J. Phys. Chem. 1994, 98, 9955–9959

Electronic Structure of the Excited States and Phenol Fluorescence

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Received: February 4, 1994; In Final Form: May 5, 1994®

The excitation energies of phenol and the deprotonated anion have been determined at geometries relevant to both the absorption and fluorescence spectra using first-order configuration interaction methods. Optimized geometries were calculated for the ground and first excited singlet and triplet state of both neutral and anion molecules. Solvatochromic shifts are predicted to be very small since the ground and singlet excited state dipole moments are very similar. The fluorescent shift is dominated by the differences in the vertical transition energies at the equilibrium geometries of the ground and excited state. Anion absorption and fluorescence shifts are substantially to the red of those found for the neutral molecule. Ordering and assignment of the triplet valence states of neutral and deprotonated phenol are determined to be different. Experimental observation that anion formation strongly deactivates fluorescence is related to these differences. Coupling of the first excited singlet to its cognate triplet state is suggested as the quenching mechanism in the anion, and the same process occurs more weakly in the neutral species.

1. Introduction

The fluorescence spectrum of phenol is studied as a simple model for tyrosine-containing proteins.[1-3] The absorption spectrum of the first excited state of phenol is observed around 275 nm with a fluorescence peak around 298 nm in water. The tyrosine absorption is reported at 277 nm and the fluorescence near 303 nm. Fluorescent efficiency is reported to be about 0.21 for both phenol and tyrosine.[2] The fluorescent shift between protic and aprotic solvents is small[4] compared to that in indole, the other model for a protein chromophore, tryptophan. The large solvatochromic effect in indole has long been linked to the second excited singlet state in absorption. The electronic properties of this state and state reversal as a function of molecular geometry and the magnitude of the dielectric constant of the solvent were found to qualitatively explain the fluorescence behavior of indole.[5] The excitation energy between the first and second excited singlet state in phenol is substantial larger than that of indole, so the coupling between these states is not significant, which suggests that the isolated excited state properties are sufficient for analyzing phenol.

Phenol also differs from indole by dissociating a proton relatively easier in both the ground and excited state. The ground state pK of the hydroxyl group is 10.0, but the pK of the first excited singlet state is between 3.6 and 4.0, while that of the first triplet state is 8.5.[1,6] There is a large shift to the red for the anion of both the absorption and fluorescence.[2] The anion differs from neutral phenol with a larger absorption coefficient[2] and a much smaller fluorescence coefficient.[2,7]

Phenol is a good model for the tyrosine spectral shift but is not completely analogous for the quenching. Evidently the presence of a carbonyl bond in tyrosine can alter the electronic response.[6] Intersystem quenching in phenol, though, models one aspect of the mechanism in tyrosine. Why the phenolate anion first singlet excited state deactivates rapidly compared to the comparable state in neutral phenol is not understood. In this study we will focus on the electronic structure of both the ground and excited states of both the neutral and anion molecules. Bent and Hayon[8] have deduced that long-lived triplet states are produced in the photolysis of phenol and tyrosine. Differences in the electronic structure of the excited states between the neutral and anion molecules provide the basis for analyzing the deactivation of the excited singlet state by radiationless transition to a lower triplet state.

Recent ab initio calculations of phenol have studied the ground state and its binding to one or small clusters of water.[9,10] However, there has been only a single ab initio exploration of the excited singlet states of phenol[11] and no studies of the triplet or the excited states of the phenoxide anion. These studies have evaluated the vibrational frequencies of the phenol ground state. Ground and excited state vibrational frequencies were also modeled for comparison with the cation,[12] but geometries of the states were not optimized. Anion ground state frequencies were calculated to assist the analysis of the photoelectron spectroscopy of the phenoxide anion;[13] but a consistent analysis of the vibrations of the excited states of the neutral and anion molecules is lacking.

This study of phenol parallels the previous one of indole.[5] It is restricted to phenol and phenoxide, and spectral shifts are estimated for solvent reorganization of the reaction field in the the excited state.[5] Supermolecule clustering of the radiating molecule would be more accurate, but the reaction field analysis is sufficient if the in vacuo electronic properties have not changed much from ground to excited state, as is the case here. The goals of this study are to determine the electronic origins

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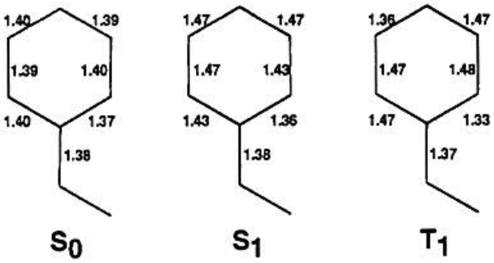
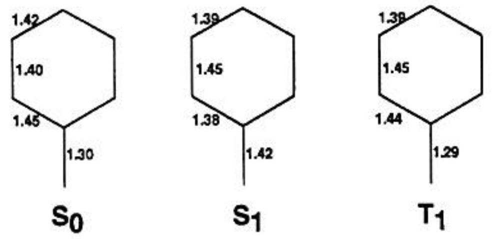
® Abstract published in *Advance ACS Abstracts*, September 1, 1994.

0022-3654/94/2098-9955$04.50/0



Neutral Conformation



Anion Conformation

Figure 1. Schematic description of the heavy-atom bond lengths in the ground and excited states of phenol and the phenoxide anion.

of the different behavior between the neutral and anion molecules of the fluorescent red-shift and the quenching mechanism.

2. Method

The electronic description of the excited states requires a multiconfiguration description. This is especially true in a study of fluorescence where geometries of the excited states are to be obtained. The ground and excited state geometries were optimized in a complete active space multiconfiguration self-consistent-field (CAS-MCSCF) calculation where four electrons were distributed among four π orbitals using a 6-31G basis.[14] Geometries are described in Figure 1 for both neutral and anion molecules for both singlet (neutral: S0, S1; anion: A0, A1) and triplet states (neutral: T1; anion: AT1). Only the bond distances for the heavy atoms are given with the bonds to hydrogen, and the angles are given in a supplementary table. All states were constrained to be planar. Vibrational harmonic frequencies, calculated with the same basis and the level of MC-SCF correlation, are given in Tables 1–6.

Excited state energies are obtained with a first-order configuration interaction calculation (FOCI) generated by all single excitations from the CAS multireference base. All FOCI calculations were done with the GAMESS system of codes modified by inclusion of the dipole reaction field into the Hamiltonian.[5,15] The reaction field for the dipole–dipole interaction between the solute and solvent is determined by two parameters, the dipole moment of the initial state in the transition and the radius which was chosen as 6.5 bohr to match the molecular volume. The molecular orbital basis was obtained from a restricted Hartree–Fock (ROHF) calculation of the lowest triplet state. This molecular oribital basis is separated into frozen, active, and virtual orbitals. The number of configurations is mostly determined by the number of active orbitals, which is restricted here to nine. Seven of the active orbitals are chosen from the occupied space of the ROHF orbitals, and the remaining two represent the lowest energy π^* orbitals. The remaining occupied ROHF orbitals are frozen.

The dominant configurations and coefficients are presented in Table 7 for the excited singlet and triplet states at their respective optimized geometries. Analysis of the quenching of the first excited singlet state requires a comparison of the electronic structure between the neutral and anion species. Total energies, excitation energies, and dipole moments are given in Table 8. The effect of the reaction field on both the absorption and fluorescence is determined with the energies obtained at the S0 and S1 geometries. Oscillator strengths are compared between the neutral and anion species in Table 9.

TABLE 1: Vibrational Frequencies of Ground State Phenol S0[a]

mode	calc	assignment	corrected	exp
		In-Plane		
1	428.3	C—O bend	404	404
2	580.3	C—C bend	530	527
3	694.0	C—C bend	634	619
4	886.0	C—C bend	809	823
5	1073.2	C—C bend	980	1000
6	1124.0	C—C bend	1026	1026
7	1160.8	C—H bend	1066	1070
8	1216.8	C—C bend	1111	1150
9	1290.0	C—H bend	1184	1169
10	1296.8	C—H bend	1190	1177
11	1362.4	O—H bend, C—H bend	1251	1262
12	1385.0	C—O stretch	1292	1277
13	1506.7	C—H bend	1375	1343
14	1625.2	C—H bend	1492	1472
15	1664.4	C—C stretch	1519	1502
16	1755.9	C—C stretch	1602	1604
17	1762.5	C—C stretch	1608	1610
18	3344.4	C—H stretch	3044	3027
19	3356.3	C—H stretch	3055	3049
20	3370.8	C—H stretch	3069	3063
21	3386.8	C—H stretch	3083	3070
22	3403.8	C—H stretch	3099	3087
23	4046.9	O—H stretch	3717	3656
		Out-of-Plane		
1	257.3	C—O bend	236	244
2	327.7	O—H bend	301	309
3	458.7	C—C bend	414	410
4	560.7	C—C bend	506	503
5	757.0	C—C bend	683	687
6	829.9	C—H bend	738	752
7	921.0	C—H bend	832	817
8	1004.7	C—H bend	907	881
9	1071.1	C—H bend	967	973
10	1092.7	C—H bend	986	995

assignment	correction factor
C—H stretch	0.910 32
O—H stretch	0.918 45
C—C stretch	0.912 40
C—O stretch	0.912 40
C—O stretch	0.933 13
C—C bend	0.912 92 (in), 0.902 82 (out)
O—H, C—H bend	0.917 90 (in), 0.918 22 (O—H, out), 0.889 02 (C—H, out)
C—O bend	0.942 17 (in), 0.915 88 (out)

[a] exp: Bist, H. D.; Brand, J. C. D.; Williams, D. R. *J. Mol. Spectrosc.* **1967**, *24*, 402; all frequencies in cm^{-1}. Correction factors were obtained by fitting analogous vibrational modes to experimental values.

3. Results and Discussion

The vibrational frequency data in Tables 1–6 illustrates the changes that accompany excitation into the lowest singlet or triplet state for both the neutral and anion molecules. Frequencies of modes that are dominantly in the carbon ring are reduced upon excitation from S0 to S1. Several frequencies have been compared for ground and excited phenol[16] which show the reduction. Frequencies observed in the ground state at 521, 825, and 997 cm^{-1} shift down by 47, 42, and 63 cm^{-1}, while the calculated shifts are 55, 45, and 124 cm^{-1}. Out-of-plane

TABLE 2: Vibrational Frequencies of Excited Singlet Phenol S1

mode	calc	assignment	corrected
		In-Plane	
1	423.9	C—O bend	399
2	520.2	C—C bend	475
3	603.9	C—C bend	551
4	837.0	C—C bend	764
5	937.3	C—C bend	856
6	993.9	C—C bend	907
7	1079.2	C—C bend	985
8	1217.7	C—H bend	1118
9	1235.1	O—H bend, C—H bend	1134
10	1279.9	O—H bend, C—H bend	1175
11	1357.3	C—O stretch	1267
12	1469.7	C—H bend	1349
13	1520.6	C—H bend	1396
14	1554.3	C—H bend	1427
15	1601.1	C—C stretch	1461
16	1664.6	C—C stretch	1519
17	1802.3	C—C stretch	1644
18	3343.4	C—H stretch	3044
19	3381.3	C—H stretch	3087
20	3404.9	C—H stretch	3100
21	3415.1	C—H stretch	3109
22	3431.8	C—H stretch	3124
23	4041.9	O—H stretch	3712
		Out-of-Plane	
1	146.5	C—H bend	130
2	173.7	C—H bend	154
3	275.9	C—C bend	249
4	307.8	C—C bend	278
5	371.6	O—H bend	341
6	396.0	C—C bend	358
7	484.4	C—H bend	431
8	521.3	C—H bend	463
9	637.1	C—O bend	583
10	969.4	C—H bend	862

TABLE 3: Vibrational Frequencies of Triplet State Phenol T1

mode	mode	assignment	corrected
		In-Plane	
1	409.0	C—O bend	385
2	522.4	C—C bend	447
3	619.7	C—C bend	566
4	822.9	C—C bend	751
5	928.2	C—C bend	847
6	1036.3	C—C bend	946
7	1070.2	C—C bend	984
8	1100.8	C—H bend	1010
9	1256.9	O—H bend	1154
10	1312.2	C—H bend	1204
11	1346.6	C—O stretch	1257
12	1457.8	C—H bend	1338
13	1479.6	C—H bend	1358
14	1538.6	C—C stretch	1404
15	1556.2	C—H bend	1428
16	1736.6	C—C stretch	1584
17	1851.9	C—C stretch	1690
18	3349.9	C—H stretch	3049
19	3360.0	C—H stretch	3059
20	3384.9	C—H stretch	3081
21	3408.8	C—H stretch	3103
22	3433.7	C—H stretch	3126
23	4039.0	O—H stretch	3710
		Out-of-Plane	
1	92.6	C—C bend	84
2	168.9	C—H bend	150
3	219.0	C—H bend	195
4	296.2	C—C bend	267
5	360.7	O—H bend	331
6	462.2	C—C bend	417
7	557.3	C—H bend	495
8	822.3	C—O bend	753
9	832.5	C—H bend	740
10	1141.4	C—H bend	1015

TABLE 4: Vibrational Frequencies of Ground State Phenoxide S0

mode	calc	assignment	corrected
		In-Plane	
1	457.8	C—O bend	431
2	582.4	C—C bend	532
3	680.5	C—C bend	621
4	888.1	C—C bend	811
5	1064.0	C—C bend	972
6	1091.7	C—C bend	997
7	1156.4	C—H bend	1061
8	1219.0	C—H bend	1119
9	1276.2	C—H bend	1171
10	1291.3	C—H bend	1185
11	1454.8	C—H bend	1335
12	1491.8	C—O stretch	1392
13	1595.6	C—C stretch	1456
14	1650.4	C—C stretch	1506
15	1695.8	C—C stretch	1547
16	1739.5	C—C stretch	1587
17	3269.8	C—H stretch	2977
18	3278.8	C—H stretch	2985
19	3320.8	C—H stretch	3023
20	3332.4	C—H stretch	3034
21	3342.2	C—H stretch	3042
		Out-of-Plane	
1	235.0	C—O bend	215
2	467.3	C—C bend	422
3	560.9	C—C bend	506
4	754.5	C—H bend	671
5	769.5	C—C bend	695
6	877.1	C—H bend	780
7	934.3	C—H bend	831
8	1023.4	C—H bend	910
9	1062.7	C—H bend	945

TABLE 5: Vibrational Frequencies of Excited Singlet Phenoxide S1

mode	calc	assignment	corrected
		In-Plane	
1	530.8	C—O bend	500
2	567.4	C—C bend	518
3	648.2	C—C bend	592
4	859.2	C—C bend	784
5	989.3	C—C bend	903
6	1061.7	C—C bend	969
7	1125.0	C—H bend	1033
8	1234.7	C—H bend	1133
9	1244.2	C—O stretch, C—H bend	1161
10	1250.9	C—O stretch, C—H bend	1167
11	1351.5	C—C stretch	1233
12	1424.6	C—H bend	1308
13	1560.2	C—H bend	1432
14	1626.3	C—C stretch	1483
15	1679.7	C—C stretch	1532
16	1740.1	C—C stretch	1588
17	3249.7	C—H stretch	2958
18	3302.1	C—H stretch	3006
19	3320.0	C—H stretch	3022
20	3362.7	C—H stretch	3061
21	3372.8	C—H stretch	3070
		Out-of-Plane	
1	177.5	C—O bend	163
2	281.6	C—C bend	254
3	443.0	C—C bend	400
4	503.2	C—C bend	454
5	618.5	C—H bend	550
6	632.7	C—H bend	562
7	674.2	C—H bend	599
8	735.2	C—H bend	654
9	1067.4	C—H bend	949

modes are affected even more with larger reductions from S0 to S1 states. The accurcy of these predictions is not sufficient to distinguish between the S1 and T1 states, but the trends in classes of modes should be followed.

TABLE 6: Vibrational Frequencies of Triplet State Phenoxide T1

mode	calc	assignment	corrected
		In-Plane	
1	471.3	C—O bend	444
2	568.2	C—C bend	519
3	609.2	C—C bend	556
4	864.9	C—C bend	790
5	941.0	C—C bend	859
6	1068.5	C—C bend	975
7	1083.7	C—H bend	995
8	1132.5	C—H bend	1040
9	1228.3	C—H bend	1127
10	1326.3	C—H bend	1217
11	1389.2	C—O stretch	1296
12	1457.2	C—H bend	1338
13	1475.5	C—C stretch	1346
14	1543.4	C—C stretch	1408
15	1615.2	C—C stretch	1473
16	1629.3	C—C stretch	1487
17	3246.3	C—H stretch	2955
18	3315.5	C—H stretch	3018
19	3324.2	C—H stretch	3026
20	3344.0	C—H stretch	3044
21	3354.4	C—H stretch	3054
		Out-of-Plane	
1	202.2	C—O bend	185
2	263.5	C—C bend	238
3	465.8	C—H bend	414
4	545.4	C—C bend	492
5	562.1	C—H bend	500
6	584.3	C—H bend	519
7	664.0	C—C bend	599
8	693.3	C—H bend	616
9	1087.2	C—H bend	967

TABLE 7: Dominant Configurations in FOCI for Comparison of Excited Singlet and Triplet Electronic Structure

			orbital occupancies[a]			
geometry	state	$\pi1$	$\pi2$	$\pi3$	$\pi4$	coefficient
			Neutral			
S1	S1	2	1	0	1	−0.521
		1	2	1	0	0.640
		2	1	1	0	−0.198
	S2	2	1	1	0	0.654
		1	2	0	1	0.399
		2	1	0	1	−0.264
		2	2	1	0	0.263
T1	S1	2	1	0	1	−0.517
		1	2	1	0	0.648
		2	1	1	0	−0.194
	T1	2	1	1	0	0.932
		1	2	0	1	−0.175
			Anion			
A0	S1	1	2	1	0	0.744
		2	1	0	1	−0.174
		1	2	2	1	0.134
A1	S1	2	1	1	0	0.801
		1	2	0	1	0.126
AT1	S1	2	1	1	0	0.841
		1	2	0	1	−0.180
		1	2	2	1	0.134
	T1	2	1	1	0	0.939

[a] There are 16 doubly occupied orbitals in these configurations. Not all important anion configurations are given since excitations are found from other more deeply bound orbitals, but those configurations are not significant in the analysis of quenching for which this table is used.

TABLE 8: Energies and Dipole Moments of the S0, S1, and T1 States of Phenol and the Phenoxide Anion[a]

	$-E$ (au); dipole (D); $\Delta E(1-2)$ (cm^{-1})		
geometry	state 1[b]	state 2[b]	spin
	Neutral		
S0	52.066 110 1.81	51.876 207 1.89 41 678.8 (239.9 nm)	0
S1	52.060 641 1.84	51.888 072 1.92 37 874.5 (264.0 nm)	0
T1[c]	52.049 856 1.79	51.868 849 1.88	0
T1	51.924 802 1.50	51.870 042 1.68	1
S0[c]	51.913 000 1.80	51.883 911 1.92	1
S0 reaction field	52.067 157 2.10	51.877 272 2.12 41 675.1 (240.0 nm)	0
S1 reaction field	52.061 735 2.17	51.889 229 2.18 37 860.8 (264.1 nm)	0
	Anion		
A0	51.493 343	51.350 568 31 334.8 (319.1 nm)	0
A1	51.470 158	51.360 890 23 981.5 (417.0 nm)	0
AT1[d]	51.471 701	51.341 657	0
AT1	51.370 739	51.330 406	1

[a] In addition to the total energy of the FOCI calculation, the dipole moment is given in debyes, the excitation energy in wavenumbers, and the wavelength in nanometers. [b] State 1 is the ground state, S0 for S = 0 and T1 for S = 1, and state 2 is the lowest excited state, S1 for S = 0 and T2 for S = 1. [c] Triplet states calculates at the geometry of the ground singlet state. [d] Singlet states calculated at the geometry of the ground triplet state.

TABLE 9: Oscillator Strengths[a]

	$f(D)$	$f(V)$
	Neutral	
S0	0.0158	0.0099
S1	0.0132	0.0079
	Anion	
A0	0.0778	0.0471
A1	0.0254	0.0169

[a] The dipole oscillator strength is represented by D, and V is the analogous velocity term.

Reaction field calculation of the excitation energy at either the S0 or S1 geometry determines a small shift. This result is in qualitative agreement with fluorescent studies of clusters of phenol with increasing numbers of water molecules[17] which show that a small shift is observed. However, the fluorescent shift in cyclohexane is about 2100 cm^{-1}. The present calculation estimates a shift closer to 3700 cm^{-1}. The calculated fluorescent shift is probably too large because the excitation energy to the S0 state is too high because of deficiencies in both the basis set and the level of correlation. For closed shell molecules whose first excitation energy is in the UV, there is mixing in the excited electronic structure of diffuse Rydberg components, which are not represented in the present calculation. When the geometry of the excited stae is optimized to S1, there is a greater lowering of the valence-type configurations relative to ionic Rydberg ones. The contribution of Rydberg configurations is less at the S1 or T1 geometry. The triplet energetics are, again, relatively less perturbed by Rydberg components for the valence states considered here. Higher order correlation calculations would also improve the singlet states more than the triplet states, which are calculated relatively lower in energy than the excited singlet states at the FOCI level. The phosphoresence energy is calculated at the T1 geometry as 28 200 cm^{-1} which is in good agreement with the experimental value of 28 500 cm^{-1}.[1]

The calculated anion energetics are relatively lower in energy than the apparent experimental values.[1-3] This reverses the situation for the neutral S1 state. The caveat about the basis set is stronger for this system. However, there also can be some difficulty in interpreting the experimental fluorescence energy. The fluorescence from the anion is known to be strongly quenched,[6,7] but a fluorescence spectrum is reported. The provenance of spectra attributed to the anion species has been questioned.[18] Hydrogen-bonded excited states are deduced also to fluoresce further to the red than the isolated phenol. Analysis of the quenching will shed light on this problem.

The quenching mechanism of the first excited singlet can be discussed in terms of the electronic structure of the excited states of the neutral and anion species. The dominant configurations of the neutral S1 excited state are different from the analogous anion state, as seen in Table 7, but the T1 state of both the neutral and anion species has the same dominant configuration. The fluorescing neutral S1 state is substantially higher in energy than the T1 state and is inhibited from quenching by this energy gap as well as the small configuration coefficient for a one-electron spin−orbit coupling. The S1 state is probably not as high in energy as the T2 state as calculated because of the larger error in calculating the singlet state relative to the triplet. On the other hand, the anion A1 state is much closer in energy to a T1 state. At the anion A1 geometry both states are dominated by the same electron configuration, allowing for direct spin−orbit coupling. The lifetime for fluorescence is short in the anion as a result. Coupling from the neutral singlet to the triplet at the S1 geometry is at least a factor of 4 smaller than the anion coupling just from the configuration coefficients. At the S0 geometry the neutral spin−orbit coupling should increase, but there is no evidence of a change in the fluorescent efficiency as a function of excitation energy in the first excited state band.[19] Relaxation in solution to the S1 geometry apparently prevails.

On the other hand, the anion may not have time to completely relax to the equilibrium geometry of the A1 state, depending on the rapidity of change of the electronic structure with geometry. The experimentally observed anion spectra would then be further to the blue than predicted here. The singlet dominant configurations change as a function of geometry for the anion. The difference in the electronic structure at A0 and A1 geometries is reflected in the difference in the absorption and emission oscillator strengths seen in Table 9. The larger calculated absorption oscillator strength agrees with the observations of increased absorption in the anion.[2]

Quenching in the neutral first excited state to the triplet has been reported by Bent and Hayon.[8] The anion triplet is not observed. The weak spin−orbit coupling would account for the observation of the neutral triplet. The anion triplet is predicted to form more readily with a dominant configuration that is just a single excitation from the dominant configuration of the ground state. However, the triplet is above the electron affinity of the phenoxyl radical[13] and will readily autodetach.

Supplementary Material Available: Tables listing the internal coordinates of the six optimized geometries, neutral S0, neutral S1, neutral T1, anion S0, anion S1, and anion T1 (6 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Becker, R. S. *Theory and Interpretation of Fluorescence and Phosphorescence*; Wiley-Interscience: New York, 1969.

(2) Creed, D. *Photochem. Photobiol.* **1984**, *39*, 563.

(3) Ross, J. B. A.; Laws, W. R.; Rousslang, K. W.; Wyssbrod, H. R. In *Topics in Fluorescence Spectroscopy, Vol. 3, Biochemical Applications*; Lakowicz, J. R., Ed.; Plenum Press: New York, 1992, pp 1−62.

(4) Berlman, I. *Handbook of Fluorescent Spectra of Aromatic Molecules*; Academic Press: New York, 1969.

(5) Chabalowski, C. F.; Garmer, D. R.; Jensen, J. O.; Krauss, M. *J. Phys. Chem.* **1993**, *97*, 4608.

(6) Feitelson, J. *J. Phys. Chem.* **1964**, *68*, 391.

(7) Grabner, G.; Kohler, G.; Zechner, J.; Getoff, N. *Photochem. Photobiol.* **1977**, *26*, 449.

(8) Bent, D. V.; Hayon, E. *J. Am. Chem. Soc.* **1975**, *97*, 2599.

(9) Schutz, M.; Burgi, T.; Leutwyler, S. *J. Mol. Struct.* (*Theochem*) **1992**, *276*, 117.

(10) Schutz, M.; Burgi, T.; Leutwyler, S.; Fischer, T. *J. Chem. Phys.* **1993**, *98*, 3763.

(11) Malmqvist, P.-A.; Roos, B. O. *Chem. Phys. Lett.* **1989**, *155*, 189.

(12) Anderson, S. L.; Goodman, L.; Krogh-Jespersen, K.; Ozkabek, A. G.; Zare, R. N.; Zheng, C. *J. Chem. Phys.* **1985**, *82*, 5329.

(13) Gunion, R. F.; Gilles, M. K.; Polak, M. L.; Lineberger, W. C. *Int. J. Mass Spectrom. Ion Processes* **1992**, *117*, 601.

(14) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *Gaussian 92*; Gaussian, Inc.: Pittsburgh, PA, 1992.

(15) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, A.; Matsunaga, S.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347.

(16) Abe, H.; Mikami, N.; Ito, M.; Udagawa, Y. *Chem. Phys. Lett.* **1982**, *93*, 217.

(17) Fuke, K.,; Kaya, K. *Chem. Phys. Lett.* **1983**, *94*, 97.

(18) Willis, K. J.; Szabo, A. G. *J. Phys. Chem.* **1991**, *95*, 1585.

(19) Kohler, G.; Getoff, N. *J. Chem. Soc., Faraday Trans. 1* **1976**, *73*, 2101.