters are given in the eV unit.**

Vibrational mode	frequencies	E_0	γ	C
ν_6 (a_2)	0.0077	2.4260	-0.0042	
ν_7 (a_2)	0.0229	2.4248	-0.0066	
ν_8 (a_2)	0.0303	2.4250	-0.0040	
ν_9 (b_1)	0.0233	2.4265	0.0047	
ν_{10} (b_1)	0.0337	2.4246	-0.0064	
ν_{11} (b_1)	0.0661	2.4261	-0.0041	
ν_{12} (b_2)	0.0098	2.4252	-0.0095	0.00001
ν_{13} (b_2)	0.0132	2.4251	-0.0042	
ν_{14} (b_2)	0.0310	2.4251	-0.0049	0.000004
ν_{15} (b_2)	0.0650	2.4251	-0.0001	-0.000002

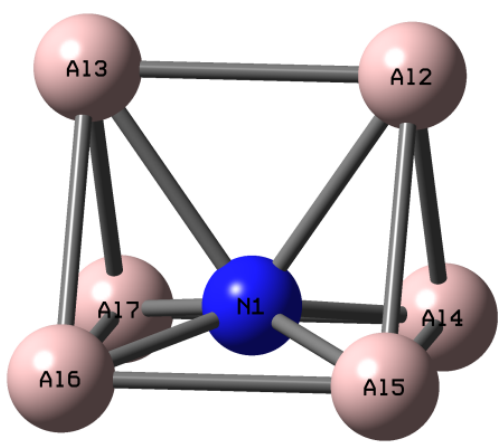


Figure S1. **The optimized structure of neutral Al_6N.**

Table S.III. **Quadratic and higher-order coupling parameters for $\tilde{A}^2A_1$ state. The parameters are given in the eV unit.**

Vibrational mode	frequencies	E_0	γ	C
ν_6 (a_2)	0.0077	3.1676	-0.0118	
ν_7 (a_2)	0.0229	3.1682	-0.0044	
ν_8 (a_2)	0.0303	3.1678	-0.0050	
ν_9 (b_1)	0.0233	3.1671	-0.0088	
ν_{10} (b_1)	0.0337	3.1673	-0.0046	
ν_{11} (b_1)	0.0661	3.1649	-0.0157	
ν_{12} (b_2)	0.0098	3.1589	-0.0673	0.0016
ν_{13} (b_2)	0.0132	3.1647	-0.0454	0.0008
ν_{14} (b_2)	0.0310	3.1671	-0.0223	0.0003
ν_{15} (b_2)	0.0650	3.1643	-0.0569	0.0009

Table S.IV. **Quadratic and higher-order coupling parameter for $\tilde{B}^2B_2$ state. The parameters are given in the eV unit.**

Vibrational mode	frequencies	E_0	γ
ν_6 (a_2)	0.0077	3.2787	0.0140
ν_7 (a_2)	0.0229	3.2784	0.0019
ν_8 (a_2)	0.0303	3.2782	-0.0047
ν_9 (b_1)	0.0233	3.2780	-0.0078
ν_{10} (b_1)	0.0337	3.2780	-0.0016
ν_{11} (b_1)	0.0661	3.2776	-0.0091
ν_{12} (b_2)	0.0098	3.2934	0.0642
ν_{13} (b_2)	0.0132	3.2840	0.0251
ν_{14} (b_2)	0.0310	3.2800	0.0122
ν_{15} (b_2)	0.0650	3.2808	0.0193

Table S.V. **Quadratic and higher-order coupling parameters for $\tilde{C}^2A_2$ state. The parameters are given in the eV unit.**

Vibrational mode	frequencies	E_0	γ	δ	C
ν_6 (a_2)	0.0077	4.2158	0.0033		
ν_7 (a_2)	0.0229	4.2123	-0.0093		
ν_8 (a_2)	0.0303	4.2151	-0.0043		
ν_9 (b_1)	0.0233	4.2147	-0.0139		0.0001
ν_{10} (b_1)	0.0337	4.2153	-0.0082		0.00002
ν_{11} (b_1)	0.0661	4.2142	-0.0110		0.0001
ν_{12} (b_2)	0.0098	4.2154	-0.0019		
ν_{13} (b_2)	0.0132	4.2148	-0.0072		
ν_{14} (b_2)	0.0310	4.2152	-0.0068	0.00003	
ν_{15} (b_2)	0.0650	4.2019	-0.0942	0.0014	

Table S.VI. **Quadratic and higher-order coupling parameters for $\tilde{D}^2B_1$ state. The parameters are given in the eV unit.**

Vibrational mode	frequencies	E_0	γ
ν_6 (a_2)	0.0077	4.2007	-0.0010
ν_7 (a_2)	0.0229	4.2005	-0.0009
ν_8 (a_2)	0.0303	4.1989	-0.0010
ν_9 (b_1)	0.0233	4.2008	0.0202
ν_{10} (b_1)	0.0337	4.2012	0.0077
ν_{11} (b_1)	0.0661	4.2035	0.0105
ν_{12} (b_2)	0.0098	4.2014	0.0013
ν_{13} (b_2)	0.0132	4.2009	0.0021
ν_{14} (b_2)	0.0310	4.2033	0.0168
ν_{15} (b_2)	0.0650	4.5246	0.0051

Table S.VII. **Quadratic and higher-order coupling parameters for $\tilde{E}^2A_1$ state. The parameters are given in the eV unit.**

Vibrational mode	frequencies	E_0	γ
ν_6 (a_2)	0.0077	4.5310	0.0005
ν_7 (a_2)	0.0229	4.5326	0.0049
ν_8 (a_2)	0.0303	4.5310	0.0051
ν_9 (b_1)	0.0233	4.5305	0.0005
ν_{10} (b_1)	0.0337	4.5273	0.0153
ν_{11} (b_1)	0.0661	4.5294	0.0242
ν_{12} (b_2)	0.0098	4.5277	-0.0162
ν_{13} (b_2)	0.0132	4.511	-0.0124
ν_{14} (b_2)	0.0310	4.5297	0.0007
ν_{15} (b_2)	0.0650	4.2696	0.0536

Table S.VIII. **Quadratic and higher-order coupling parameters for $\tilde{F}^2B_2$ state. The parameters are given in the eV unit.**

Vibrational mode	frequencies	E_0	γ
ν_6 (a_2)	0.0077	4.7526	-0.0004
ν_7 (a_2)	0.0229	4.7527	0.0096
ν_8 (a_2)	0.0303	4.7532	0.0142
ν_9 (b_1)	0.0233	4.7591	0.0276
ν_{10} (b_1)	0.0337	4.7534	0.0092
ν_{11} (b_1)	0.0661	4.7610	0.0298
ν_{12} (b_2)	0.0098	4.7541	0.0021
ν_{13} (b_2)	0.0132	4.7693	0.0289
ν_{14} (b_2)	0.0310	4.7541	0.0126
ν_{15} (b_2)	0.0650	4.7630	0.0237

Table S.IX. **Normal modes combination, size of the primitive basis and single particle function (SPF) for uncoupled and coupled (TD and TI) calculations of Al_6N^- using the MCTDH approach.**

Combination of normal modes	Primitive basis	SPF
ν_2	8	[12,12,12,12,12,12,12]
ν_1,ν_3	8,10	[10,10,10,10,10,10,10]
ν_4	10	[9,9,9,9,9,9,9]
ν_5	8	[7,7,7,7,7,7,7]
ν_2,ν_6,ν_{12},ν_{13}	10,10,10,10	[12,12,12,12,12,12,12]
ν_1,ν_3,ν_7,ν_8,ν_9	8,8,8,8,8,	[10,10,10,10,10,10,10]
ν_5,ν_{10},ν_{11},ν_{14},ν_{15},ν_4	6,6,6,6,6,6	[8,8,8,8,8,8,8]
ν_2	12	[12,12,12,12,12,12,12]
ν_1,ν_3	8,10	[10,10,10,10,10,10,10]
ν_4	10	[9,9,9,9,9,9,9]
ν_5	8	[7,7,7,7,7,7,7]
ν_2,ν_6,ν_{12}	8,8,8	[6,6,6,6,6,6,6]
ν_1,ν_3,ν_7,ν_9	6,6,6,6	[5,5,5,5,5,5,5]
ν_5,ν_4	5,5	[3,3,3,3,3,3,3]

Table S.X. **Vibronic level assignments for fundamental and first overtone excitation (in cm^{-1}) of tuning modes for $\tilde{A}$ state.**

No.	Vibronic Energy Level	Assignments
1	0	0
2	280	ν_1
3	352	ν_2
4	542	ν_3
5	547	ν_4
6	633	ν_5
7	716	$2\nu_2$

Table S.XI. **Vibronic level assignments for fundamental excitation (in cm^{-1}) of tuning modes for $\tilde{B}$ state.**

No.	Vibronic Energy Level	Assignments
1	0	0
2	261	ν_1
3	683	ν_2
4	808	ν_3
5	915	ν_4
6	924	ν_5

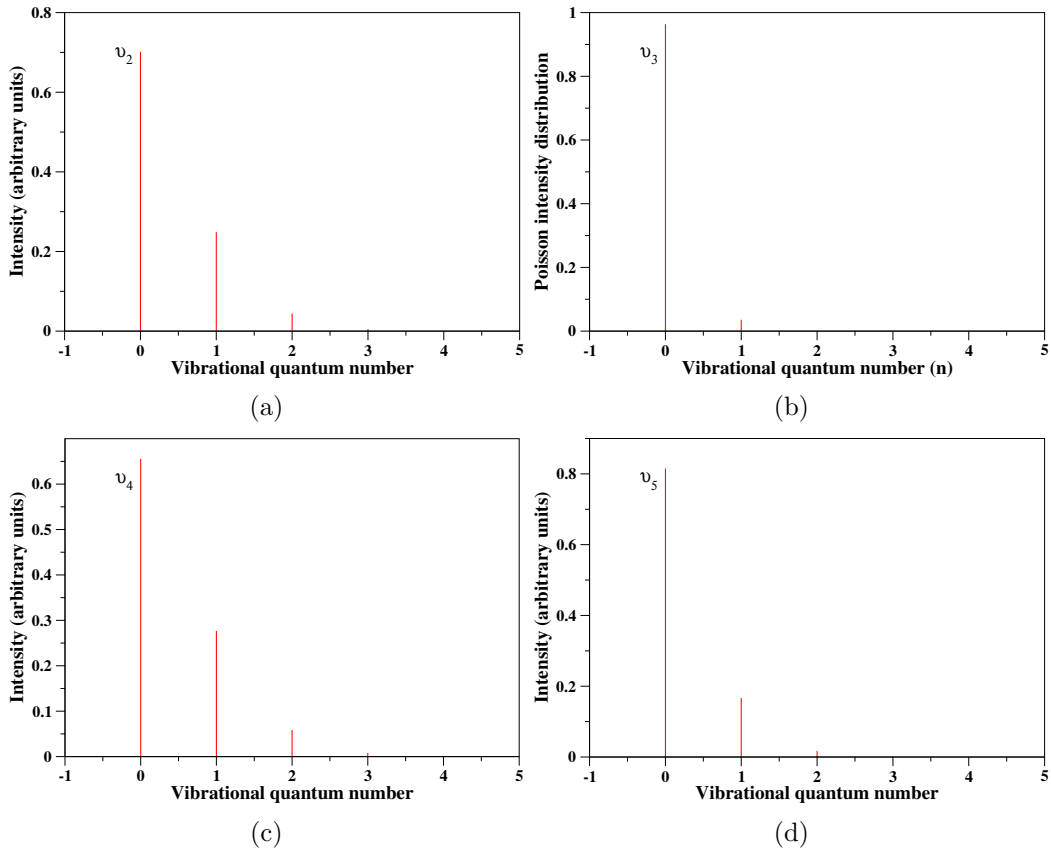


Figure S2. **Poisson intensity distribution for tuning vibrational modes of $\tilde{X}^2B_1$ electronic state of Al_6N along vibrational quantum number.**

Table S.XII. **Vibronic level assignments for fundamental excitation (in cm^{-1}) of tuning modes for $\tilde{C}$ state.**

No.	Vibronic Energy Level	Assignments
1	0	0
2	551	ν_2
3	693	ν_4

Table S.XIII. **Vibronic level assignments for fundamental excitation (in cm^{-1}) of tuning modes for $\tilde{D}$ state.**

No.	Vibronic Energy Level	Assignments
1	0	0
2	473	ν_2
3	547	ν_3

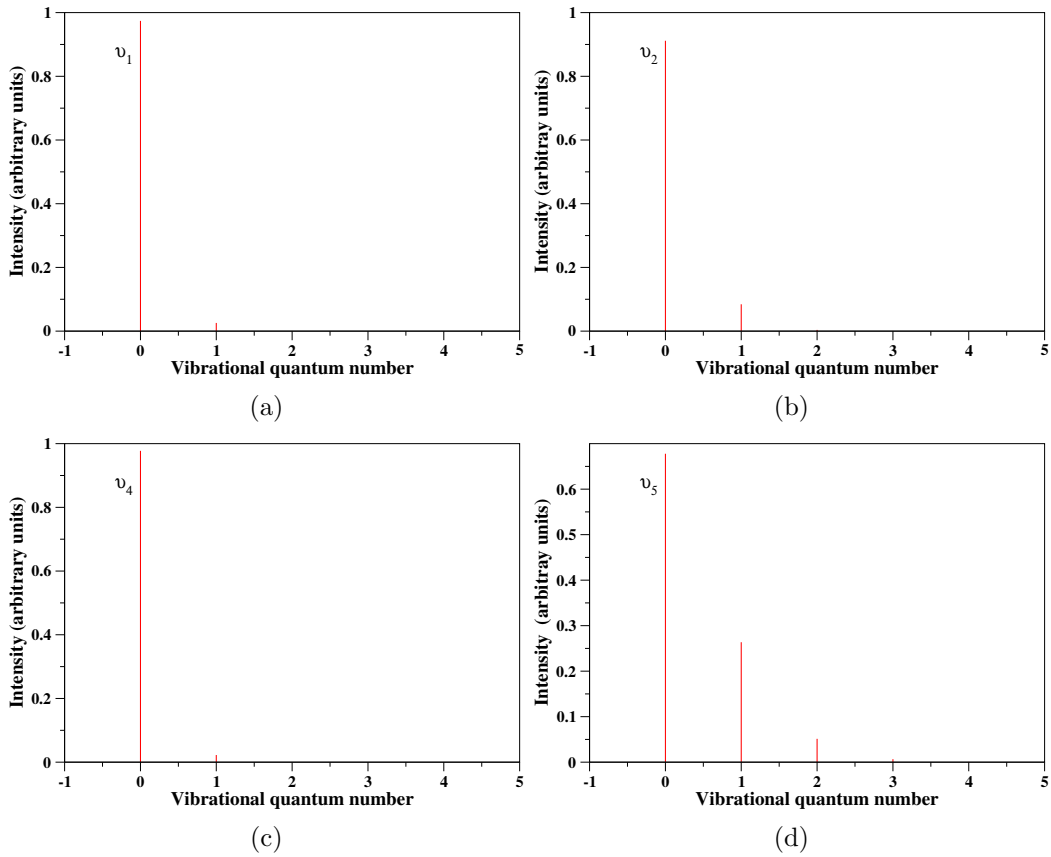


Figure S3. **Poisson intensity distribution for tuning vibrational modes of $\tilde{A}^2A_1$ electronic state of Al_6N along vibrational quantum number.**

Table S.XIV. **Vibronic level assignments for fundamental excitation (in cm^{-1}) of tuning modes for $\tilde{E}$ state.**

No.	Vibronic Energy Level	Assignments
1	0	0
2	545	ν_2
3	984	ν_5

Table S.XV. **Vibronic level assignments for fundamental excitation (in cm^{-1}) of tuning modes for $\tilde{F}$ state.**

No.	Vibronic Energy Level	Assignments
1	0	0
2	208	ν_1
3	358	ν_3
4	488	ν_4
5	538	ν_5

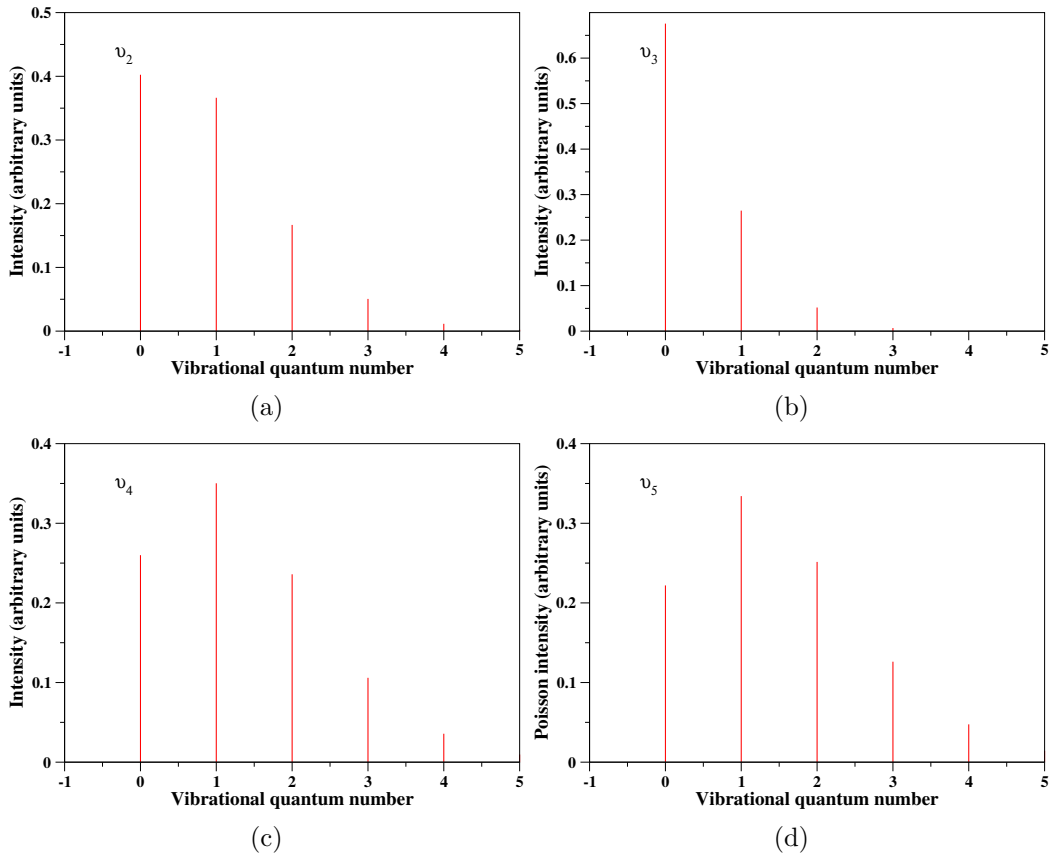


Figure S4. **Poisson intensity distribution for tuning vibrational modes of $\tilde{B}^2B_2$ electronic state of Al_6N along vibrational quantum number.**

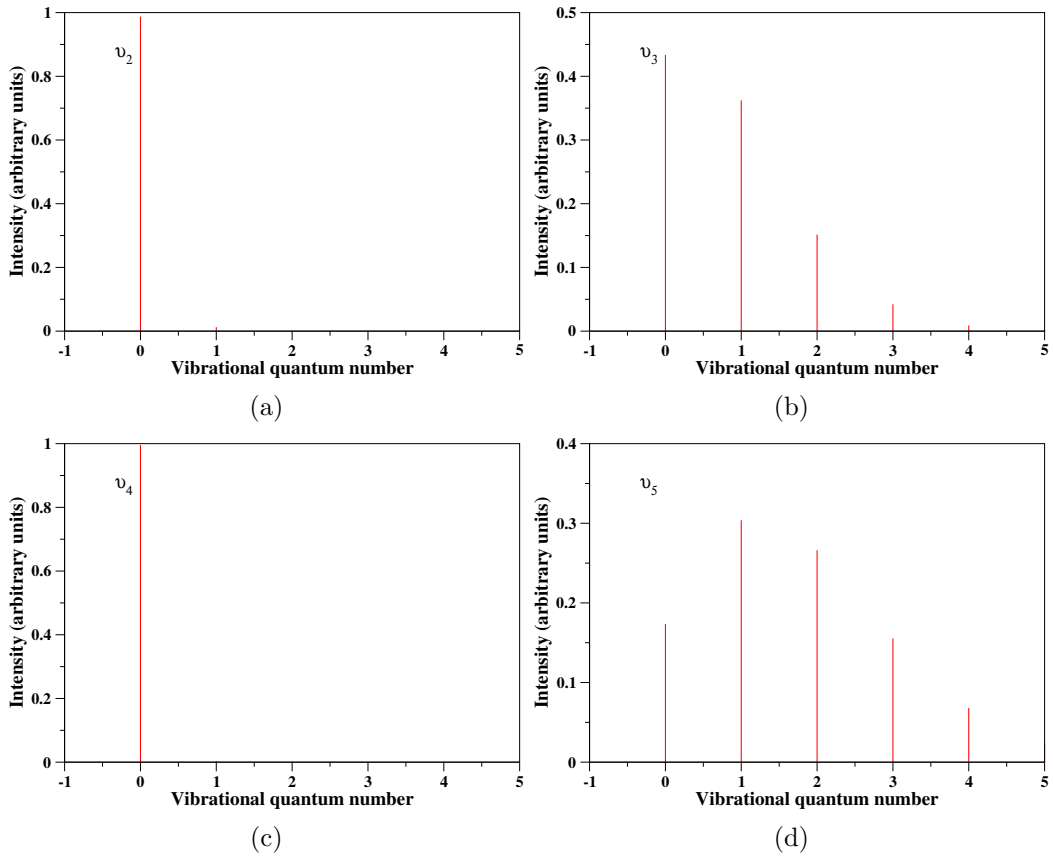


Figure S5. **Poisson intensity distribution for tuning modes of $\tilde{C}^2A_2$ electronic state of Al_6N along vibrational quantum number.**

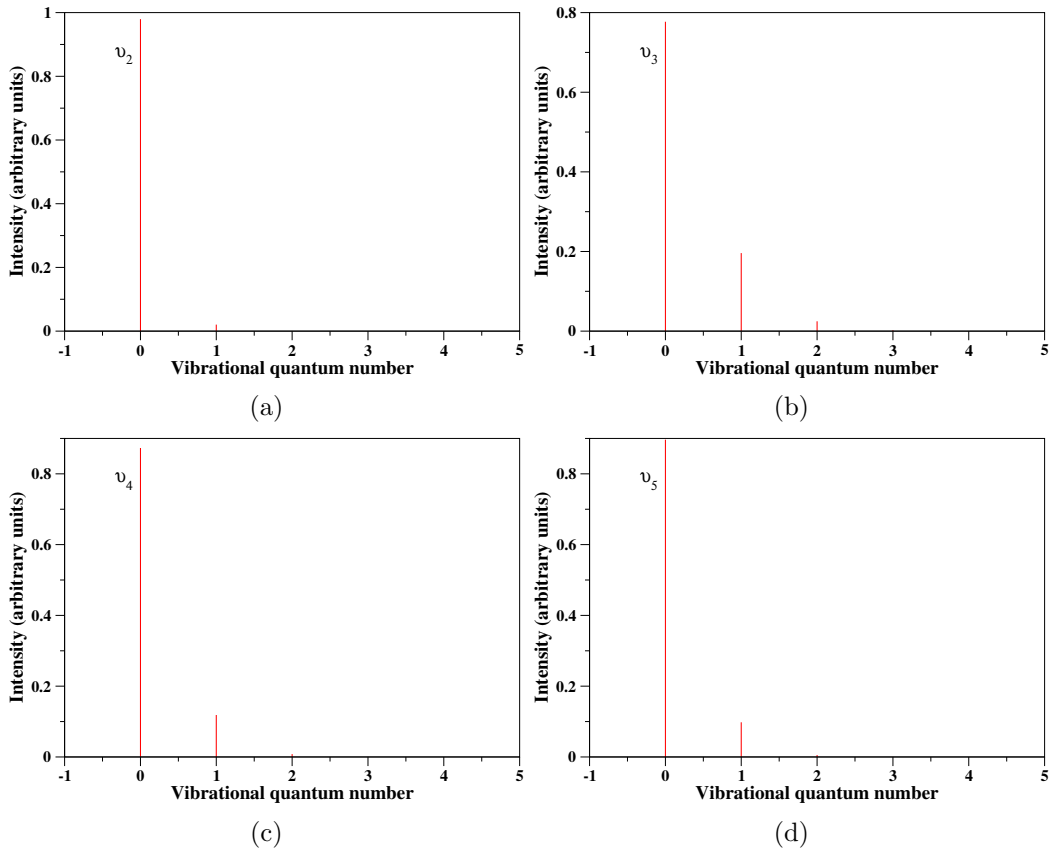


Figure S6. **Poisson intensity distribution for tuning modes of $\tilde{D}^2B_1$ electronic state of Al_6N along vibrational quantum number.**

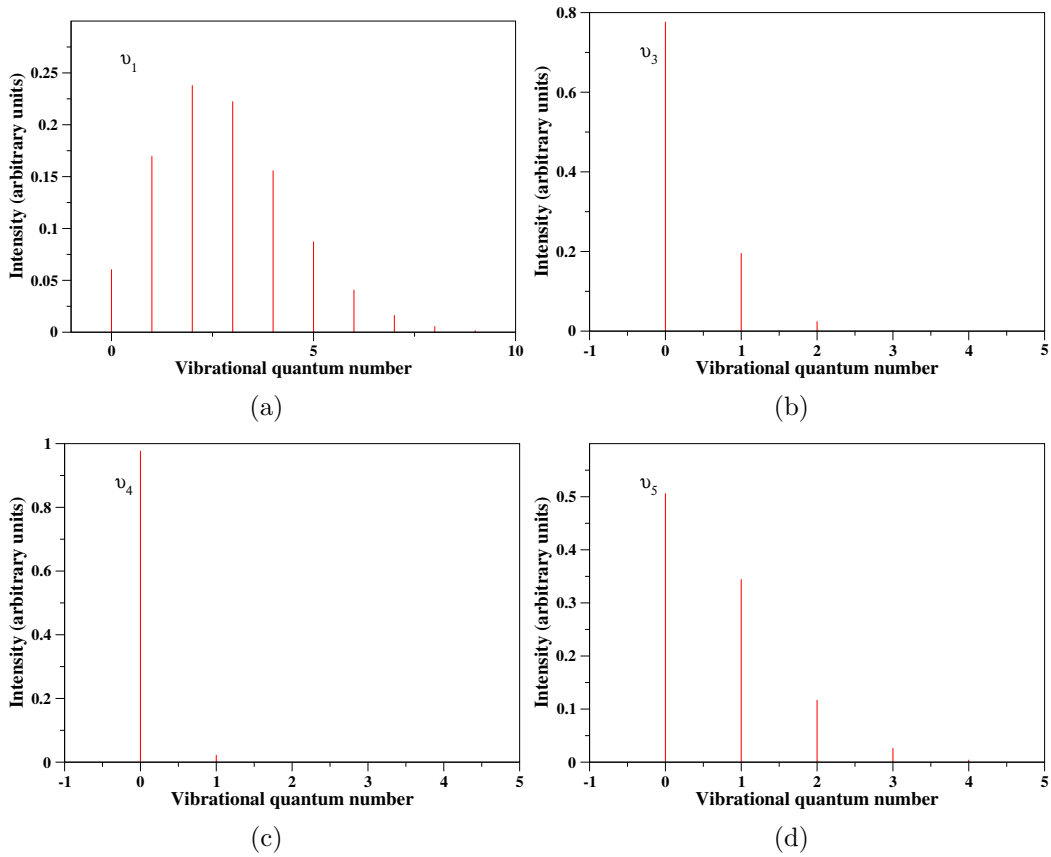


Figure S7. **Poisson intensity distribution for tuning modes of $\tilde{E}^2A_1$ electronic state of Al_6N along vibrational quantum number.**

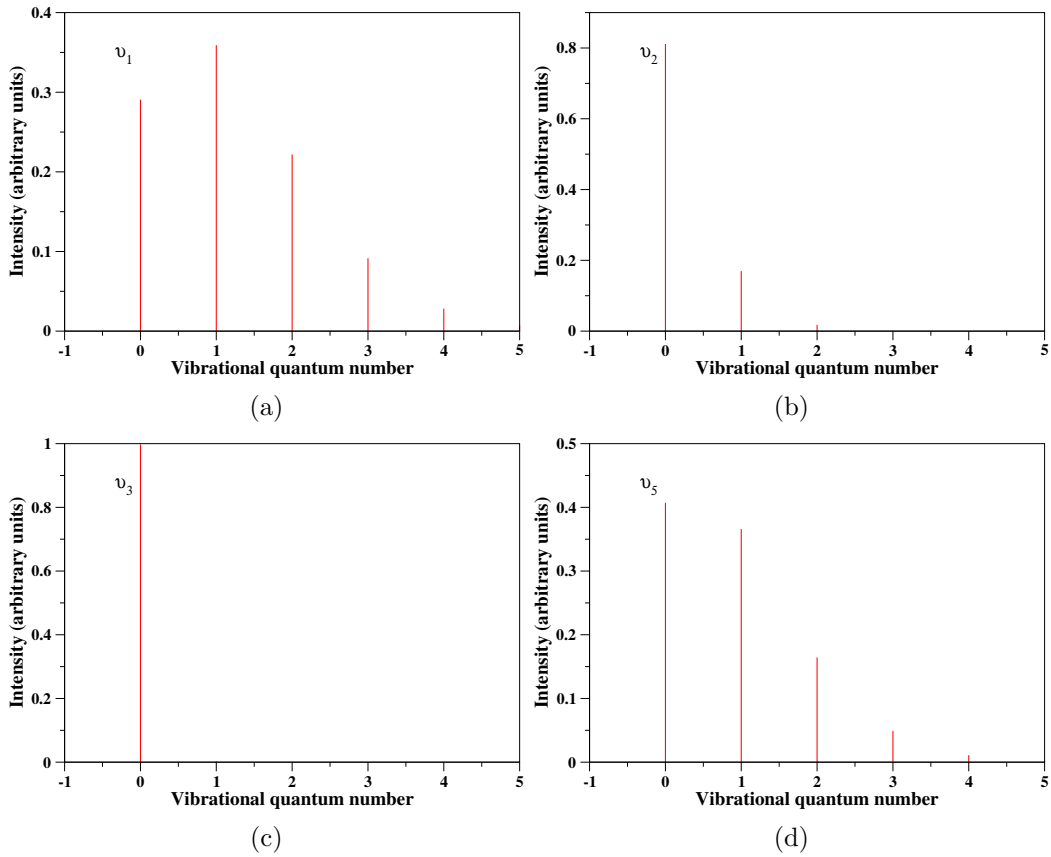
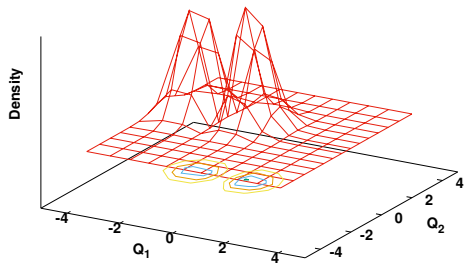
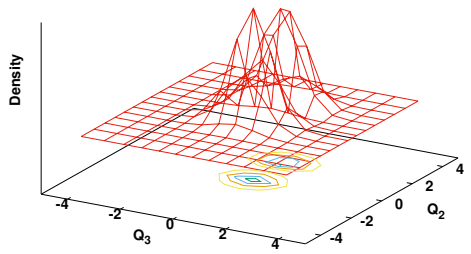


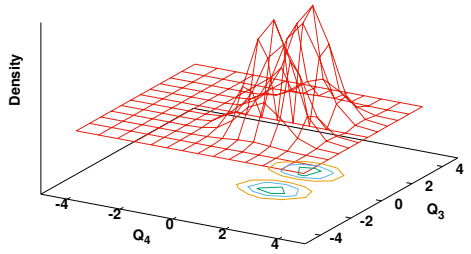
Figure S8. **Poisson intensity distribution for tuning modes of $\tilde{F}^2B_2$ electronic state of Al_6N along vibrational quantum number.**



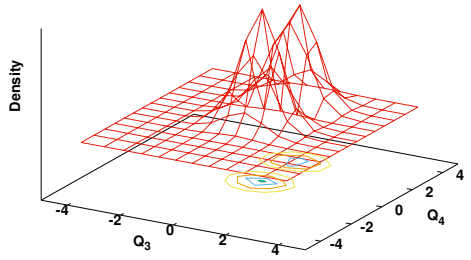
(a)280 cm^{-1}



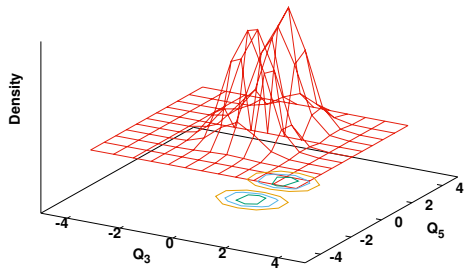
(b)352 cm^{-1}



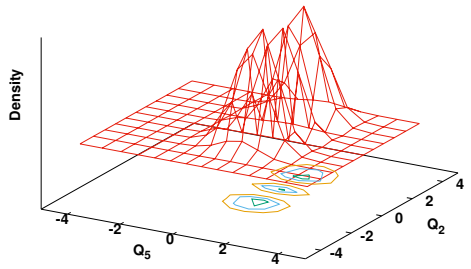
(c)542 cm^{-1}



(d)547 cm^{-1}

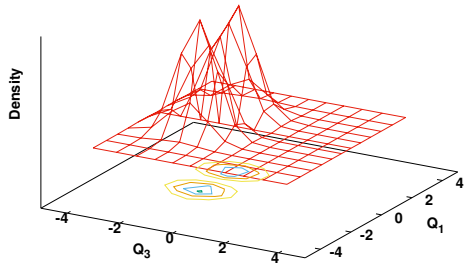


(e)633 cm^{-1}

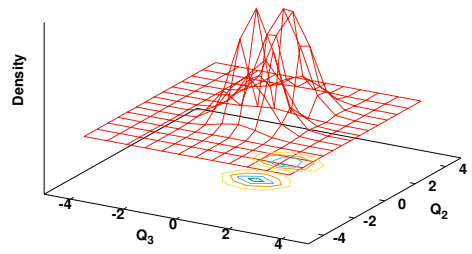


(f)716 cm^{-1}

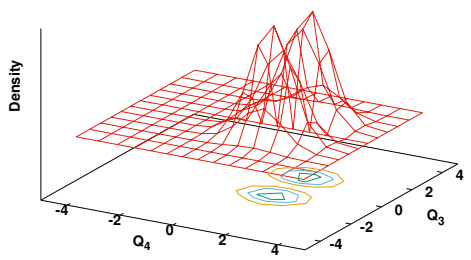
Figure S9. **WP density plot for assignment of fundamental and first overtone of corresponding tuning modes for ground electronic state $\tilde{A}$.**



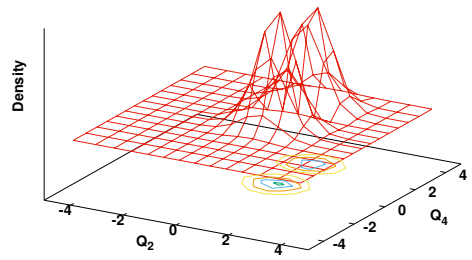
(a)261 cm^{-1}



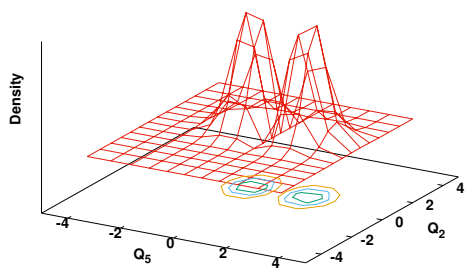
(b)683 cm^{-1}



(c)808 cm^{-1}

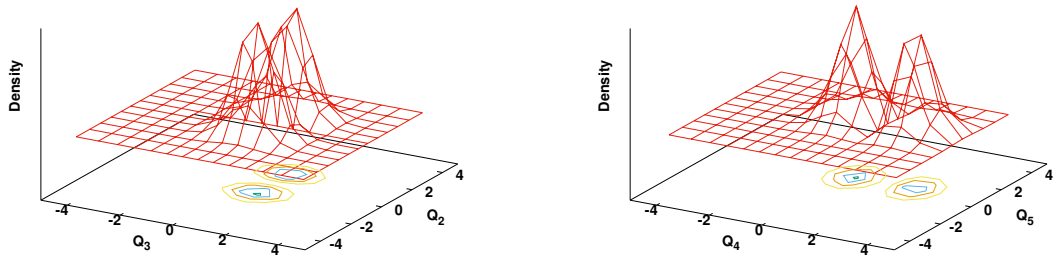


(d)915 cm^{-1}



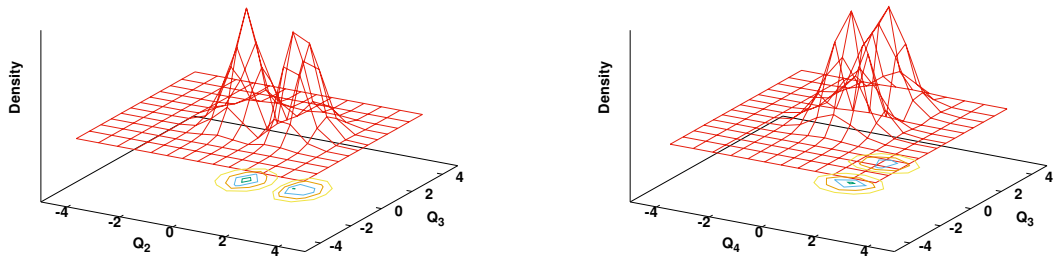
(e)924 cm^{-1}

Figure S10. **WP density plot for assignment of fundamental bands of corresponding tuning modes for $\tilde{B}$ state.**



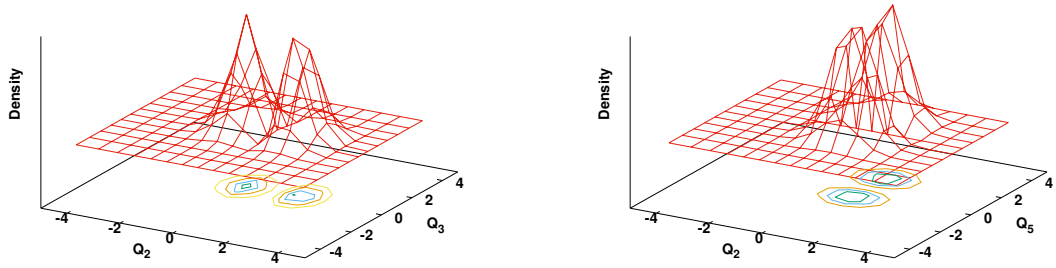
(a)551 cm^{-1} (b)693 cm^{-1}

Figure S11. **WP density plot for assignment of fundamental bands of corresponding tuning modes for $\tilde{C}$ state.**



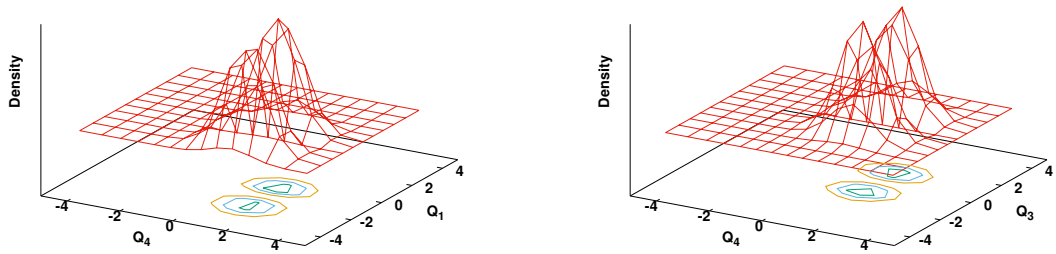
(a)473 cm^{-1} (b)547 cm^{-1}

Figure S12. **WP density plot for assignment of fundamental bands of corresponding tuning modes for $\tilde{D}$ state.**

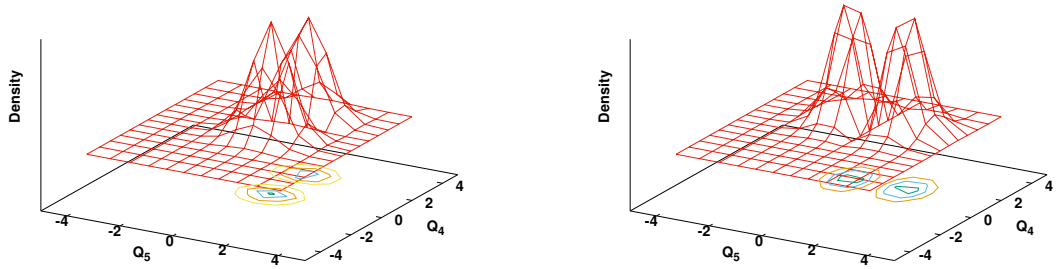


(a)545 cm^{-1} (b)984 cm^{-1}

Figure S13. **WP density plot for assignment of fundamental bands of corresponding tuning modes for $\tilde{E}$ state.**



(a)208 cm^{-1} (b)358 cm^{-1}



(c)488 cm^{-1} (d)538 cm^{-1}

Figure S14. **WP density plot for assignment of fundamental bands of corresponding tuning modes for $\tilde{F}$ state.**

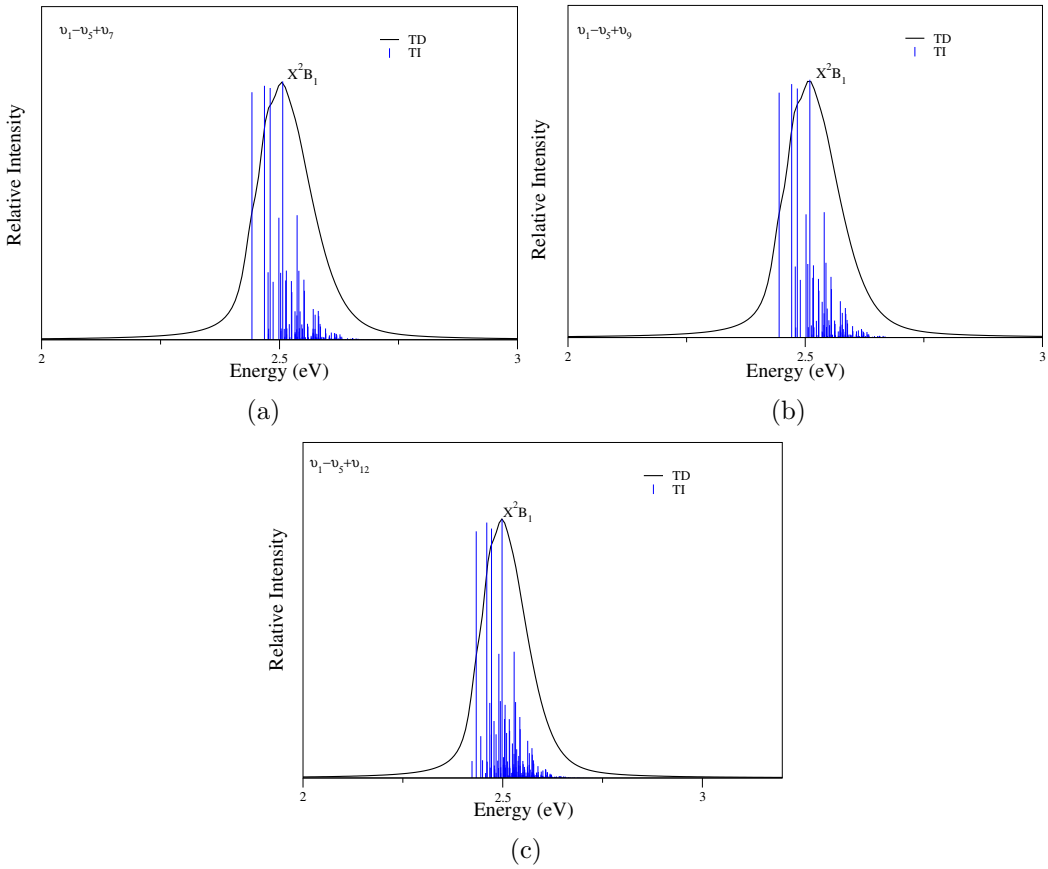


Figure S15. **Comparison of TD and TI spectra for $\tilde{X}^2B_1$ electronic state including ν_6, ν_7, ν_9 and ν_{12} vibrational modes along with totally symmetric vibrational modes for Al_6N.**

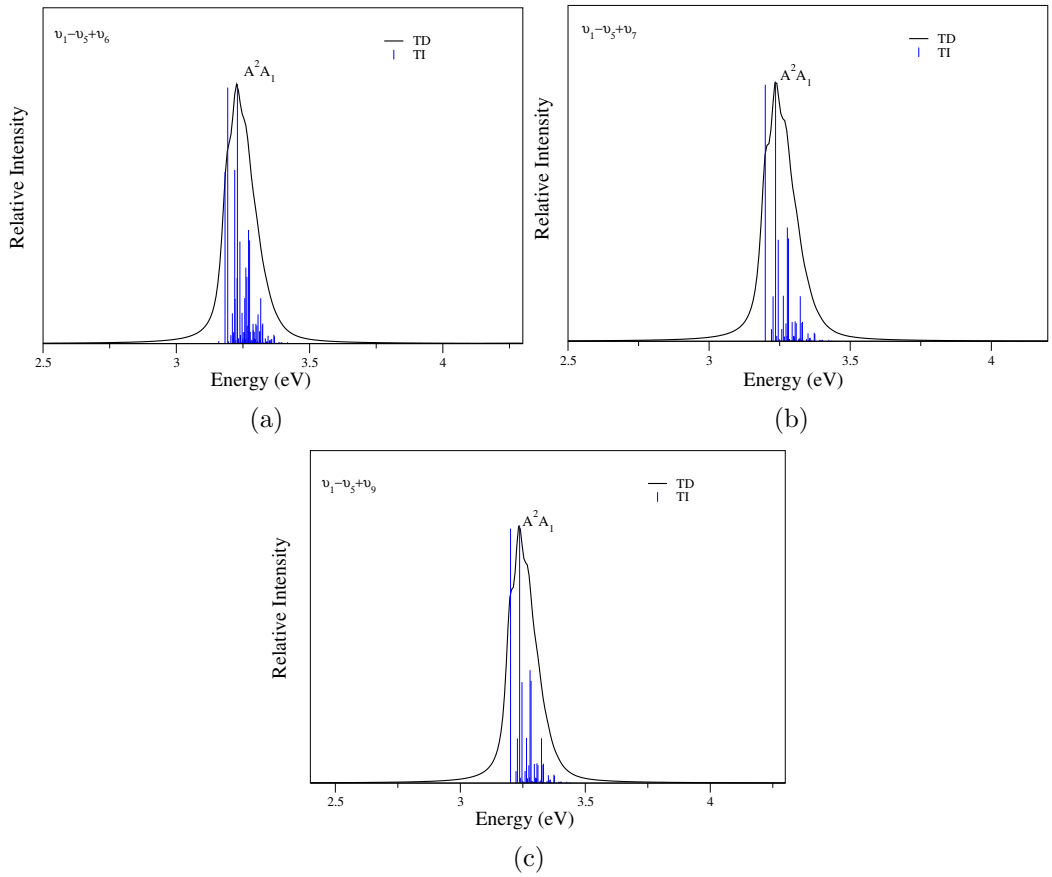


Figure S16. **Comparison of TD and TI spectra for $\tilde{A}^2A_1$ electronic state including ν_6, ν_7 and ν_9 vibrational mode along with totally symmetric vibrational modes for Al_6N.**

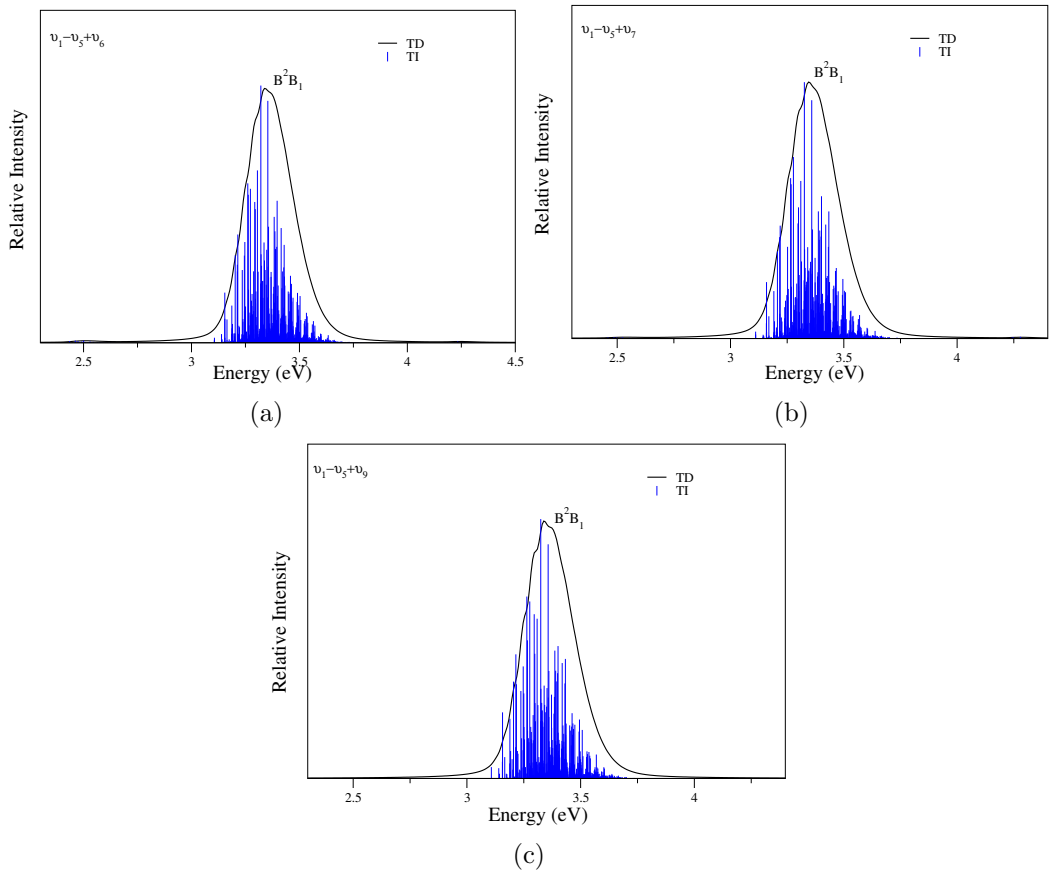


Figure S17. **Comparison of TD and TI spectra for $\tilde{B}^2B_2$ electronic state including ν_6, ν_7 and ν_9 vibrational mode along with totally symmetric vibrational modes for Al_6N.**

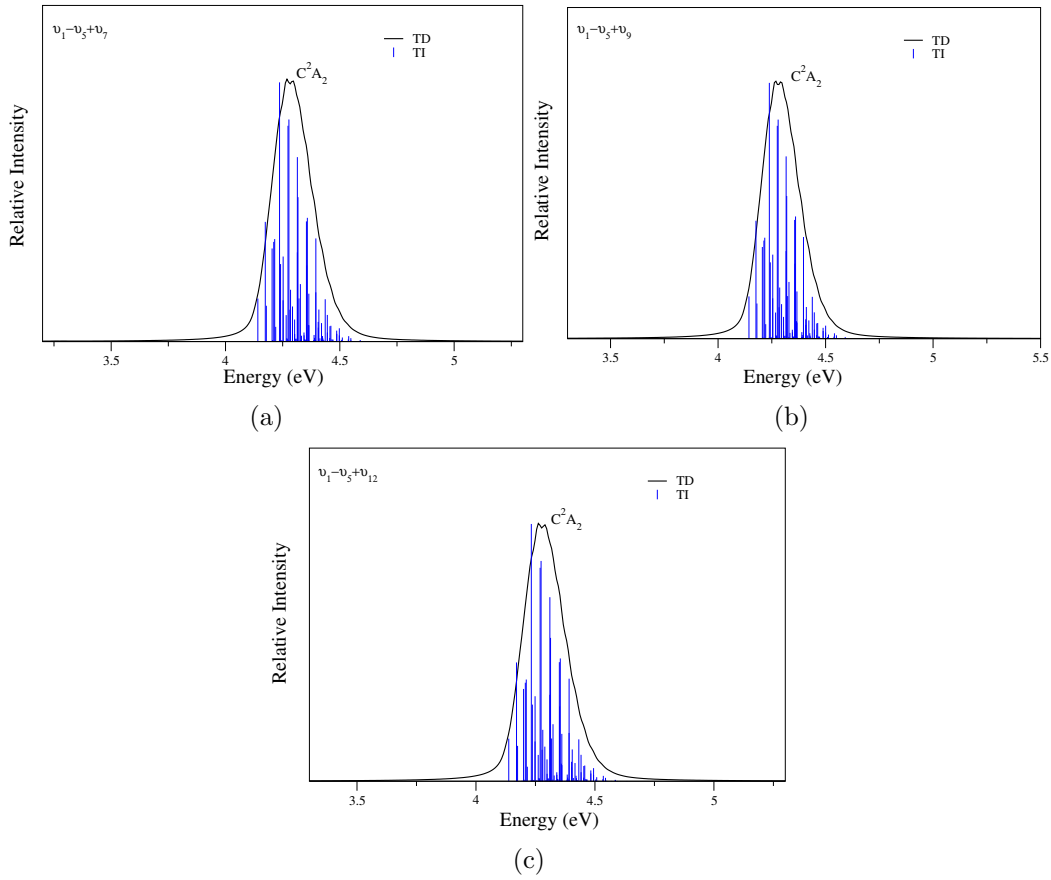


Figure S18. **Comparison of TD and TI spectra for $\tilde{C}^2A_2$ electronic state including ν_6, ν_7, ν_9 and ν_{12} vibrational mode along with totally symmetric vibrational modes for Al_6N.**

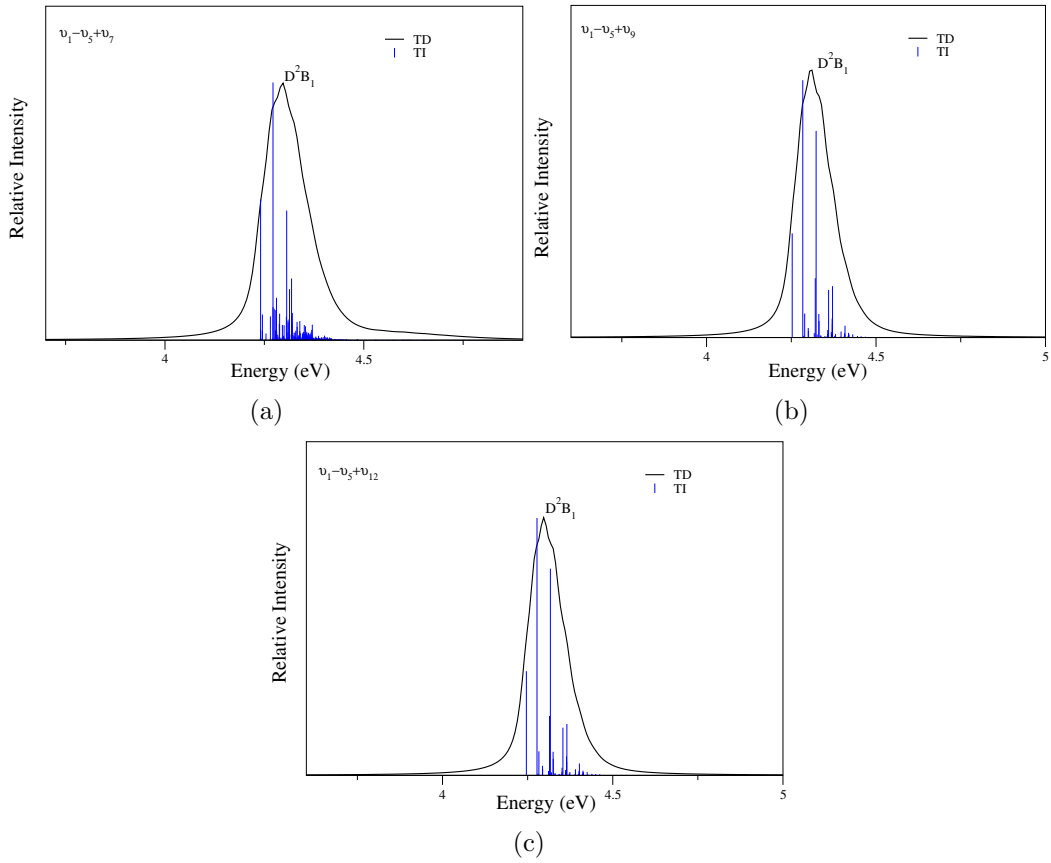


Figure S19. **Comparison of TD and TI spectra for $\tilde{D}^2B_1$ electronic state including ν_9 and ν_{12} vibrational mode along with totally symmetric vibrational modes for Al_6N.**

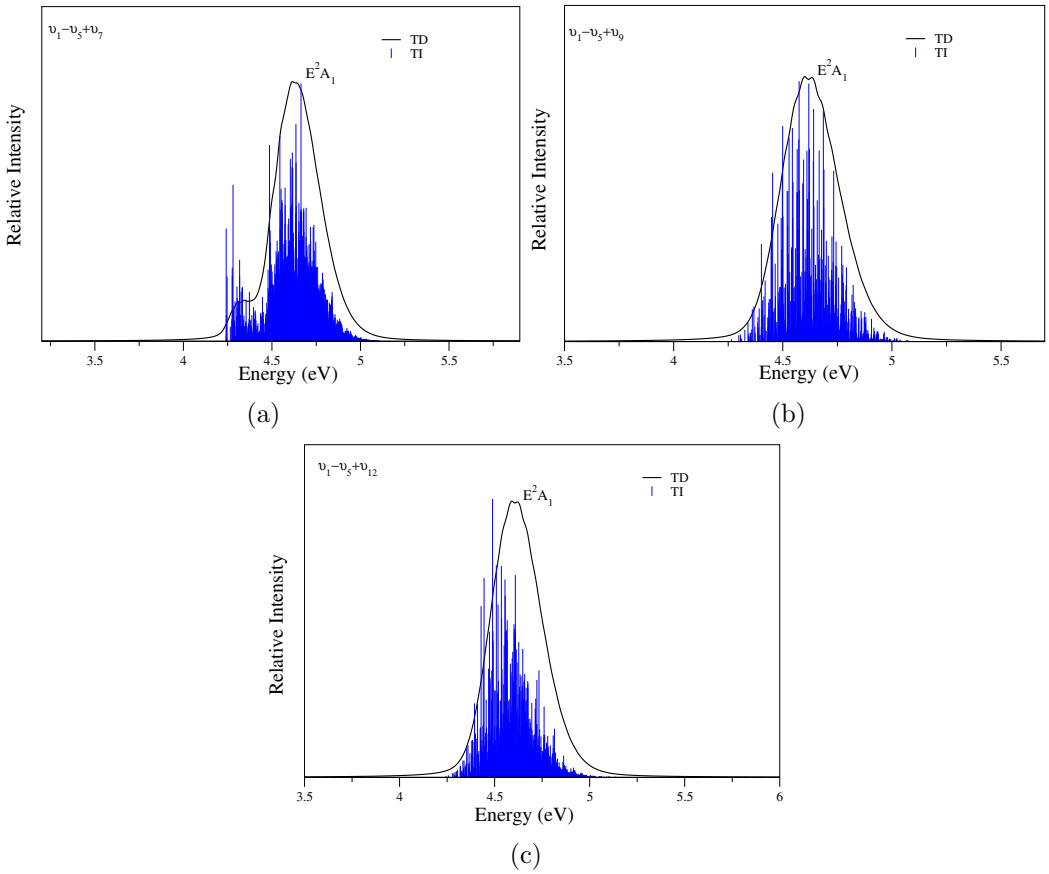


Figure S20. **Comparison of TD and TI spectra for $\tilde{E}^2A_1$ electronic state including ν_9 and ν_{12} vibrational mode along with totally symmetric vibrational modes for Al_6N.**

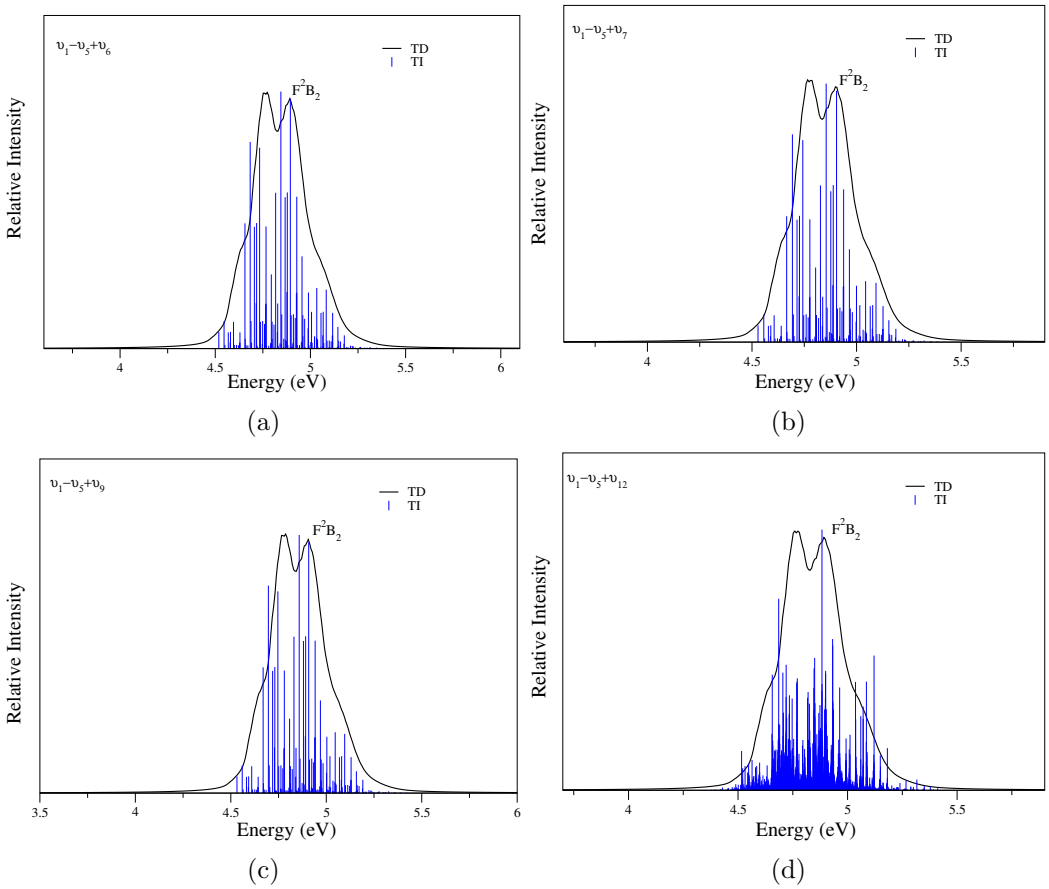


Figure S21. **Comparison of TD and TI spectra for $\tilde{F}^2B_2$ electronic state including ν_6, ν_7, ν_9 and ν_{12} vibrational mode along with totally symmetric vibrational modes for Al_6N.**