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Density Functional Theory Study of Vibrational Spectra of Anthracene Neutral and Radical Cation

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Ab initio Hartree-Fock and Becke 3-Lee-Yang-Parr (B3LYP) density functional theory calculations using 6-31G* basis set were carried out to study the vibrational spectra of anthracene neutral (h_{10} and d_{10}) and radical cation (h_{10}). We report results of the fundamental vibrational frequencies obtained on the basis of the calculations. The assignments of fundamentals show a one-to-one correspondence between the observed and calculated fundamentals.

Introduction

Of growing interest is density functional theory (DFT) study since the methods predict relatively accurate molecular structures and vibrations with moderate computational effort.[1~8] It is indicated in the published results that DFT method reproduces experimental vibrational frequencies with higher accuracy than do the Hartree-Fock (HF) and second order Møller-Plesset perturbation theory (MP2) calculations.[1~8] Even when a uniform scaling is performed for the computed vibrational frequencies, DFT methods show better agreement with experiment than do the HF and MP2 methods.[1a,2,3] Some examples of the calculation on the vibrational frequencies of benzene are represented by Handy *et al.*[2] and Wheeless *et al.*,[4] in which MP2 calculations obtained by using 6-311G(d, p) basis set still underestimate the vibrational frequencies corresponding to the CCC out-of-plane bending, and overestimate that corresponding to a b2u mode which tends to dissociate into three acetylene molecules. On the other hand, these frequencies are accurately predicted by DFT methods using the Becke-Lee-Yang-Parr (BLYP) functional.[2,4]

Rauhut and Pulay (RP) applied the BLYP and B3LYP functional methods to 20 small molecules such as benzene, ether and methanol, etc. whose vibrational frequencies are exactly assigned, and they then derived uniform scaling factors, 0.995 and 0.963, having root mean square (rms) deviations of 26.2 and 18.5 cm^{-1}, respectively.[5] When these workers also applied these scaling factors to another 11 molecules such as aniline, ethanol and oxetane, etc., the rms deviations turned out to be 26.9 and 19.7 cm^{-1} for the BLYP and B3LYP methods, respectively.

The electronic-vibrational structures of anthracene (AN) and its derivatives are the subject of ongoing spectroscopic[9,10] and theoretical[11,12] investigations. It is well known in the literature that AN molecule fluoresces efficiently upon excitation of S_0 to S_1. Also the ultrafast dynamics of the van der Waals complexes of anthracene derivatives has been studied by time-resolved fluorescence spectroscopy.[10] Published results indicate that the vibrational frequencies appended to the 0_0^0 band origin in AN consist of fundamentals, overtones, second overtones, and combination bands.[9,10a-c] Thus the determination of fundamental vibrational frequencies and modes in

the ground-state is necessary to elucidate the vibronic spectra.

Numerous vibrational spectroscopic data have been reported on ground-state AN neutral (AN-h_{10}[14] and AN-d_{10}[15,16]), and on the radical cation (AN$^+$-h_{10}) in a matrix-isolated system.[17,18] Although the experimental works are excellent in the assignment of symmetry to the observed vibrational frequencies, there are, however, no assignment to a_u modes owing to the forbidden infrared and Raman selection rule. And also there is some ambiguity in the assignments of fundamental modes of AN-d_{10} and AN$^+$-h_{10}. Many workers have endeavoured to unambiguosly reproduce fundamentals of AN-h_{10}[11,12,17] and AN$^+$-h_{10}[17] and to assign their modes with *ab initio* HF calculations. Still large deviations are found between experiment and the calculations. Recently, the infrared spectra of AN-h_{10} and AN$^+$-h_{10} are more reliably reproduced by Langhoff with the B3LYP calculation using the 4-31G* basis set, in which multiple scaling factors were employed to reduce rms deviations.[7] Unfortuately, comparison between experiment and the calculations could be made for only some frequencies having relatively high intensities in the infrared spectra.[7]

By using the HF and B3LYP methods, we performed the normal vibrational mode analysis of AN-h_{10}, AN-d_{10}, and AN$^+$-h_{10} with the use of the expanded basis set 6-31G* to predict the spectral positions of the missing lines and to select fundamentals from the various vibrational frequencies reported experimentally. By using the uniform scaling factor reported by RP, we could predict the spectral positions of the molecules with the similar accuracy as predicted by Langhoff with the multiple scaling factors.[7] It is found in this study that DFT methods are sufficiently powerful to predict fundamentals and their intensities.

Calculations

The molecular vibrations were calculated at the HF and B3LYP levels of theory with 6-31G* basis set by using the Gaussian 94 program.[19] Vibrational frequencies were computed with the HF and B3LYP methods. They were scaled by 0.8929 (HF/6-31G*) and 0.963 (B3LYP/6-31G*). The frequencies and normal modes for AN were determined by dia-

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gonalizing the mass-weighted force constant matrix.

Results and Discussion

Our calculations show that anthracene radical cation turned out to have D_{2h} symmetry like anthracene neutral in the ground-state. The AN neutral and radical cation involve 66 fundamentals having the various symmetries of $12a_g + 5 a_u + 4b_{1g} + 11b_{1u} + 6b_{2g} + 11b_{2u} + 11b_{3g} + 6b_{3u}$. We seek to determine fundamentals making a one-to-one correspondence between the observed and calculated frequencies. Fundamentals having the same symmetries are well separated and thus the assignment is straight forward. The scaled vibrational frequencies and modes of AN-h_{10} and AN-d_{10} calculated with the HF and B3LYP methods are represented in Table 1. Our scaled frequencies of AN-h_{10} obtained from the B3LYP calculation are in excellent agreement with experiment and are found to have rms deviations of 30.98 and 19.30 cm^{-1} for the HF and B3LYP, respectively. Therefore we conclude that among the methods the B3LYP calculations are quite reliable in predicting the fundamentals.

However, the assignments of fundamentals of AN-d_{10} are less straightforward due to the missing lines. But reliable prediction of many fundamentals and modes of AN-d_{10} could be made by comparing the frequencies and modes of the protiated system with those of the deuterated counterpart. Our scaled frequencies obtained from the B3LYP calculation are in excellent agreement with experiments and are found to have rms deviations of 12.97 cm^{-1}. As expected, the ring torsional and deformation modes are not so sensitive to the deuterium substitution. However, the C-H stretching and bending frequencies correctly reflect the deuterium isotope effect.

For the AN$^+$-h_{10} system, we represent in Table 2 the calculated results along with a few observed vibrational peaks. The experimental frequencies are well correlated with the calculated values. It is quite interesting that the observed frequencies are also found to have the high intensities in the B3LYP and HF calculations.

Almost all the modes are delocalized over whole molecule and thus can not be assigned to several local bonds. This is a characteristic feature of cyclic compounds, particularly aromatic compounds.[17] Therefore we represent in Table 1 only the approximate mode descriptions.

a_g **symmetry.** Under D_{2h} symmetry, a_g modes are infrared inactive and Raman active. On the basis of our calculations and the reported infrared and Raman spectra of AN-h_{10}, we made a reliable one-to-one correspondence between the fundamentals reported experimentally and our calculated frequencies with the B3LYP and HF methods. Twelve frequencies which we identify as a_1 fundamentals are 397, 625, 754, 1007, 1164, 1264, 1412, 1480, 1556, 3027, 3048 and 3072 cm^{-1}. It is shown that the HF values deviate from the experimental data, particularly in the C-H stretching region.

For AN-d_{10}, among the twelve fundamentals, eleven fundamentals can be identified as 382, 602, 709, 842, 1156, 1388, 1402, 1534, 2258, 2266, and 2288 cm^{-1}, the frequencies based on the reported Raman spectra by Bree and Kidd.[15b]

For the radical cation, almost all of the frequencies are close to those of the protiated counterpart except those in the C-H stretching region in which the frequencies are found to be higher than those of the neutral system.

It is shown in the B3LYP calculation that most of the fundamentals involve more or less ring deformation and in-

Table 1. Comparison of the observed and calculated vibrational spectra of anthracene[a]

sym	No	Anthracene (h10)							Anthracene (d10)			Approx.[h] mode
		HF				B3LYP			B3LYP			
		freq	I_{IR}	I_{Ram}	DP[b]	freq	I_{IR}	exp[c]	freq	I_{IR}	exp[f]	
a_g	1	376	0.00	15.99	0.24	384	0.00	397	370	0.00	382	ring defm
	2	611	0.00	1.66	0.47	618	0.00	625	594	0.00	602	ring defm
	3	735	0.00	42.94	0.10	738	0.00	754	693	0.00	709	ring defm
	4	971	0.00	22.41	0.44	1002	0.00	1007	828	0.00	−	ip C-H bend, ring defm
	5	1152	0.00	27.05	0.18	1155	0.00	1164	835	0.00	842	ip C-H bend
	6	1225	0.00	203.89	0.19	1255	0.00	1264	1149	0.00	1156	ring defm, ip C-H bend
	7	1398	0.00	860.51	0.21	1391	0.00	1412	1378	0.00	1388	ring defm, ip C-H bend
	8	1468	0.00	71.19	0.57	1478	0.00	1480	1399	0.00	**1402**	ip C-H bend, ring defm
	9	1577	0.00	143.22	0.52	1550	0.00	1556	1526	0.00	1534	ring defm, ip C-H bend
	10	2993	0.00	19.34	0.13	3056	0.00	3027	2257	0.00	2258	sym $C_{9,10}$-H str
	11	3002	0.00	305.06	0.61	3065	0.00	3048	2262	0.00	2266	C-H str
	12	3024	0.00	688.06	0.13	3089	0.00	3072	2290	0.00	2288	tot sym C-H str
a_u	1	120	0.00	0.00	0.00	120	0.00	137[d]	109	0.00	**110**	ring tor
	2	486	0.00	0.00	0.00	489	0.00	552[d]	437	0.00	−	ring tor
	3	734	0.00	0.00	0.75	731	0.00	743	621	0.00	−	ring tor
	4	855	0.00	0.00	0.00	839	0.00	858	729	0.00	−	oop C-H bend
	5	1001	0.00	0.00	0.75	953	0.00	958[d]	796	0.00	−	oop C-H bend
b_{1g}	1	227	0.00	7.14	0.75	230	0.00	244	215	0.00	228	ring tor
	2	474	0.00	3.80	0.75	471	0.00	479	405	0.00	**415**	ring tor

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Table 1. Continued

sym	No	HF				B3LYP			B3LYP			Approx.[h] mode
		freq	I_{IR}	I_{Ram}	DP[b]	freq	I_{IR}	exp[c]	freq	I_{IR}	exp[f]	
	3	762	0.00	11.14	0.75	747	0.00	747[d]	601	0.00	613	oop C-H bend
	4	978	0.00	4.76	0.75	922	0.00	956	745	0.00	—	oop C-H bend
b_{1u}	1	224	1.79	0.00	0.38	227	1.29	234	211	1.10	220	ring defm
	2	625	3.43	0.00	0.75	637	0.80	653	607	0.47	592[g]	ring defm
	3	882	4.70	0.00	0.36	884	1.72	906	813	0.56	822[g]	ring defm, ip C-H bend
	4	1139	5.35	0.00	0.74	1138	4.68	1147	868	7.83	879	ip C-H bend, ring defm
	5	1242	5.88	0.00	0.40	1250	8.21	1272	1022	0.46	—	ip C-H bend, ring defm
	6	1298	3.09	0.00	0.44	1298	4.23	1317	1238	5.92	1258	ring defm, C-H bend
	7	1440	0.42	0.00	0.54	1445	1.22	1448	1378	0.01	1406	ip C-H bend, ring defm
	8	1648	11.87	0.00	0.43	1625	6.85	1620	1588	1.56	1584	ring defm, ip C-H bend
	9	2991	2.87	0.00	0.58	3054	10.71	3007	2253	1.41	2248	antisym $C_{9,10}$-H str
	10	2996	13.32	0.00	0.55	3060	16.42	3053	2258	13.29	2264	C-H str
	11	3013	95.01	0.00	0.75	3077	73.50	3084	2280	48.59	2283	C-H str
b_{2g}	1	261	0.00	0.01	0.75	263	0.00	287	239	0.00	261	ring tor
	2	567	0.00	0.08	0.75	569	0.00	580	497	0.00	—	ring tor
	3	760	0.00	14.66	0.75	754	0.00	773	627	0.00	644	oop C-H bend
	4	838	0.00	4.10	0.75	820	0.00	—	642	0.00	659	oop C-H bend
	5	913	0.00	0.67	0.75	886	0.00	896	764	0.00	761	oop $C_{9,10}$-H bend
	6	1002	0.00	5.02	0.75	954	0.00	952[d]	827	0.00	—	oop C-H bend
b_{2u}	1	582	10.25	0.00	0.71	595	8.18	601	573	8.06	575	ring defm
	2	767	0.20	0.00	0.62	795	0.00	809	693	0.23	703	ring defm
	3	950	1.69	0.00	0.61	998	3.94	998	823	0.01	**824?**	ip C-H bend
	4	1032	2.43	0.00	0.40	1132	1.33	1124	824	5.06	824	ip C-H bend
	5	1150	0.45	0.00	0.67	1156	1.62	1167	933	0.01	**941**	ip C-H bend
	6	1266	5.64	0.00	0.72	1342	3.98	1346[e]	1261	0.00	**1245**	ring defm, ip C-H bend
	7	1381	0.02	0.00	0.73	1381	0.61	1397	1300	1.32	**1298**	ip C-H bend, ring defm
	8	1441	1.83	0.00	0.71	1445	1.87	1460[e]	1369	0.79	1335?	ip C-H bend, ring defm
	9	1548	8.46	0.00	0.68	1538	4.45	1534	1501	3.67	1493	ip C-H bend, rinf defm
	10	2999	0.74	0.00	0.66	3063	0.00	3021	2260	0.13	2267	C-H str
	11	3024	94.45	0.00	0.12	3089	77.47	3048	2290	38.60	—	C-H str
b_{3g}	1	378	0.00	3.56	0.75	379	0.00	397	353	0.00	**369**	ring defm
	2	510	0.00	12.95	0.75	515	0.00	522	493	0.00	502	ring defm
	3	888	0.00	0.86	0.75	893	0.00	903	798	0.00	816	ring defm, ip C-H bend
	4	1082	0.00	0.91	0.75	1093	0.00	1102	870	0.00	**886**	ip C-H bend
	5	1169	0.00	58.40	0.75	1178	0.00	1187	925	0.00	943	ip C-H bend
	6	1259	0.00	0.37	0.75	1259	0.00	1273	1020	0.00	—	ip C-H bend
	7	1374	0.00	2.22	0.75	1375	0.00	—	1219	0.00	1233	ip C-H bend, ring defm
	8	1595	0.00	4.85	0.75	1580	0.00	1574	1537	0.00	—	ring defm, ip C-H bend
	9	1653	0.00	39.12	0.75	1623	0.00	1632	1596	0.00	1615	ring defm, ip C-H bend
	10	2994	0.00	30.01	0.75	3054	0.00	3017	2254	0.00	—	C-H str
	11	3012	0.00	208.91	0.75	3077	0.00	3054	2279	0.00	2276	C-H str
b_{3u}	1	89	1.10	0.00	0.00	90	0.86	106	85	0.80	102	ring tor
	2	376	0.31	0.00	0.75	374	0.08	380	332	0.11	**349**	ring tor
	3	470	21.09	0.00	0.75	468	12.77	474	396	16.57	397	ring tor
	4	736	89.31	0.00	0.00	718	60.23	737	550	26.41	560	oop C-H bend
	5	901	71.72	0.00	0.00	860	54.70	883	702	14.68	722	oop $C_{9,10}$-H bend
	6	982	6.10	0.00	0.00	927	6.47	956	764	16.40	784	oop C-H bend

[a] Vibrational frequencies in cm^{-1}. [b] Depolarization ratio. [c] Otherwise noted elsewhere, the frequencies from the result of Bakke *et al.* (ref 14d). [d] ref 14a-c. [e] ref 17. [f] ref 15, the numbers noted by bold face refer to our new assignment based on the deuterium isotope effect in the vibrational shift, [g] ref 16, [h] Mode descriptions are from the B3LYP/6-31G*, ip: in-plane; oop: out-of-plane, the modes assigned are sorted in the order of their contributions to the vibrational motions.

Table 2. Comparison of observed and calculated vibrational spectra of anthracene radical cation[a]

sym	No.	HF/6-31G*				B3LYP/6-31G*		exp[c]	exp[d]
		freq	I_{IR}	I_{Ram}	DP[b]	freq	I_{IR}		
a_g	1	371	0.00	269.14	0.14	381	0.00		
	2	590	0.00	375.24	0.50	604	0.00		
	3	726	0.00	770.74	0.17	738	0.00		
	4	1006	0.00	2745.65	0.50	1020	0.00		
	5	1153	0.00	351.16	0.16	1167	0.00		
	6	1209	0.01	5687.58	0.29	1249	0.00		
	7	1309	0.00	741.86	0.72	1374	0.00		
	8	1490	0.00	1869.33	0.58	1493	0.00		
	9	1569	0.00	269.45	0.38	1553	0.00		
	10	3021	0.00	88.69	0.30	3083	0.00		
	11	3028	0.00	153.91	0.75	3093	0.00		
	12	3049	0.00	591.86	0.40	3114	0.00		
a_u	1	117	0.00	0.00	0.75	117	0.00		
	2	471	0.00	0.00	0.75	467	0.00		
	3	708	0.00	0.00	0.75	711	0.00		
	4	892	0.00	0.00	0.75	871	0.00		
	5	1028	0.00	0.00	0.75	986	0.00		
b_{1g}	1	214	0.00	5.17	0.75	214	0.00		
	2	448	0.00	1.80	0.75	447	0.00		
	3	769	0.00	0.01	0.75	748	0.00		
	4	988	0.00	2.69	0.75	951	0.00		
b_{1u}	1	236	14.41	0.00	0.74	225	0.42		
	2	631	0.50	0.00	0.74	643	0.01		
	3	876	4.82	0.00	0.73	881	0.53		
	4	1112	4.64	0.00	0.39	1123	0.12		
	5	1232	3.29	0.00	0.73	1266	21.42	1291(0.07)[e]	1290(0.06)
	6	1269	27.46	0.00	0.74	1277	5.77		1315(0.06)
	7	1442	84.41	0.00	0.74	1442	19.41		1430(0.01)
	8	1582	18.52	0.00	0.35	1570	58.05		1586(0.14)
	9	3019	0.11	0.00	0.75	3081	0.32		
	10	3026	31.98	0.00	0.75	3090	0.48		
	11	3039	5.32	0.00	0.44	3105	1.73		
b_{2g}	1	266	0.00	7.94	0.75	264	0.00		
	2	540	0.00	1.15	0.75	541	0.00		
	3	716	0.00	3.77	0.75	732	0.00		
	4	863	0.00	1.33	0.75	841	0.00		
	5	926	0.00	50.31	0.75	919	0.00		
	6	1029	0.00	19.17	0.75	988	0.00		
b_{2u}	1	580	2.29	0.00	0.60	587	1.87		
	2	793	32.86	0.00	0.22	805	3.36		
	3	1008	31.12	0.00	0.16	1020	6.01	1034(0.20)	
	4	1086	30.21	0.00	0.18	1155	0.75		1183(0.01)?
	5	1136	2030.51	0.00	0.13	1179	161.32	1188(0.98)	1189(0.70)
	6	1209	1138.72	0.04	0.29	1341	310.77	1341(1.00)	1341(1.00)
	7	1322	449.39	0.00	0.26	1395	143.87	1418(0.97)	1418(0.86)
	8	1447	31.07	0.00	0.53	1447	55.86	1457(0.05)	1457(0.07)
	9	1534	41.51	0.00	0.16	1528	83.14	1540(0.04)	1540(0.15)
	10	3027	8.80	0.00	0.19	3092	1.42		
	11	3048	18.09	0.00	0.45	3114	3.16		
b_{3g}	1	401	0.00	5284.88	0.75	371	0.00		
	2	537	0.00	7358.39	0.75	499	0.00		
	3	885	0.00	17.43	0.75	891	0.00		
	4	1082	0.00	207.36	0.75	1086	0.00		

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Table 2. Continued

sym	No.	HF/6-31G*				B3LYP/6-31G*		exp[c]	exp[d]
		freq	I_{IR}	I_{Ram}	DP[b]	freq	I_{IR}		
	5	1213	0.00	9619.26	0.75	1176	0.00		
	6	1266	0.00	4159.98	0.75	1264	0.00		
	7	1391	0.00	19.15	0.75	1387	0.00		
	8	1531	0.00	1033.58	0.75	1509	0.00		
	9	2401	0.00	>9999.99	0.75	1530	0.00		
	10	3025	0.00	5777.89	0.75	3090	0.00		
	11	3039	0.00	3915.57	0.75	3105	0.00		
b_{3u}	1	83	1.59	0.00	0.75	85	1.62		
	2	372	2.71	0.00	0.75	372	0.12		
	3	423	31.54	0.00	0.75	432	22.79	432(0.07)	
	4	759	102.49	0.00	0.75	740	77.61		748(0.26)
	5	907	38.37	0.00	0.75	895	31.05	912(0.15)	912(0.09)
	6	992	5.64	0.00	0.75	959	8.19		

[a] Vibrational frequencies in cm^{-1}. [b] Depolarization ratio. [c] ref 17. [d] ref 18. [e] The numbers in the parentheses are relative intensities.

plane C-H bending.

a$_u$ **symmetry.** The modes are infrared and Raman inactive vibrations. Five fundamentals at 137, 552, 743, 858 and 958 cm^{-1} are observed in the Raman spectrum.[14] For the perdeuterated anthracene, only one fundamental is found at 110 cm^{-1}. Most of the fundamentals include more or less ring torsions and out-of-plane C-H bending. The calculated fundamentals in the deuterated and radical cation systems can not be compared with the experimental values due to the missing lines.

b$_{1g}$ **symmetry.** Four fundamentals attributable to b_{1g} mode are 244, 479, 747, and 956 cm^{-1}. For the deuterated molecule, only three fundamentals are identified as 228, 415, and 613 cm^{-1}. In the ring torsional modes, the isotope effect is quite small, reflecting the skeletal vibration of the molecule. The frequencies of the radical cation are very close to those of the neutral molecule. Almost all of the vibrations include out-of-plane bending modes, and some of them involve the ring torsion.

b$_{1u}$ **symmetry.** Eleven modes which we identify as b_{1u} are 234, 653, 906, 1147, 1272, 1317, 1448, 1620, 3007, 3053, and 3084 cm^{-1}. Except fundamental $9b_{1u}$ (3007 cm^{-1}), the B3LYP calculation reproduces quite accurately the experimental data. It is shown that the HF values greatly underestimate the experimental frequencies particularly in the C-H stretching region. In the deuterated analog, only ten fundamentals are identified as b_{1u}. These are 220, 592, 822, 879, 1258, 1406, 1584, 2248, 2264, and 2283 cm^{-1}. These fundamentals are well correlated with our B3LYP calculation, correctly reflecting the isotope effect. The B3LYP method is also found to correctly reproduce the vibrational frequencies of the radical cation.

Almost all of the vibrations include the ring deformation, in-plane C-H bending and stretching.

b$_{2g}$ **symmetry.** Five fundamentals attributable to b_{2g} mode are 287, 580, 773, 896, and 952 cm^{-1}. The previously assigned fundamentals corresponding to the $4b_{2g}$ and $5b_{2g}$, 896 and 916 cm^{-1} are not correlated with the calculated frequencies. But the corresponding frequencies in the deu-

terated molecules are well predicted. As seen in Table 1, we leave the $4b_{2g}$ fundamental unassigned and assume that the peak at 896 cm^{-1} is attributed to the $5b_{2g}$.

For AN-d_{10}, only four fundamentals are identified as b_{2g}. These are 261, 644, 659, and 761 cm^{-1}. However, it is found in the deuterated system that the $4b_{2g}$ value (659 cm^{-1}) is found to be very close to the B3LYP value.

Almost all of the vibrations include the out-of-plane bending and ring torsional modes.

b$_{2u}$ **symmetry.** Eleven modes which we identify as b_{2u} are 601, 809, 998, 1124, 1167, 1346, 1397, 1460, 1534, 3021, and 3048 cm^{-1}. Two fundamentals, 1346 ($6b_{2u}$) and 1460 cm^{-1} ($8b_{2u}$), are from the result of Szczepanski.[17] The Bakke's value, 1494 cm^{-1}, is found to deviate very much from our calculated value, 1445 cm^{-1}. For AN-d_{10}, nine fundamentals could be identified as b_{2u}. These are 575, 703, 824, 941, 1245, 1298, 1335, 1493, and 2267 cm^{-1}. It is assumed that the $3b_{2u}$ peak is immersed in the $4b_{2u}$ peak (824 cm^{-1}).

Here it is also found that the C-H frequencies of AN$^+$-h_{10} are higher than those of AN-h_{10}.

Most of the vibrations include in-plane C-H bending, ring deformation, and C-H stretching modes.

b$_{3g}$ **symmetry.** Ten fundamentals attributable to the b_{3g} mode are 397, 522, 903, 1102, 1187, 1273, 1574, 1632, 3017 and 3054 cm^{-1}. Like the $4b_{2g}$ fundamental, the previously assigned fundamental $7b_{3g}$, 1433 cm^{-1} deviate very much from the calculated value, and thus we leave it unassigned.

For AN-d_{10}, only eight fundamentals are identified as b_{3g}. These are 367, 502, 816, 886, 943, 1233, 1615, and 2276 cm^{-1} whose values are very close to our B3LYP frequencies. The fundamentals at 367 and 886 cm^{-1} are newly assigned.

In the skeletal ring deformation, the frequencies such as fundamentals $8b_{3g}$ and $9b_{3g}$ of the cation are much lower than those corresponding to the neutral system, reflecting the decrease of the bond orders in the rings.

Almost all the vibrations include the out-of-plane bending and ring torsional modes.

b$_{3u}$ **symmetry.** Six modes which we identify as b_{3u} are 106, 380, 474, 737, 883, and 956 cm^{-1}. For AN-d_{10}, fundamen-

tals we identify as b_{3u} are 102, 349, 397, 560, 722, and 784 cm^{-1} which correctly match the calculated fundamentals. Most of the vibrations include in-plane C-H bending, ring deformation, and C-H stretching modes.

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