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SUPPORTING INFORMATION

1. CASSCF and CASPT2 active spaces

CASSCF and CASPT2 calculations require the specification of (n_e, n_a) where n_e is the number of active electrons distributed in n_a active orbitals. We evaluate vertical excitation energies using the small active space, (10,12), in which all π and lone-pair electrons are active. For irreducible representations of [a_1, b_1, b_2, a_2] symmetry, this involves [4,0,2,0] frozen core orbitals, [6,0,4,0] inactive doubly occupied orbitals, and [5,4,1,2] active orbitals. Using this active space, the reference weight is too low for reliable CASPT2 calculations for $(2)^1A_2$, $(3)^1A_1$, and $(2)^1B_2$ and hence results for these are not included. For normal-mode analysis of the $^1B_1$ and $^3B_1$ states, the smallest active space which provides a continuous potential-energy surface as a function of an arbitrary nuclear displacement is (18,16). As this is prohibitively large, we employ different active spaces for each type of asymmetric displacement, evaluating the Hessian matrix numerically. For b_1, b_2, and a_2 modes, the active spaces are (18,15), (18,12), and (18,13), respectively. For irreducible representations of [symmetric, antisymmetric] symmetry, these calculations require core and inactive of [4,2], [6,0], and [4,2], and active spaces of [10,5], [6,6], and [5,8], respectively. Unfortunately, these calculations for the b_1 modes are still prohibitive and hence we report vibration frequencies for the a_2 and b_2 modes only.

2. Geometrical properties calculated for the ground and excited states of pyrimidine, as well as some approximate structures for transition states and conical intersections.

Calc		N-C_1	N-C_2	C_2-C_3	N-C_1-N	C_1-N-C_2	N-C_2-C_3	C_3-C_4-C_3	θ	φ
$^1A_1$	CCSD C_{2v}	1.345	1.345	1.401	128	115	123	116	0	0
$^1B_1$	EOM-CCSD C_{2v}	1.326	1.395	1.402	118	123	119	118	0	0
$^1A_2$	EOM-CCSD C_{2v}	1.382	1.304	1.436	112	126	123	111	0	0
$^1A_2$	EOM-CCSD C_s	1.389	1.305	1.432	111	126	123	111	9	2
$^1B_2$	EOM-CCSD C_{2v}	1.377	1.380	1.439	130	115	121	118	0	0
2^1A_2	EOM-CCSD C_{2v}	1.308	1.420	1.399	132	117	115	127	0	0
2^1B_1	EOM-CCSD C_{2v}	1.368	1.317	1.438	123	121	118	121	0	0
2^1B_1	EOM-CCSD C_s	1.369	1.332	1.442	122	116	119	117	32	9
2^1A_1	EOM-CCSD C_{2v}	1.419	1.309	1.468	130	113	124	116	0	0
2^1B_2	EOM-CCSD C_{2v}	1.389	1.370	1.442	127	115	124	115	0	0
$^3B_1$	EOM-CCSD C_{2v}	1.328	1.394	1.401	119	123	118	118	0	0
$^3B_1$	EOM-CCSD C_s	1.334	1.404	1.401	120	121	119	118	15	4
$(\alpha)^3A_1$	EOM-CCSD C_{2v}	1.421	1.301	1.484	127	116	122	116	0	0
$(\alpha)^3A_1$	EOM-CCSD C_s	1.420	1.299	1.485	124	114	121	114	28	21
$(\beta)^3A_1$	EOM-CCSD C_{2v}	1.352	1.452	1.406	129	115	121	119	0	0
$^3A_2$	EOM-CCSD C_{2v}	1.388	1.306	1.429	112	125	123	112	0	0
$^3A_2$	EOM-CCSD C_s	1.399	1.308	1.424	110	126	123	112	11	1
$^3B_2$	EOM-CCSD C_{2v}	1.364	1.383	1.436	132	114	120	120	0	0
$(\alpha)^3A_1$-$^3B_1$ CI	EOM-CCSD C_{2v}	1.374	1.347	1.442	123	120	120	117	0	0
$(\beta)^3A_1$-$^3B_1$ CI	EOM-CCSD C_{2v}	1.349	1.446	1.405	128	116	121	119	0	0
$(\alpha)^3A_1$-$^3B_1$ TS	EOM-CCSD C_s	1.370	1.356	1.430	122	118	120	117	21	8
$(\alpha)^3A_1$-$(\beta)^3A_1$ TS	EOM-CCSD C_{2v}	1.373	1.407	1.429	128	115	122	118	0	0
$^3B_1$-$^3A_2$ CI	EOM-CCSD C_{2v}	1.372	1.329	1.421	114	125	121	114	0	0
$(\alpha)^3A_1$-$^3A_2$ CI	EOM-CCSD C_{2v}	1.395	1.305	1.444	116	123	122	113	0	0

$(\beta)^3A_1$-$^3A_2$ CI	EOM-CCSD	C_{2v}	1.373	1.356	1.420	118	122	122	114	0	0
$^1A_1$	MP2	C_{2v}	1.347	1.348	1.401	128	115	122	117	0	0
$^1B_1$	CASPT2	C_{2v}	1.331	1.400	1.404	119	123	119	118	0	0
$^1B_1$	CASPT2	C_{2v}	1.331	1.400	1.404	119	123	119	118	0	0
$^3B_1$	CASPT2	C_{2v}	1.334	1.396	1.403	119	123	119	118	0	0
$^3B_1$	CASPT2	C_{2v}	1.334	1.396	1.403	119	123	119	118	0	0
$^1A_1$	B3LYP	C_{2v}	1.339	1.340	1.395	128	116	122	117	0	0
$^1B_1$	TD-B3LYP	C_{2v}	1.322	1.390	1.394	118	123	119	118	0	0
$^3B_1$	B3LYP	C_{2v}	1.322	1.392	1.394	118	123	118	118	0	0
$(\alpha)^3A_1$	B3LYP	C_{2v}	1.420	1.285	1.486	127	116	123	116	0	0
$(\alpha)^3A_1$	B3LYP	C_s	1.411	1.288	1.482	123	114	121	113	33	22
$(\beta)^3A_1$	B3LYP	C_{2v}	1.334	1.482	1.384	129	115	121	119	0	0
$^3A_2$	B3LYP	C_{2v}	1.384	1.297	1.429	112	126	123	112	0	0
$^3A_2$	B3LYP	C_s	1.395	1.299	1.423	110	126	123	112	10	1
$^3B_2$	B3LYP	C_{2v}	1.357	1.378	1.433	132	114	120	120	0	0
$(2)^3A_2$	B3LYP	C_{2v}	1.301	1.419	1.390	132	116	115	127	0	0
$(2)^3B_2$	B3LYP	C_{2v}	1.389	1.372	1.417	123	117	124	114	0	0
$(2)^3B_1$	B3LYP	C_{2v}	1.365	1.309	1.432	123	121	118	121	0	0
$^1A_1$	CASSCF	C_{2v}	1.337	1.332	1.392	127	116	122	117	0	0
$^1B_1$	CASSCF	C_{2v}	1.310	1.403	1.390	119	123	118	118	0	0
$^1B_1$	CASSCF	C_{2v}	1.316	1.396	1.392	118	124	118	118	0	0
$^1A_2$	CASSCF	C_{2v}	1.389	1.299	1.411	112	125	123	113	0	0
$^1B_2$	CASSCF	C_{2v}	1.375	1.373	1.434	128	116	121	118	0	0
2^1A_2	CASSCF	C_{2v}	1.275	1.427	1.389	134	115	115	126	0	0
2^1B_1	CASSCF	C_{2v}	1.346	1.305	1.429	122	122	117	120	0	0
2^1A_1	CASSCF	C_{2v}	1.452	1.293	1.473	131	112	124	117	0	0
3^1A_1	CASSCF	C_{2v}	1.362	1.371	1.436	127	117	121	117	0	0

$^3B_1$	CASSCF	C_{2v}	1.311	1.395	1.390	119	123	118	118	0	0
$(\alpha)^3A_1$	CASSCF	C_{2v}	1.413	1.287	1.476	126	117	122	116	0	0
$(a)^3A_1$	CASSCF	C_s	1.410	1.288	1.474	124	116	121	115	23	17
$(\beta)^3A_1$	CASSCF	C_{2v}	1.335	1.446	1.396	128	116	121	119	0	0
$^3A_2$	CASSCF	C_{2v}	1.392	1.302	1.402	112	125	123	114	0	0
$^3B_2$	CASSCF	C_{2v}	1.359	1.371	1.429	130	115	120	120	0	0
2^3A_2	CASSCF	C_{2v}	1.279	1.423	1.388	134	116	115	126	0	0
2^3B_1	CASSCF	C_{2v}	1.350	1.304	1.424	122	121	117	121	0	0
$^1A_1$	SCF	C_{2v}	1.319	1.321	1.382	127	116	122	116	0	0
$^1B_1$	CIS	C_{2v}	1.306	1.363	1.383	116	125	118	118	0	0
$^1A_2$	CIS	C_{2v}	1.368	1.276	1.411	111	126	122	112	0	0
$^1A_2$	CIS	C_s	1.377	1.280	1.406	110	126	122	112	12	1
$^1B_2$	CIS	C_{2v}	1.343	1.348	1.417	129	116	121	118	0	0
2^1A_2	CIS	C_{2v}	1.297	1.349	1.409	125	120	117	121	0	0
2^1B_1	CIS	C_{2v}	1.329	1.292	1.424	124	121	117	121	0	0
2^1A_1	CIS	C_{2v}	1.377	1.290	1.452	127	117	121	117	0	0
3^1A_1	CIS	C_{2v}	1.377	1.290	1.452	127	117	121	117	0	0
2^1B_2	CIS	C_{2v}	1.362	1.346	1.417	125	117	123	115	0	0
$^3B_1$	CIS	C_{2v}	1.312	1.363	1.381	117	125	118	119	0	0
$(\alpha)^3A_1$	CIS	C_{2v}	1.388	1.278	1.466	125	118	121	116	0	0
$^3A_2$	CIS	C_{2v}	1.375	1.293	1.395	113	125	121	115	0	0
$^3A_2$	CIS	C_s	1.386	1.296	1.393	110	125	121	114	16	1
$(2)^3A_1$	CIS	C_{2v}	1.339	1.354	1.416	126	118	121	117	0	0
$^3B_2$	CIS	C_{2v}	1.332	1.359	1.414	131	115	120	120	0	0
2^3A_2	CIS	C_{2v}	1.305	1.326	1.425	123	121	118	117	0	0
2^3B_2	CIS	C_{2v}	1.365	1.350	1.396	123	118	124	115	0	0
2^3B_1	CIS	C_{2v}	1.324	1.295	1.425	125	120	117	120	0	0

3: RMS deviations from experiment for calculated properties of the ground state $^1A_1$ (S_0) of pyrmidine[a]

Method	Basis Set	R / Å	θ / deg.	Vibrations	
				Scale[c]	ν / cm^{-1}
CCSD	cc-pVDZ	0.013	0.84	0.95	24
CASSCF(8/11)	cc-pVDZ	0.009	0.62	0.91	40
B3LYP	cc-pVDZ	0.011	0.72	0.9614	26
HF	cc-pVDZ	0.013	1.00	0.8935	40
B3LYP[b]	cc-pVTZ	0.008	0.33	0.9614	23

a: Averaged over the six unique bond lengths R, the seven unique bond angles θ, and all 24 vibrational frequencies ν; full details are given in the Supporting Information.

b: From ref.[59].

c: All vibration frequencies are scaled by this factor[60].

4. Calculated rotational constants A, B, and C, in cm^{-1}, for the S_1 (n,π^*) state of pyrimidine[a]

Method	A	B	C
EOM-CCSD	0.20911	0.19278	0.10031
CASSCF	0.21316	0.19348	0.10142
TD-B3LYP	0.21099	0.19433	0.10116
CASPT2	0.20735	0.19228	0.09976
CIS	0.21720	0.19943	0.10397
Obs.[b]	0.2128 ± 0.001	0.1948 ± 0.001	0.1017 ± 0.001

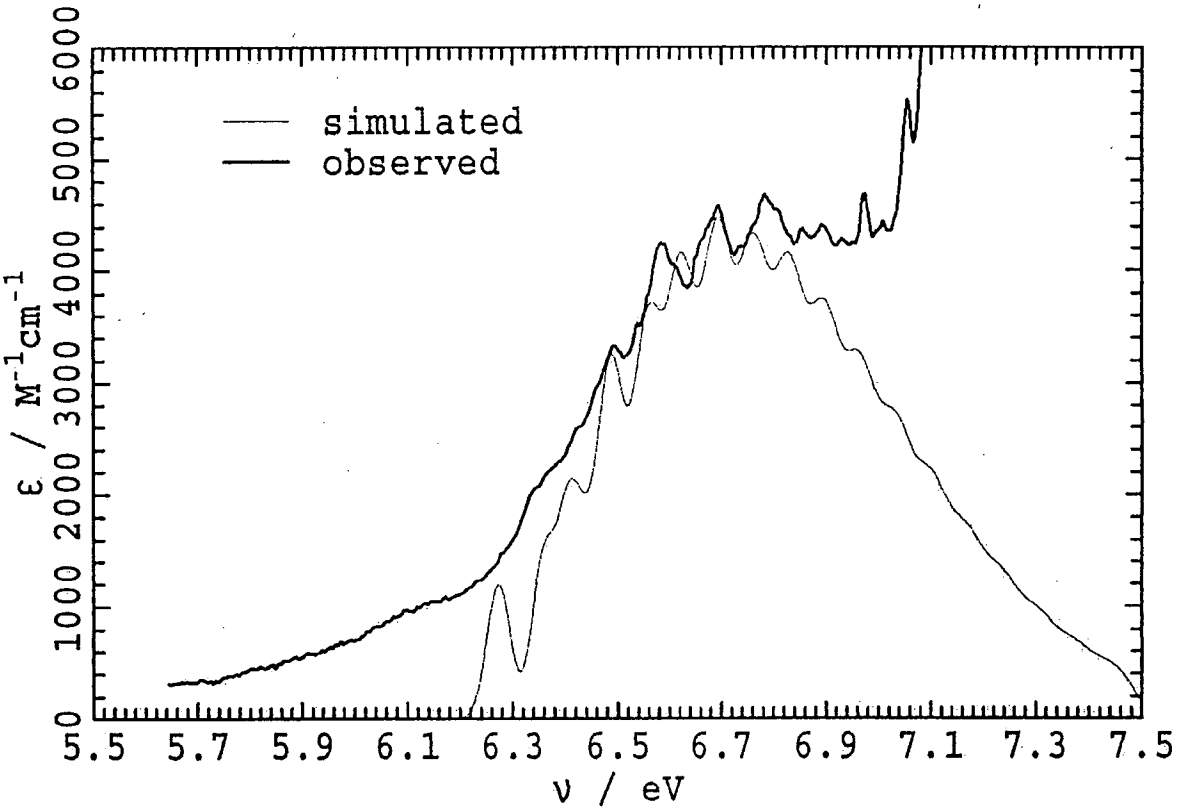
a: All results obtained using the cc-pVDZ basis set at the C_{2v} optimized geometry. *b*: from ref [61].

4b. Calculated rotational constants A, B, and C, in cm^{-1}, for the T_1 (n,π^*) state of pyrimidine[a]

Method	Symmetry	A	B	C
EOM-CCSD	C_{2v}	0.20842	0.19435	0.10033
EOM-CCSD	C_s	0.20649	0.19300	0.10006
CASSCF	C_{2v}	0.21280	0.19490	0.10173
B3LYP	C_{2v}	0.21064	0.19407	0.10101
CASPT2	C_{2v}	0.20688	0.19319	0.09990
CIS	C_{2v}	0.21513	0.20051	0.10376

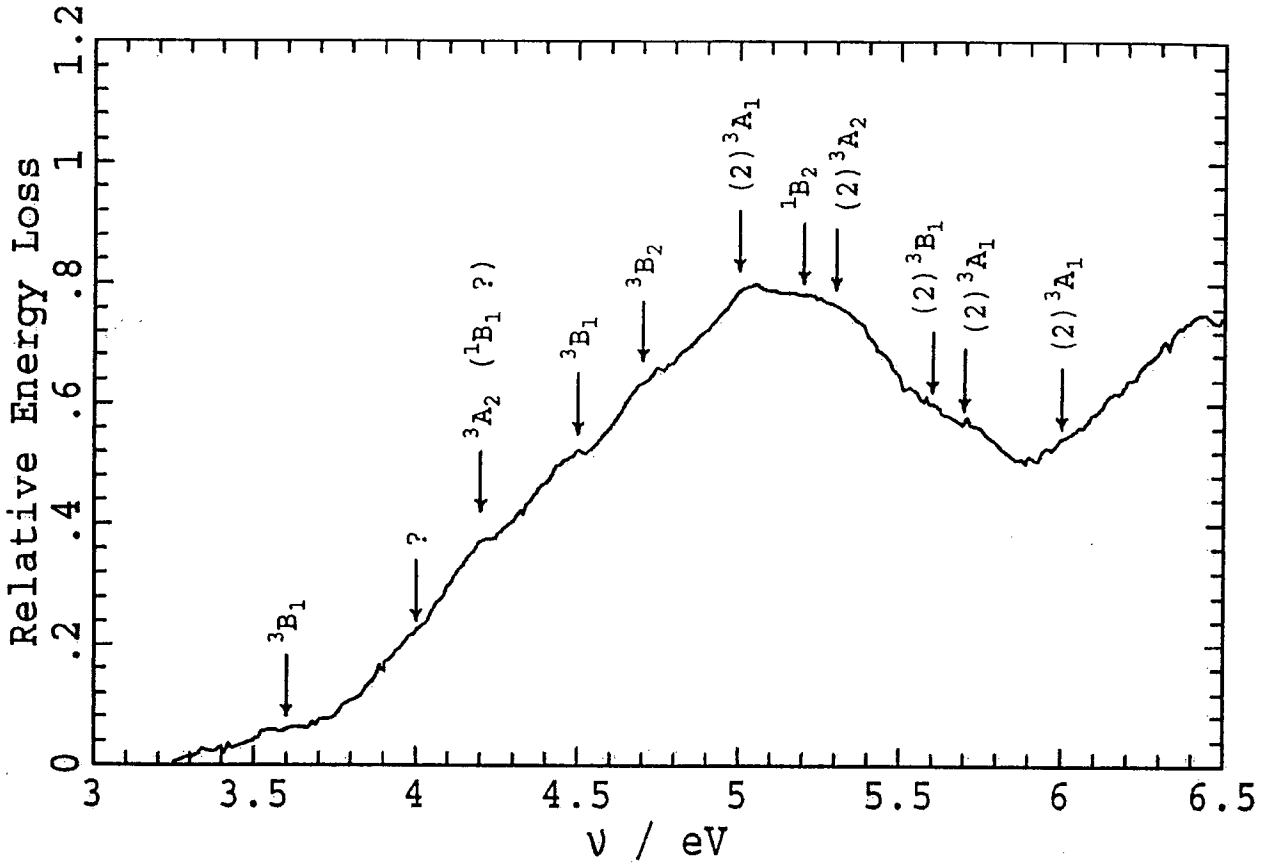
a: All results obtained using the cc-pVDZ basis set

5. Simulation of the absorption spectrum of $(2)^1A_1$



The simulations use the EOM-CCSD calculated vibrational properties for the excited state, but the 0-0 energy (6.26 eV) and the intensity are set to match the observed spectrum.[48]

6. Assignment of the EEL spectrum of Palmer et al.[17]



7: Calculated (B3LYP/cc-pVDZ) and observed (in Benzene crystal 1.2 K) excess alpha spin densities for triplet states of pyrimidine

State	Sym.	N	C_1	C_3	C_4
$(\alpha)\ ^3A_1$	C_{2v}	0.06	0.83	0.12	0.91
$(\alpha)\ ^3A_1$	C_s	0.16	0.80	0.08	0.87
$(\beta)\ ^3A_1$	C_{2v}	0.61	-0.23	0.64	-0.22
$^3B_1$	C_{2v}	0.64	-0.07	0.44	-0.08
$^3B_2$	C_{2v}	0.26	0.23	0.40	0.53
$^3A_2$	C_{2v}	-0.51	0.59	-0.05	0.48
$^3A_2$	C_s	0.53	0.60	-0.06	0.44
Obs.[a]		~ 0.60	0.0	~ 0.42	0.0

a: from ref. [49]

8. Calculated changes E_{00} - E_0 to the 0-0 excitation energies of pyrimidine at singlet excited states arising from zero-point vibrational motion, in eV[a]

Method	$^1B_1(S_1)$	$^1A_2$		$^1B_2$	$(2)^1A_2$	$(2)^1B_1$	$(2)^1A_1$	$(3)^1A_1$	$(2)^1B_2$
	C_{2v}	C_{2v}	C_s	C_{2v}	C_{2v}	C_{2v}	C_{2v}	C_{2v}	C_{2v}
EOM-CCSD	-0.11	-0.12	-0.17	-0.07	-0.16	-0.10	-0.09		-0.02
CIS	-0.19	-0.22	-0.19	-0.16	-0.05	-0.03	-0.17	-0.04	-0.13
best	-0.11	-0.17		-0.07	-0.16	-0.10	-0.09	-0.04	-0.02

a: For states whose minimum is of C_s symmetry, values at the C_{2v}-optimized geometry are also listed obtained using numerical calculations to estimate the zero-point energy associated with the modes of imaginary frequency. All calculations are performed using the cc-pVDZ basis set.

8a. Calculated changes E_{00} - E_0 to the 0-0 excitation energies of pyrimidine at triplet excited states arising from zero-point vibrational motion, in eV[a]

Method	$(\alpha)^3A_1$		$(\beta)^3A_1$	$(2)^3A_1$	$^3B_1$		$(2)^3B_1$	$^3A_2$	$(2)^3A_2$	$^3B_2$	$(2)^3B_2$
	C_{2v}	C_s	C_{2v}	C_{2v}	C_{2v}	C_s	C_{2v}	C_s	C_{2v}	C_{2v}	C_{2v}
EOM-CCSD		-0.18	-0.24		-0.08	-0.18		-0.18		-0.18	
B3LYP		-0.20			-0.18			-0.18	-0.13	-0.08	-0.03
CIS	-0.24	0	-	-0.11	-0.16		-0.06	-0.18	-0.19	-0.09	-0.09
best	-0.19		-0.24	-0.11	-0.18		-0.06	-0.18	-0.13	-0.13	-0.03

a: For states whose minimum is of C_s symmetry, values at the C_{2v}-optimized geometry are also listed obtained using numerical calculations to estimate the zero-point energy associated with the modes of imaginary frequency. All calculations are performed using the cc-pVDZ basis

9: Some calculated vibration frequencies, in cm^{-1}, for pyrimidine excited states[a]

State	Method	ν_1	ν_4	ν_5	ν_{6a}	ν_{6b}	ν_{8a}	ν_{8b}	ν_{9a}	ν_{10b}	ν_{12}	ν_{14}	ν_{16a}	ν_{16b}	ν_{17b}
$(\alpha)^3A_1$ (C_{2v})	EOM-CCSD	938	576	848	588	520	1575	877	853	386	1063	1309	389	**152i**	**70i**
	CASSCF	974	678	890	621	586	1452	735	894	385	1118	1391	421	**39i**	225
	B3LYP	582	607	876	924	591	1719	**377i**	1054	365	805	1363	**338i**	**162i**	609
$(\alpha)^3A_1$ (C_s)	EOM-CCSD	959	481	852	634	588	1627	931	888	310	1058	1321	377	175	550
	CASSCF	992	545	467	640	622	1712	970	927	877	1112	1412	426	129	348
	B3LYP	942	442	833	664	559	1676	915	899	294	1043	1286	338	112	520
$(\beta)\ ^3A_1$ (C_{2v})	EOM-CCSD	1007	**1646i**	850	592	811	1427	**1126i**	1141	563	1043	1234	29	324	872
	CASSCF	968	**496i**	925	676	592	1535	**1246i**	1142	540	1094	1301	235	369	**4694i**
	B3LYP	657	884	1181	894	554	1484	**695i**	1123	564	1038	1323	**194i**	346	944
$(\beta)\ ^3A_1$ (C_s)	EOM-CCSD	865	446	900	639	489	1476	1629	1120	610	1088	936	**175i**	329	932
$^3B_1$ (C_{2v})	EOM-CCSD	963	**298i**	886	647	412	1554	996	1128	626	1044	1320	282	396	939
	CASSCF	1003	**901i**	914	692	661	1643	1385	1187	610	1101	1142	296	387	978
	B3LYP	652	238	898	1029	437	1518	737	1114	619	956	943	288	431	943
$^3A_2$ (C_{2v})	EOM-CCSD	941	466	854	578	524	1682	**1038i**	1076	623	1033	1242	456	260	**369i**
	CASSCF	978	531	982	604	490	1781	3728	1130	741	1103	1329	489	283	**714i**
	B3LYP	585	475	841	1007	562	1668	**1031i**	1063	603	929	1300	483	260	**408i**
$^3A_2$ (C_s)	EOM-CCSD	943	474	874	552	560	1673	362	1082	648	1043	1283	490	264	666
	B3LYP	932	478	864	529	582	1658	377	1064	611	1021	1260	478	266	643

a: Mode assignments are made by examination of the Duschinsky matrix elements.

10: Properties and anharmonic vibrational analysis of all double-well potentials (cm^{-1})

State	Mode	Symm.	Method.	Harmonic	Anharmonic	Well
$^1B_1$ (S_1)	6b	b_2	EOM-CCSD	58	371	0.2
	6b	b_2	TD-B3LYP	339	493	15
$^1A_2$ (S_2)	8b	b_2	EOM-CCSD	464	537	32
	8b	b_2	CIS	1201	461	426
	17b	b_1	EOM-CCSD	311	397	24
	17b	b_1	CIS	413	379	61
	17b	b_1	CASSCF	311	397	24
$^1B_2$ (S_3)	16b	b_1	EOM-CCSD	287	309	27
	10b	b_1	CIS	595	209	263
	4	b_1	CIS	211	355	7
(2) $^1A_2$ (S_4)	10b	b_1	EOM-CCSD	302	58	190
	16a	a_2	CIS	967	215	558
	8b	b_2	CIS	506	850	16
(2) $^1B_1$ (S_5)	8b	b_2	EOM-CCSD	1519	499	734
	10b	b_1	EOM-CCSD	793	20	1065
	16b	b_1	EOM-CCSD	131	289	3
(2) $^1A_1$ (S_6)	16b	b_1	EOM-CCSD	271	15	323
	16b	b_1	CIS	404	263	121
	10b	b_2	CIS	1678	1157	432
(2) $^1B_2$ (S_8)	16b	b_1	EOM-CCSD	438	0	113
	16b	b_1	CIS	400	181	200
(α)$^3A_1$	16b	b_1	EOM-CCSD	152	169	17
	17b	b_1	EOM-CCSD	71	316	0.4
(β)$^3A_1$	8b	b_2	EOM-CCSD	1045	409	398
	4	b_1	EOM-CCSD	840	12	1253
(2)$^3A_1$	16a	a_2	CIS	229	364	9
	18b	b_2	CIS	980	663	263
$^3B_1$	4	b_1	EOM-CCSD	286	174	73
(2) $^3B_1$	16b	b_1	CIS	157	233	9
$^3B_2$	10b	b_1	CIS	232	265	22
	17a	a_2	CIS	71	431	0.1
(2) $^3B_2$	16b	b_1	CIS	195	172	35
(2) $^3A_2$	4	b_1	CIS	1115	160	777
	8b	b_2	CIS	1261	479	485