Supplementary Table 1. Calculated and experimental bond lengths (Å) **and bond angles** (°) **of ethyl bromide at the B3LYP/631+(2d,2p) level of theory**

	Experimental	**Theoretical**					
Parameter	**Neutral**	**Neutral**	**Ionic**	**2A"(5s)$_{1/2}$**	**3A′(5s)$_{1/2}$**	**3A" (5pa$_1$)$_{1/2}$**	**5A′ (5pe)$_{1/2}$**
r-CBr	1.950	1.990	2.013	2.025	2.062	2.046	2.252
r-CC	1.518	1.516	1.534	1.491	1.504	1.516	1.490
r-CH(CH3)	1.093	1.097	1.09	1.09	1.12	1.09	1.10
r-CH(CH_2,CH)	1.087	1.088	1.09	1.10	1.09	1.10	1.09
∠CCBr	111.0	111.6	103.3	117.7	112.1	111.2	103.9
∠HCH (CH_3)	108.9	108.4	107.8	107.9	107.8	105.9	104.3
∠HCH (CH_2)	109.9	109.7	114.2	108.1	113.5	106.5	113.6
∠HCBr	105.4	104.7	104.3	98.5	100.2	98.2	96.8

Supplementary Table 2. Vibrational frequencies (in cm^{-1}) of ethyl bromide in a few excited states at the B3LYP/6-31+(2d,2p) level of theory

	2A"(5s)$_{1/2}$		**3A′(5s)$_{1/2}$**		**3A"(5pa$_1$)$_{1/2}$**		**5A′(5pe)$_{1/2}$**	
Vibrational Mode	**C_2H_5Br**	**C_2D_5Br**	**C_2H_5Br**	**C_2D_5Br**	**C_2H_5Br**	**C_2D_5Br**	**C_2H_5Br**	**C_2D_5Br**
A'								
ν_1(CH_3 d-str)	3095	2262	3089	2259	3088	2282	3031	2225
ν_2 (CH_2 s-str)	2918	2122	2993	2174	2980	2161	3006	2187
ν_3 (CH_3 s-str)	2763	2008	2795	2030	2903	2100	2906	2098
ν_4 (CH_3 d-deform)	1480	1183	1482	1132	1429	1105	1471	1153
ν_5 (CH_2 scis)	1395	1053	1390	1055	1394	1031	1418	1065
ν_6 (CH_3 s-deform)	1357	1028	1379	1032	1367	1018	1289	1028
ν_7 (CH_2 wag)	1234	934	1252	949	1213	941	1190	919
ν_8 (CH_3 rock; in-plane)	1109	887	1045	878	987	815	1036	838
ν_9 (CC str)	901	712	885	694	870	699	773	587
ν_{10} (CBr str)	435	415	418	396	397	370	448	414
ν_{11} (CCBr deform)	270	240	199	179	245	221	165	148
A"								
ν_{12} (CH_2 a-str)	3151	2337	3164	2365	3088	2232	3118	2324
ν_{13} (CH_3 d-str)	2913	2141	3126	2321	2900	2160	2916	2168
ν_{14} (CH_3 d-deform)	1416	1019	1414	1029	1415	1024	1227	900
ν_{15} (CH_2 twist)	1230	952	1244	977	1078	830	1115	859
ν_{16} (CH_3 rock; out of plane)	916	662	1155	835	871	626	781	562
ν_{17} (CH_2 rock)	482	362	806	587	607	457	716	527
ν_{18} (Torsion)	213	160	254	184	230	167	232	166
ZPE (cm^{-1})	13,639	10,239	14,045	10,538	13,531	10,120	13,419	10,084

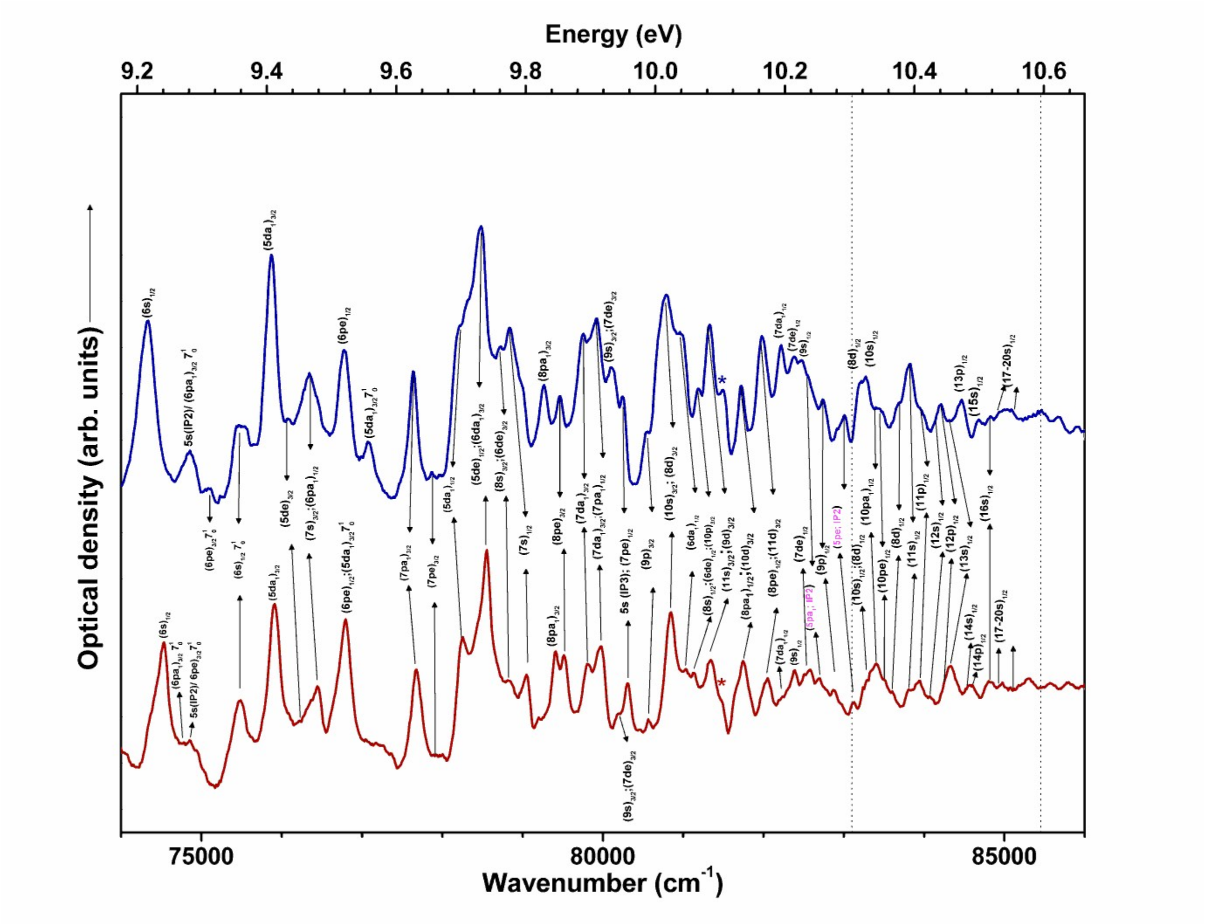
Supplementary Table 3. Vertical Excited state energies at the CAM-B3LYP/aug-cc-pVTZ level of theory[#]

Sym	VEE (eV)	*f*	Λ	Transition	Weight	Ass.	EXPT	O-C
^{3}A"	6.181	0	0.276	7a"-21a'	0.53			
^{3}A'	6.231	0	0.290	19a'-21a'	-0.52			
^{1}A"	**6.126**	**0.0004**	**0.277**	**7a"-21a'**	**0.53**	**V**	**~5.2 – 6.7**	
^{1}A'	**6.177**	**0.0005**	**0.290**	**19a'-21a'**	**0.52**			
^{3}A"	7.067	0	0.248	7a"-20a'	-0.77	5s-3/2	7.026	-0.063
^{3}A'	7.111	0	0.254	19a'-20a'	-0.75			
^{1}A"	**7.001**	**0.0433**	**0.249**	**7a"-20a'**	**0.76**	**5s-1/2**	**7.348**	**0.319**
^{1}A'	**7.057**	**0.0562**	**0.255**	**19a'-20a'**	**-0.75**			
^{3}A"	7.840	0	0.273	7a"-21a'	0.75			
^{3}A'	7.909	0	0.277	19a'-21a'	-0.72			
^{1}A"	**7.807**	**0.0063**	**0.238**	**7a"-21a'**	**0.66**	**V?**	**--**	
^{1}A'	**7.866**	**0.0138**	**0.290**	**19a'-21a'**	**-0.75**			

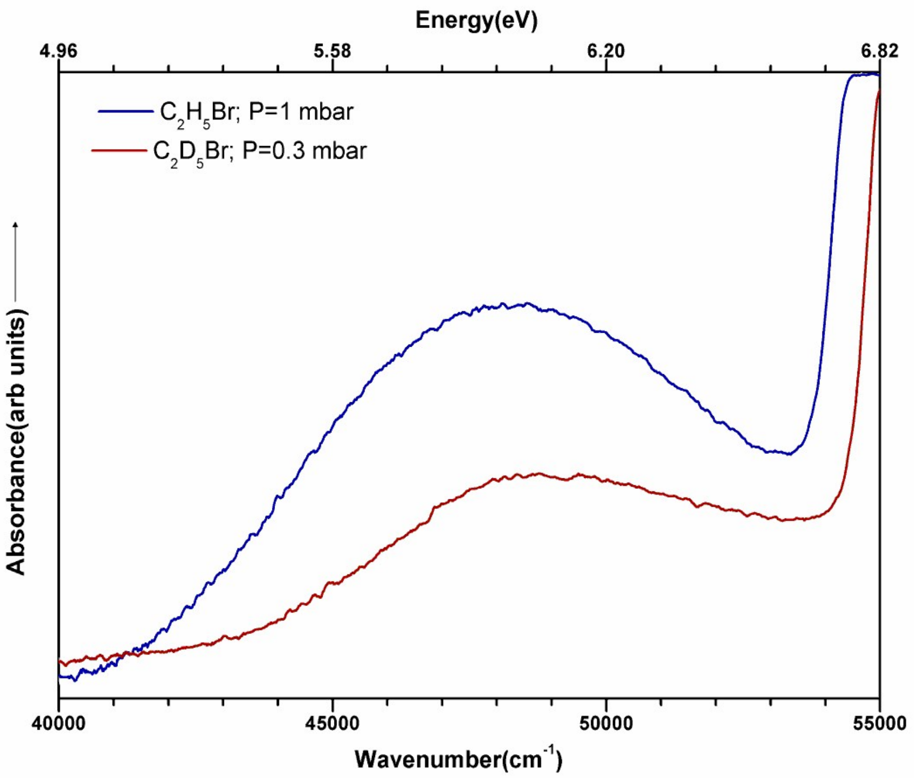
^{3}A'	7.845	0	0.179	7a"-8a"	0.88	5pe-3/2	7.969	0.111
^{3}A"	7.870	0	0.123	19a'-8a"	-0.93			
^{1}A'	**7.805**	**0.0175**	**0.167**	**7a"-8a"**	**-0.92**	**5pe-1/2**	**8.296**	**0.463**
^{1}A"	**7.861**	**0.0001**	**0.158**	**19a'-8a"**	**0.82**			
^{3}A"	8.052	0	0.279	7a"-23a'	-0.55	4da$_1$-3/2	8.727	0.651
				7a"-22a'	0.52	5pa$_1$-3/2	7.903	-0.173
^{3}A'	8.101	0	0.289	19a'-23a'	-0.56			
				19a'-22a'	0.53			
^{1}A"	**8.022**	**0.0288**	**0.277**	**7a"-23a'**	**-0.53**	**4da$_1$-1/2**	**9.035**	**0.992**
				7a"-22a'	**0.51**	**5pa$_1$-1/2**	**8.236**	**0.193**
^{1}A'	**8.064**	**0.0352**	**0.288**	**19a'-23a'**	**-0.54**			
				19a'-22a'	**0.52**			
^{3}A'	8.685	0	0.158	7a"-9a"	-0.91	4de-3/2	8.793	0.102
^{3}A"	8.696	0	0.192	19a'-9a"	-0.71			
^{1}A'	**8.652**	**0.0021**	**0.167**	**7a"-9a"**	**-0.88**	**4de-1/2**	**9.094**	**0.421**
^{1}A"	**8.695**	**0.0116**	**0.177**	**19a'-9a"**	**-0.77**			
^{3}A"	8.725	0	0.206	19a'-25a'	0.58	6pa$_1$-3/2	9.133	0.359
^{3}A'	8.823	0	0.293	19a'-25a'	0.66			
^{1}A"	**8.654**	**0.0001**	**0.222**	**7a"-25a'**	**0.67**	**6pa$_1$-1/2**	**9.465**	**0.747**
^{1}A'	**8.783**	**0.0224**	**0.306**	**19a'-25a'**	**0.80**			
^{3}A'	8.827	0	0.311	18a'-20a'	0.67			
^{1}A'	**8.771**	**0.0721**	**0.292**	**18a'-20a'**	**0.77**	**5s(18a')**	**9.281**	**0.510**
^{3}A"	8.973	0	0.254	7a"-24a'	0.61	6s-3/2	8.908	-0.069
^{3}A'	8.982	0	0.263	19a'-24a'	0.72			
^{1}A"	**8.938**	**0.0135**	**0.254**	**7a"-24a'**	**0.53**	**6s-1/2**	**9.215**	**0.274**
^{1}A'	**8.943**	**0.0223**	**0.268**	**19a'-24a'**	**-0.65**			
^{3}A"	9.022	0	0.26	7a"-26a'	-0.69	5da$_1$-3/2	9.708	0.651
^{3}A'	9.092	0	0.281	19a'-26a'	-0.67			
^{1}A"	**8.988**	**0.0001**	**0.259**	**7a"-26a'**	**-0.62**	**5da$_1$-1/2**	**9.405**	**0.399**
^{1}A'	**9.024**	**0.0155**	**0.278**	**19a'-26a'**	**0.63**			
^{3}A"	9.140	0	0.18	19a'-10a"	0.95	6pe-3/2	9.163	-0.062
^{3}A'	9.310	0	0.305	7a"-10a"	-0.62			
^{1}A"	**9.104**	**0.0015**	**0.180**	**19a'-10a"**	**-0.94**	**6pe-1/2**	**9.518**	**0.368**
^{1}A'	**9.196**	**0.2500**	**0.293**	**7a"-10a"**	**0.69**			
^{3}A"	9.268	0	0.261	6a"-20a'	0.70			
^{1}A"	**9.223**	**0.0000**	**0.262**	**6a"-20a'**	**0.71**	**5s(6a")**	**9.948**	**0.725**
^{3}A'	9.430	0	0.315	18a'-21a'	0.50			
^{1}A'	**9.364**	**0.1091**	**0.324**	**18a'-21a'**	**0.55**	**V?**	**--**	
^{3}A"	9.532	0	0.252	7a"-28a'	0.64	7pa$_1$-3/2	9.626	0.060
^{3}A'	9.601	0	0.283	19a'-28a'	0.61			
^{1}A"	**9.502**	**0.0131**	**0.252**	**7a"-28a'**	**0.63**	**7pa$_1$-1/2**	**9.908**	**0.383**
^{1}A'	**9.548**	**0.0279**	**0.282**	**19a'-28a'**	**-0.59**			
^{3}A"	9.748	0	0.241	6a"-20a'	0.52			
				6a"-21a'	**0.51**			
^{1}A"	**9.709**	**0.0064**	**0.252**	**6a"-21a'**	**-0.57**	**V?**	**--**	
				6a"-20a'	**-0.53**			
^{3}A'	9.756	0	0.349	18a'-22a'	0.69			
^{1}A'	**9.720**	**0.0275**	**0.346**	**18a'-22a'**	**-0.71**	**5pa$_1$(18a')**	**10.236**	**0.516**
^{3}A"	9.806	0	0.168	18a'-8a"	-0.86			
^{1}A"	**9.779**	**0.0168**	**0.160**	**18a'-8a"**	**-0.89**	**5pe(18a')**	**10.259**	**0.480**
^{3}A"	9.830	0	0.226	7a"-27a'	-0.63	7s-3/2	9.465	-0.385
^{3}A'	9.869	0	0.277	19a'-27a'	-0.57			
^{1}A"	**9.805**	**0.0052**	**0.224**	**7a"-27a'**	**-0.62**	**7s-1/2**	**9.776**	**-0.041**
^{1}A'	**9.829**	**0.0197**	**0.285**	**19a'-27a'**	**0.53**			
^{3}A'	9.972	0	0.355	18a'-23a'	-0.69			
^{1}A'	**9.934**	**0.0233**	**0.352**	**18a'-23a'**	**-0.68**	**4da$_1$(18a')**	**10.623**	**0.689**
^{3}A'	10.078	0	0.26	7a"-11a"	0.59	5de-3/2	9.435	-0.661
^{3}A"	10.114	0	0.183	19a'-11a"	-0.74			
^{1}A'	**10.040**	**0.0125**	**0.264**	**7a"-11a"**	**-0.51**	**5de-1/2**	**9.73**	**-0.344**
^{1}A"	**10.107**	**0.0015**	**0.189**	**19a'-11a"**	**0.69**			
^{3}A"	10.106	0	0.223	7a"-30a'	0.68	8s-3/2	9.76	-0.391
^{3}A'	10.195	0	0.287	19a'-30a'	-0.66			
^{1}A"	**10.075**	**0.0194**	**0.217**	**7a"-30a'**	**0.64**	**8s-1/2**	**10.064**	**-0.045**
^{1}A'	**10.143**	**0.0556**	**0.285**	**19a'-30a'**	**0.65**			
^{3}A'	10.132	0	0.278	7a"-12a"	-0.40			

^{1}A'	**10.098**	**0.0181**	**0.275**	**7a"-12a"**	**0.46**	**--**		
^{3}A"	10.246	0	0.226	7a"-29a'	-0.74	6da$_1$-3/2	9.73	-0.541
^{3}A'	10.295	0	0.273	19a'-29a'	-0.79			
^{1}A"	**10.226**	**0.0072**	**0.226**	**7a"-29a'**	**0.72**	**6da$_1$-1/2**	**10.04**	**-0.203**
^{1}A'	**10.260**	**0.0070**	**0.273**	**19a'-29a'**	**0.79**			
^{3}A"	10.314	0	0.199	19a'-12a"	0.67	7pe-3/2	9.654	-0.714
^{3}A'	10.422	0	0.231	7a"-12a"	0.67			
^{1}A"	**10.290**	**0.0020**	**0.206**	**19a'-12a"**	**-0.62**	**7pe-1/2**	**9.948**	**-0.380**
^{1}A'	**10.365**	**0.1296**	**0.234**	**7a"-12a"**	**0.66**			
^{3}A"	10.361	0	0.244	6a"-21a'	0.61			
^{1}A"	**10.311**	**0.0487**	**0.239**	**6a"-21a'**	**0.55**	**V**	**--**	
^{3}A'	10.497	0	0.224	6a"-8a"	-0.80			
^{1}A'	**10.443**	**0.0887**	**0.225**	**6a"-8a"**	**0.79**	**5pe(6a")**	**11.049**	**0.606**
^{3}A"	10.582	0	0.237	6a"-22a'	0.67			
^{1}A"	**10.554**	**0.0013**	**0.236**	**6a"-22a'**	**0.66**	**5pa$_1$(6a")**	**10.993**	**0.439**
^{3}A'	10.615	0	0.275	17a'-20a'	-0.73			
^{1}A'	**10.589**	**0.0023**	**0.276**	**17a'-20a'**	**-0.73**	**5s(17a′)**	**--**	
^{3}A"	10.647	0	0.136	18a'-9a"	-0.95			
^{1}A"	**10.629**	**0.0022**	**0.142**	**18a'-9a"**	**-0.93**	**4de(18a')**	**--**	
^{3}A"	10.741	0	0.269	19a'-13a"	0.66			
				19a'-14a"	0.44	--	--	
^{1}A"	**10.692**	**0.0088**	**0.268**	**19a'-13a"**	**-0.64**			
				19a'-14a"	**-0.44**			
^{3}A'	10.756	0	0.34	18a'-25a'	0.64			
				7a"-13a"	-0.39	--	--	
^{3}A'	10.822	0	0.302	19a'-31a'	-0.54			
				7a"-13a"	-0.42			
^{1}A'	**10.710**	**0.0218**	**0.336**	**7a"-13a"**	**0.51**			
				18a'-32a'	**-0.51**	**--**	**--**	
^{1}A'	**10.773**	**0.0147**	**0.319**	**18a'-24a'**	**0.52**			
				18a'-25a'	**-0.49**			
^{3}A"	10.867	0	0.233	7a"-31a'	-0.82	8pa$_1$-3/2	9.828	-1.057
^{3}A'	10.903	0	0.284	19a'-31a'	0.65			
^{1}A"	**10.849**	**0.0052**	**0.233**	**7a"-31a'**	**-0.83**	**8pa$_1$-1/2**	**10.134**	**-0.726**
^{1}A'	**10.872**	**0.0630**	**0.272**	**19a'-31a'**	**0.73**			
^{3}A'	11.048	0	0.318	18a'-26a'	0.6286			
^{1}A'	**11.003**	**0.0068**	**0.318**	**18a'-26a'**	**0.622**	5da$_1$(18a′)	**--**	
^{3}A'	11.167	0	0.293	19a'-32a′	0.678	--	--	
^{1}A'	**11.125**	**0.0142**	**0.294**	**19a'-32a′**	**0.6577**			
^{3}A"	11.185	0	0.175	18a'-10a"	-0.757			
^{1}A"	**11.154**	**0.0013**	**0.18**	**18a'-10a"**	**-0.74**	**6pe(18a′)**	**--**	
^{3}A"	11.257	0	0.272	7a"-32a'	0.8675	7da$_1$-3/2	9.908	-1.328
^{1}A"	**11.214**	**0.0195**	**0.267**	**7a"-32a'**	**0.8461**			
^{3}A'	11.251	0	0.287	19a'-32a'	-0.489	7da$_1$-1/2	10.215	-1.018
^{1}A'	**11.215**	**0.0995**	**0.286**	**19a'-32a'**	**-0.534**			

$^\#$**Singlet state energies are in bold type;** all energies in eV; Unassigned lines are either not observed in the present experiment or show too much orbital mixing to be unambiguously assigned. EXPT: present experimental study; VEE: vertical excited energy; *f*: oscillator strength; Λ: lambda diagnostic value; Ass: assignment; R: Rydberg; V: Valence



Supplementary Figure 1: Expanded view of the 74,000–86000 cm^{-1} region



Supplementary Figure 2: Absorption spectra of C_2H_5Br and C_2D_5Br in the UV region

Appendix 1: Note on spectroscopic notations

We recapitulate here the various spectroscopic notations that have been used to describe the Rydberg spectra of alkyl bromides. The similarity in the structure and spectra of HBr, CH_3Br and CH_3CH_2Br leads one naturally to consider the $C_{\infty V}$ or C_{3V} limiting cases and then follow what happens when the symmetry is lowered to C_s. The other important consideration is the correlation of the relatively weaker spin orbit coupling in the neutral molecule with the strong spin orbit coupling seen in the cationic ground state. We also note that the concept of double groups has to be used in derivation of the possible Rydberg states in order to allow for the half integral values of spin[1, 2]. In correlating the C_{3V} case with the linear limit $C_{\infty V}$, we note that a_1 and e symmetries correspond to σ and π respectively[3, 4]. In the linear molecule limit, the first *ns* Rydberg excitation may be taken as $\pi^4 \rightarrow \pi^3\sigma$, giving rise to four states, three of Π symmetry (dipole allowed) and one of Δ symmetry (dipole forbidden). In the C_{3V} limit, this correlates with three states of E symmetry and one each of A_1 and A_2 symmetry (jointly referred to as state 3). In the intermediate or strong spin-orbit coupling limit, only two of the four states, viz. 2 and 4 are strongly allowed[2, 4]. Of these, the $^3\Pi_1$ correlates with the $^2E_{3/2}$ component of the cationic ground state while $^1\Pi_1$ correlates with the $^2E_{1/2}$ component. In the C_s case, strictly speaking all transitions are allowed, however transitions observed experimentally follow the C_{3V} case, thus validating the assumption that the additional methyl group has negligible influence on the Rydberg spectra of ethyl bromide. The expected states for *np* and *nd* Rydberg excitations can also be worked out in a similar way.

State	$C_{\infty V}$[4]	C_{3V}[2]	C_s[2]	Ionic limit	Current designation
1	$^3\Pi_2(\Delta)$	E(2)	(A′, A")	$^2E_{3/2}$	--
2	$^3\Pi_1(\Pi)$	E(1)	(A′, A")	$^2E_{3/2}$	5s ($^2E_{3/2}$)
3*	$^3\Pi_{0\pm}(\Sigma^+, \Sigma^-)$	A_1, A_2(0)	(A′, A")	$^2E_{1/2}$	--
4	$^1\Pi_1$	E(1)	(A′, A")	$^2E_{1/2}$	5s ($^2E_{1/2}$)

*These two states are very close in energy and have been designated jointly as state 3[2, 4].

References

1. G. Herzberg, *Molecular Spectra and Molecular Structure Vol. III Electronic Spectra and Electronic Structure of Polyatomic Molecules*, D.VAN NOSTRAND COMPANY, INC., Princeton, New Jersey, 1966.
2. N. L. Baker and B. R. Russell, *Journal of Molecular Spectroscopy*, 1978, 69, 211-224.
3. R. S. Mulliken, *Physical Review*, 1942, 61, 277-283.

4. S. Felps, P. Hochmann, P. Brint and S. P. McGlynn, *Journal of Molecular Spectroscopy*, 1976, 59, 355-379.