

# 1 Supplementary Materials

Table S1: Harmonic Frequencies at Ground and Excited State Minima. Frequencies in  $\text{cm}^{-1}$  and quasi- $D_{3h}$  symmetry labels are employed, although the actual symmetry of  $S_0$ ,  $S_1$ , and the Jahn-Teller distorted  $S_2$  minima are  $D_3$ ,  $C_3$ , and  $C_{2v}$ , respectively. The splitting of non-degenerate components for  $S_2$  state minimum are shown in final column.

Mode	$R_{min}[S_0]$	$R_{min}[S_1]$	$R_{min}[S_{2x}]$	
$\omega_1(a_1)$	3218	3239	3203	
$\omega_2(a_1)$	1615	1639	1643	
$\omega_3(a_1)$	1474	1386	1409	
$\omega_4(a_1)$	1059	1017	970	
$\omega_5(a_1)$	873	864	854	
$\omega_6(a_1)$	634	767	731	
$\omega_7(a_2)$	3270	3313	3283	
$\omega_8(a_2)$	1258	1251	1255	
$\omega_9(a_2)$	858	871	871	
$\omega_{10}(a_1)$	3249	3297	3269	
$\omega_{11}(a_1)$	1337	1279	1267	
$\omega_{12}(a_1)$	1077	1072	1080	
$\omega_{13}(a_1)$	112	84	70	
$\omega_{14}(a_2)$	3199	3222	3199	
$\omega_{15}(a_2)$	1595	1612	1708	
$\omega_{16}(a_2)$	1476	1454	1552	
$\omega_{17}(a_2)$	1054	908	1316	
$\omega_{18}(a_2)$	829	555	911	
$\omega_{19}(e')$	3279	3307	3296 3287	9
$\omega_{20}(e')$	3208	3224	3199 3189	10
$\omega_{21}(e')$	1598	1601	1601 1491	110
$\omega_{22}(e')$	1452	1462	1467 160	1307
$\omega_{23}(e')$	1418	1338	1363 1322	41
$\omega_{24}(e')$	1191	1116	1126 1105	21
$\omega_{25}(e')$	973	910	941 921	20
$\omega_{26}(e')$	883	843	778 771	7
$\omega_{27}(e')$	448	473	653 479	174
$\omega_{28}(e'')$	3252	3296	3278 3275	3
$\omega_{29}(e'')$	3195	3219	3189 3189	0
$\omega_{30}(e'')$	1582	1585	1584 1582	2
$\omega_{31}(e'')$	1437	1447	1465 1464	1
$\omega_{32}(e'')$	1388	1374	1382 1382	0
$\omega_{33}(e'')$	1287	1245	1237 1236	1
$\omega_{34}(e'')$	1123	1139	1152 1149	3
$\omega_{35}(e'')$	620	2 577	585 585	0
$\omega_{36}(e'')$	339	358	380 379	1

Table S2: Minimum Energy Cartesian Geometry of  $X^1A'_1$  State

N	1.27919980	0.00101494	0.00001575
N	-1.27919980	-0.00101494	0.00001575
C	0.77587276	0.05426160	1.37052511
C	-0.77587276	-0.05426160	1.37052511
C	0.77500100	1.16070239	-0.73167683
C	-0.77500100	-1.16070239	-0.73167683
C	0.77688035	-1.21308940	-0.63880350
C	-0.77688035	1.21308940	-0.63880350
H	1.10565679	0.99445028	1.81427108
H	-1.10565679	-0.99445028	1.81427108
H	1.10562565	1.07533973	-1.76754690
H	-1.10562565	-1.07533973	-1.76754690
H	1.10811759	-2.06710030	-0.04671220
H	-1.10811759	2.06710030	-0.04671220
H	1.23175486	-0.75563208	1.94138849
H	-1.23175486	0.75563208	1.94138849
H	1.22950611	2.06056062	-0.31536245
H	-1.22950611	-2.06056062	-0.31536245
H	1.23217238	-1.30193567	-1.62594762
H	-1.23217238	1.30193567	-1.62594762

Table S3: Minimum Energy Cartesian Geometry of  $A^1A'_1$  State

N	0.00286784	1.25000571	0.00041973
N	0.00468498	-1.20319066	-0.00074895
C	1.36553627	0.78992782	-0.05025603
C	1.38385439	-0.81592717	0.05091969
C	-0.63426444	0.78783763	1.20523597
C	-0.72164122	0.78890007	-1.15439434
C	-0.72991362	-0.81802892	1.16833678
C	-0.64074746	-0.81682165	-1.22094957
H	1.93523052	1.19787238	0.77929055
H	1.82549945	1.09596475	-0.98488806
H	1.82363446	-1.14399428	0.98666002
H	1.92648307	-1.24679209	-0.78398099
H	-1.63780437	1.19497677	1.28437270
H	-1.76149767	1.09336879	-1.08540921
H	-0.05505102	1.09311156	2.07130875
H	-0.28868367	1.19756715	-2.06250093
H	-1.75994932	-1.14669908	1.08088583
H	-1.63445136	-1.24919353	-1.27345497
H	-0.27788019	-1.24978522	2.05512932
H	-0.04977264	-1.14394511	-2.06970403

Table S4: Minimum Energy Cartesian Geometry of  $B^1A_1$  State

N	0.00280783	1.20923810	0.00000000
N	0.00189554	-1.23840208	0.00000000
C	1.36913484	0.79636144	0.00000000
C	1.36852905	-0.82653706	0.00000000
C	-0.68340299	0.79704399	1.18268417
C	-0.68340299	0.79704399	-1.18268417
C	-0.68400334	-0.82568591	1.18268528
C	-0.68400334	-0.82568591	-1.18268528
H	1.88047221	1.15530396	0.88751077
H	1.88047221	1.15530396	-0.88751077
H	1.87957299	-1.18589922	0.88750595
H	1.87957299	-1.18589922	-0.88750595
H	-1.70913204	1.15186790	1.17479626
H	-1.70913204	1.15186790	-1.17479626
H	-0.16569776	1.15716141	2.06666054
H	-0.16569776	1.15716141	-2.06666054
H	-1.70998351	-1.17978385	1.17477945
H	-1.70998351	-1.17978385	-1.17477945
H	-0.16654333	-1.18622763	2.06663756
H	-0.16654333	-1.18622763	-2.06663756

Table S5: Minimum Energy Cartesian Geometry of  $D^1A_2'$  State

N	0.00286851	2.28138326	0.00000000
N	0.00102603	-2.33687317	0.00000000
C	2.58526738	1.50554054	0.00000000
C	2.58404444	-1.56308040	0.00000000
C	-1.28879483	1.50708576	2.23669100
C	-1.28879483	1.50708576	-2.23669100
C	-1.29001955	-1.56153524	2.23669190
C	-1.29001955	-1.56153524	-2.23669190
H	3.54051384	2.20027018	1.67794218
H	3.54051384	2.20027018	-1.67794218
H	3.53873180	-2.25857912	1.67793971
H	3.53873180	-2.25857912	-1.67793971
H	-3.21914123	2.20296851	2.22474613
H	-3.21914123	2.20296851	-2.22474613
H	-0.31286522	2.20180991	3.90268795
H	-0.31286522	2.20180991	-3.90268795
H	-3.22092047	-2.25588000	2.22474348
H	-3.22092047	-2.25588000	-2.22474348
H	-0.31464125	-2.25704049	3.90268746
H	-0.31464125	-2.25704049	-3.90268746

Table S6: Minimum Energy Jahn-Teller point on  $B^1E''$  State

N	0.00147488	1.20922502	0.00000000
N	0.00054162	-1.23843121	0.00000000
C	1.36830289	0.79631855	0.00000000
C	1.36769372	-0.82648516	0.00000000
C	-0.68217527	0.79710019	1.18384401
C	-0.68217527	0.79710019	-1.18384401
C	-0.68279871	-0.82570309	1.18385234
C	-0.68279871	-0.82570309	-1.18385234
H	1.87659893	1.15393380	0.89001287
H	1.87659893	1.15393380	-0.89001287
H	1.87554433	-1.18469966	0.89002761
H	1.87554433	-1.18469966	-0.89002761
H	-1.70689218	1.15530045	1.17891660
H	-1.70689218	1.15530045	-1.17891660
H	-0.16534528	1.15471271	2.06892962
H	-0.16534528	1.15471271	-2.06892962
H	-1.70771505	-1.18333374	1.17876829
H	-1.70771505	-1.18333374	-1.17876829
H	-0.16614248	-1.18392145	2.06879584
H	-0.16614248	-1.18392145	-2.06879584

Table S7: Minimum Energy Conical Intersection  $A^1A_1B^1A_1$  States

N	0.01757475	1.07095920	0.00000000
N	0.01770018	-1.09563176	0.00000000
C	1.31718418	0.83631810	0.00000000
C	1.31756746	-0.86022118	0.00000000
C	-0.68340801	0.83630271	1.13468792
C	-0.68340801	0.83630271	-1.13468792
C	-0.68331139	-0.86114073	1.13459827
C	-0.68331139	-0.86114073	-1.13459827
H	1.88092527	1.04925588	0.93875081
H	1.88092527	1.04925588	-0.93875081
H	1.88154828	-1.07288735	0.93870308
H	1.88154828	-1.07288735	-0.93870308
H	-1.78033490	1.02943059	1.09805894
H	-1.78033490	1.02943059	-1.09805894
H	-0.06942159	1.05579975	2.03713439
H	-0.06942159	1.05579975	-2.03713439
H	-1.78021272	-1.05443416	1.09797255
H	-1.78021272	-1.05443416	-1.09797255
H	-0.06951914	-1.08069477	2.03717107
H	-0.06951914	-1.08069477	-2.03717107

Table S8: Minimum Energy Conical Intersection  $A^1A_1C^1B_2$  States

N	-0.00769885	1.06548128	0.00000000
N	-0.00822547	-1.09468705	0.00000000
C	1.32596016	0.84587925	0.00000000
C	1.32523551	-0.87635494	0.00000000
C	-0.63361571	0.83759130	1.15108805
C	-0.63361571	0.83759130	-1.15108805
C	-0.63416472	-0.86615104	1.15117833
C	-0.63416472	-0.86615104	-1.15117833
H	1.80330146	1.02958512	0.98845906
H	1.80330146	1.02958512	-0.98845906
H	1.80241431	-1.06050682	0.98846190
H	1.80241431	-1.06050682	-0.98846190
H	-1.72556304	1.07107253	1.12169760
H	-1.72556304	1.07107253	-1.12169760
H	-0.09535059	1.03035591	2.10773497
H	-0.09535059	1.03035591	-2.10773497
H	-1.72625598	-1.09897525	1.12174340
H	-1.72625598	-1.09897525	-1.12174340
H	-0.09609603	-1.05917594	2.10786117
H	-0.09609603	-1.05917594	-2.10786117