Anharmonic Force Fields of Naphthalene-h_8 and Naphthalene-d_8

Elisabetta Cané, Andrea Miani,[†] and Agostino Trombetti*

Dipartimento di Chimica Fisica e Inorganica, Facoltà di Chimica Industriale, Università di Bologna, Viale Risorgimento 4, 40136 Bologna, Italy

Received: February 27, 2007; In Final Form: May 7, 2007

The cubic and the quartic semidiagonal anharmonic force fields of naphthalene-h_8 and -d_8 are obtained using density functional theory (DFT) with the B9-71 functional and a triple-ζ plus double polarization (TZ2P) basis set. The fundamental frequencies computed by second-order vibrational perturbation theory are in very good agreement with the experimental data, with a mean absolute deviation (MAD) of 4 cm^{-1} for $C_{10}H_8$ and 6 cm^{-1} for $C_{10}D_8$. Some of the fundamental frequencies have been reassigned on the basis of the present results. Only CH stretchings seem to be significantly affected by Fermi resonances, with two shifts larger than 10 cm^{-1}. Calculated infrared harmonic intensities reproduce the experimental data within 15%, with the exception of CH stretchings affected by a larger error. Scale factors from $C_{10}H_8$ have been tested by deriving the fundamental frequencies of $C_{10}D_8$ from the theoretical harmonic ones. These fundamentals are in nice agreement with those obtained from the $C_{10}D_8$ anharmonic force field. These results support the use of scale factors to calculate the vibration spectra of larger polycyclic aromatic hydrocarbons of great astrophysical interest.

1. Introduction

In recent years, ab initio calculations of the anharmonic force fields of large molecules have been found to be of great help in the assignment of their vibrational spectra.[1−5] At the moment, only density functional theory (DFT) methods can be employed to compute the cubic and quartic force field constants for large molecules[3,6] due to their favorable scaling with respect to the number of electrons when compared to other correlated methods. Benzene is one of the largest molecules whose anharmonic force field based on DFT methods has been reported on;[1,3] so far the fundamental frequencies for naphthalene have been obtained through scaling the DFT harmonic frequencies.[7−12] In this work the harmonic constants and the ab initio anharmonic force fields for naphthalene-h_8 and naphthalene-d_8 are calculated, and their vibrational spectra are thus assigned.[13] The accuracy of the calculations are tested by comparing the ab initio fundamentals with those obtained scaling the harmonic frequencies, in order to evaluate the feasibility of the scaling procedure for larger polycyclic aromatic hydrocarbons (PAHs). Naphthalene is the simplest among PAHs, which are currently of great astrophysical interest, due to the hypothesis[14,15] that they, together with the corresponding cations, are the carriers of the Unidentified Infrared Bands, first observed in the interstellar medium in 1973.[16] Due to the large computational effort required to calculate the semidiagonal quartic anharmonic force field for a polyatomic molecule and thus the ab initio spectral anharmonic shifts for the largest PAHs believed to be responsible for the signals,[15] scaling the harmonic frequencies could be the only possible way at present to predict the vibrational spectra for the molecules belonging to this very important class. The intensities of both the Raman and the infrared active bands have been calculated, at the harmonic oscillator level, and have been compared to the experimental ones of the infrared active bands.

2. Computational Details

All computations have been performed with the Gaussian 03 system programs,[17] using the B9-71 functional[18] in combination with the TZ2P basis set[19] since they provided the best performances, especially for organic molecules.[3] The B3LYP/6-31+G(d,p) method is reported[20] to provide the fundamental frequencies of molecules such as H_2CO and C_2H_4 as accurately as those obtained with the B9-71/TZ2P method. The results of the anharmonic force field calculations have been found to be very sensitive to the KS integration grid.[21] In the present study a (150,770) grid for the KS integration and a (75,194) grid for the CPKS steps have been used. A larger KS integration grid (200,974) has been recently recommended,[22] but this has shown to be too computationally demanding for naphthalene. As a test, the fundamental frequencies for the azabenzenes were recalculated using the smaller (150,770) grid and found to be within 1 cm^{-1} of those which were obtained using the larger grid.[21] A step of 25 pm has been chosen in the numerical calculation of the cubic and quartic force field constants. The fundamental frequencies for the azabenzenes obtained with this step differed at most 0.5 cm^{-1} from those obtained[3] employing an elaborate function of the harmonic frequencies. Fundamental frequencies have been obtained, correcting the harmonic frequencies by means of second-order vibrational perturbation theory, which requires the full cubic and diagonal and semidiagonal quartic force field constants only. Fermi resonances occurring between states within 100 cm^{-1} have been computed, diagonalizing the Hamiltonian matrix containing the resonant levels and the corresponding interaction terms.[2,22]

3. Results and Discussion

3.1. Naphthalene-h_8. The calculated harmonic and fundamental frequencies are listed in Table 1, together with the

---

* Corresponding author. Telephone: +390512093706. Fax: +39051209-3690. E-mail: agostino.trombetti@unibo.it.

[†] Present address: Statistical and Biological Physics Sector, SISSA/ISAS, via Beirut 4, 34014, Trieste, Italy.

10.1021/jp071610p CCC: $37.00

TABLE 1: Computed and Observed Fundamental Frequencies, Computed Harmonic Frequencies (cm^{-1}), and Computed Intensities[a] of Naphthalene-h_8

		B9-71/TZ2P calculated			experiment
	mode	harmonic frequencies	intensities	fundamental frequencies	experiment fundamental frequencies
a_g	1	3185	522	3059	3057
	2	3160	210	3044	3051
	3	1606	36	1569	1576
	4	1487	61	1460	1464
	5	1393	177	1359	1383
	6	1182	0.84	1168	1168
	7	1041	41	1025	1025
	8	769	41	757	764
	9	516	17	512	513
a_u	10	990		972	
	11	846		830	
	12	633		621	
	13	183		177	
b_{1g}	14	960	2.9	940	952
	15	725	0.59	714	726
	16	392	1.6	383	390
b_{1u}	17	3173	39	3067	3065
	18	3155	4.4	3008	3008
	19	1631	3.8	1595	1602
	20	1415	4.6	1388	1392
	21	1283	6.8	1265	1268
	22	1147	5.0	1130	1130
	23	804	0.21	794	796
	24	362	1.4	359	359
b_{2g}	25	996	0.41	977	979
	26	894	3.7	877	880
	27	783	1.2	768	773
	28	475	0.22	466	465
b_{2u}	29	3184	28	3059	3057
	30	3158	0.29	3024	3042
	31	1542	8.8	1504	1514
	32	1386	0.86	1358	1361
	33	1227	0.74	1210	1210
	34	1163	0.79	1144	1135
	35	1030	8.0	1012	1012
	36	629	3.6	624	620
b_{3g}	37	3172	138	3055	3057
	38	3154	13	3021	3018
	39	1661	9.3	1620	1629
	40	1485	3.1	1459	1458
	41	1266	4.1	1239	1240
	42	1167	6.3	1148	1145
	43	948	0.03	935	936
	44	514	9.4	508	509
b_{3u}	45	979	4.0	959	959
	46	796	124	783	782
	47	482	23	473	473
	48	170	2.9	166	166

[a] Infrared intensities are in km/mol, and Raman scattering activities are in $Å^4$/amu.

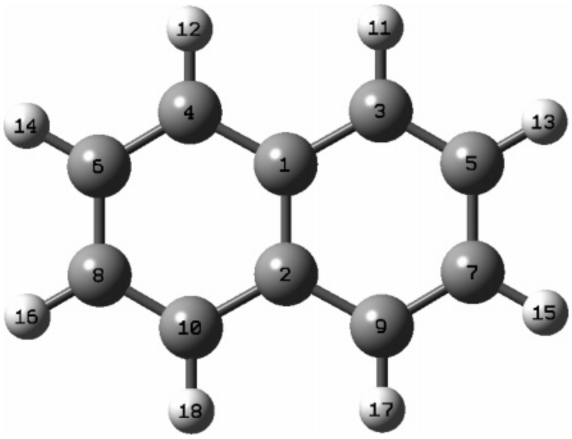

Figure 1. Atom indexing for naphthalene adopted in the force field calculation.

experimental data of fundamentals derived from infrared high-resolution gas-phase spectra,[7] Ar matrix spectra,[23] and oriented crystal spectra,[24] and from Raman spectra of powder or crystal of naphthalene.[25,26] The accuracy of experimental data ranges from 0.5 cm^{-1}, in the case of gas-phase spectra, to 4 cm^{-1} for matrix or solid-state Raman spectra. In addition, the experimental frequencies from the condensed-phase spectra are affected by a phase shift of a few wavenumbers (cm^{-1}) compared to the corresponding ones from gas-phase spectra. The assignments of naphthalene-h_8 fundamentals have been extensively discussed,[7−12] but some revisions must be made according to the results of Table 1. In the following, the discussion on CH stretching mode assignments has been moved to subsection 3.2 since they are peculiarly affected by strong Fermi resonances that complicate the interpretation of the experimental data. Six of seven a_g computed fundamentals agree fairly well with the accepted experimental assignments, with a maximum absolute deviation (MAD) of 7 cm^{-1} and a mean deviation of 3 cm^{-1}. The ν_6 mode is assigned to the experimental band centered at 1168 cm^{-1} instead of 1145 cm^{-1}, differently from that previously reported.[26] However, the ν_5 frequency is calculated at 1359 cm^{-1}, a value that differs 24 cm^{-1} from the experiment, observed at 1383 cm^{-1}. The ν_5 mode corresponds to the "double Kekulè" vibration, which was found to be quite sensitive to the basis set,[9] and involves mainly the $C_1{=}C_2$ bond stretching (see Figure 1. for atom indexing). The assignment of ν_5 to 1383 cm^{-1} has been indicated in all previous analyses of experimental spectra and must be considered right. Since the Fermi resonances involving the ν_5 mode have been accounted for in the computation procedure, it is apparent that this model fails to reproduce the "double Kekulè" vibration with the accuracy of the other a_g vibrations. In case of the a_u modes, forbidden in both infrared and Raman spectra, we fully agree with Pulay et al.[8] and Martin et al.[9] that the reported experimental frequencies are unreliable. Thus, these calculated fundamentals must be considered the closest estimates of the experimental data. The MAD of calculated frequencies of the b_{1g} fundamentals is 10 cm^{-1}, the worst performance in all symmetry classes, according to the most reliable assignments reported in Table 1, from Stenman[25] and Hanson and Gee.[26] The b_{2g} calculated fundamentals are in excellent agreement with the experimental frequencies reported by Pietilä and Stenman.[27] In the case of b_{3g} fundamentals, only one significant change has been introduced in the accepted assignments:[7,8] ν_{40}, calculated at 1459 cm^{-1}, is assigned to the band observed in the Raman spectrum at 1458 cm^{-1}. Hanson and Gee[26] favored this assignment of ν_{40} mode instead of that at 1443 cm^{-1}. The resulting MAD, 3 cm^{-1}, is very good. Gas-phase spectra[7] are the most important source of information as far as the infrared active fundamental frequencies are concerned, because it is possible to infer the symmetry of the transitions from the contours of the recorded bands. Low-temperature solid matrix spectra,[23] in which band overlaps are avoided, and oriented single-crystal spectra,[24] furnish other valuable experimental data. The b_{1u} modes are easily assigned with the exception of ν_{23}, calculated at 794 cm^{-1}. This elusive fundamental has been previously reported at about 740 and 810 cm^{-1}, but it was pointed out as "probably never identified"[8] and "probably not observed".[9] The ν_{23} calculated fundamental is very close to the strongest infrared absorption band of naphthalene-h_8, ν_{46}, at 783 cm^{-1}, with a theoretical intensity ratio $I_{23}/I_{46} = 1/550$. A weak absorption at about 796 cm^{-1} has been observed in the Ar matrix spectra, in very nice agreement with the ν_{23} calculated frequency, so this absorption band is assigned as ν_{23} in the present paper. The obtained MAD is 3 cm^{-1}. The b_{2u} fundamentals can be assigned without doubts from the B-type band contour observed

TABLE 2: Computed and Observed Fundamental Frequencies, Computed Harmonic and Deperturbed Fundamentals (cm^{-1}) of the CH Stretching Mode of Naphthalene-h_8, and Indexing of $v_n = v_m = 1$ States Involved in Fermi Resonances

		calculated			experiment	
	mode	harmonic	deperturbed	fundamental	fundamental	$v_n = v_m = 1$ states in Fermi resonance
a_g	1	3185	3060	3059	3057	3,4 3,3 31,31 19,19 40,39
	2	3160	3037	3044	3051	3,4 3,3 31,31 19,19 40,39
b_{1u}	17	3173	3052	3067	3065	3,19 4,19 31,39
	18	3155	3029	3008	3014	3,19 4,19 31,39
b_{2u}	29	3184	3056	3059	3057	3,31 19,40 20,39
	30	3158	3029	3024	3042	3,31 19,40 20,39
b_{3g}	37	3172	3049	3055	3057	31,19 3,39 4,39 5,39 3,40
	38	3154	3024	3021	3018	31,19 4,39 5,39 3,40

in gas-phase spectra. The MAD equal to 3 cm^{-1} is obtained from six b_{2u} vibration modes. The four C-type bands assigned to b_{3u} symmetry agree with the computed fundamentals within 1 cm^{-1}.

3.2. CH Stretching Modes of Naphthalene-h_8. The assignments of the CH stretching vibrations have been the most critical part in the previously reported analyses[7–12] of the vibration spectra of this molecule. Three CH stretching modes out of eight have been assigned quite firmly: ν_1 at 3057 cm^{-1},[26] ν_{17} at 3065 cm^{-1},[7] and ν_{29} at 3078 cm^{-1}.[7] Since the band intensity of the other five modes is expected to be weak, the two infrared active modes, ν_{18} and ν_{30}, could be almost completely overlapped by the ν_{17} and ν_{29} bands in the infrared gas spectrum. Furthermore, the Raman active bands are reported without reliable scattering tensors being available for the analysis. The assignments proposed in Table 2 differ from the most accepted ones. As far as the Raman active modes are concerned, ν_1 has been kept assigned to the band at 3057 cm^{-1}, while ν_2 is assigned to the 3051 cm^{-1} band,[25,26] instead of at 3008 cm^{-1}, on the basis of the calculated fundamental frequency, notwithstanding the uncertain scattering tensor data. The b_{3g} ν_{37} and ν_{38} fundamentals are assigned to 3057 and 3018 cm^{-1}, respectively, on the basis of the calculated frequencies. In the case of the infrared active modes, we agree with the previous assignment of ν_{17} to the band observed at 3065 cm^{-1}. Referring to the ν_{18}, ν_{29}, and ν_{30} modes, several experimental data sources must be considered and compared. Broude and Umarov[24] recorded the infrared polarized spectrum of crystal naphthalene and observed three absorptions of the right symmetry at 3004, 3068, and 3048 cm^{-1} that could be assigned as ν_{18}, ν_{29}, and ν_{30}, respectively. As a consequence, we assigned the three bands observed in the gas spectrum[7] at 3014, 3057, and 3042 cm^{-1} as ν_{18}, ν_{29}, and ν_{30}. The assignments from Broude and Umarov analysis[24] have been based on the measurement of the polarization direction of the infrared absorption of naphthalene single crystal. In gas-phase spectra the right band contour has been observed only for ν_{29}, while the absorptions assigned as ν_{18} and ν_{30} are too weak and are overlapped by stronger bands to draw a safe conclusion on the band symmetry. The MAD of the CH stretching modes, according to the assignments listed in Table 2, is equal to 3 cm^{-1}, based on experimental evidence corroborated by the values of the computed fundamentals. The Fermi resonances mainly affecting the eight CH modes are also listed in Table 2, together with the deperturbed frequencies of fundamentals obtained by removing the contribution of the perturbations.

The reliability of this anharmonic force field in reproducing the vibration spectrum of naphthalene-h_8 is confirmed by an overall MAD of 4 cm^{-1}, from the 44 modes considered for the assignments. This can be compared to a previous MAD obtained from scaled harmonic frequencies,[8,9] which is as twice as large.

TABLE 3: Computed and Observed Fundamental Frequencies, Computed Harmonic Frequencies (cm^{-1}), and Computed Intensities[a] of Naphthalene-d_8

		B9-71/TZ2P calculated			
	mode	harmonic frequencies	intensities	fundamental frequencies	experiment fundamental frequencies
a_g	1	2361	203	2282	2292
	2	2333	78	2251	2273
	3	1578	38	1544	1551
	4	1398	239	1364	1387
	5	1314	11	1289	1294
	6	874	54	863	862
	7	847	4.9	838	840
	8	699	19	688	697
	9	497	9.3	492	496
a_u	10	817		806	
	11	663		654	
	12	545		535	
	13	165		160	
b_{1g}	14	770	3.9	757	766
	15	547	1.6	539	547
	16	345	1.0	337	348
b_{1u}	17	2349	25	2264	2279
	18	2326	0.98	2250	2255
	19	1582	0.26	1545	1549
	20	1268	3.4	1254	1259
	21	1061	0.01	1046	1035
	22	894	7.3	885	885
	23	746	0.19	737	737
	24	330	1.2	326	326
b_{2g}	25	852	4.6	838	836
	26	781	1.8	770	762
	27	650	0.74	638	650
	28	419	0.01	411	416
b_{2u}	29	2361	13	2291	2301
	30	2330	0.56	2250	2260
	31	1472	3.4	1438	1446
	32	1336	0.14	1309	1312
	33	1105	0.28	1088	1084
	34	848	0.28	839	836
	35	841	6.6	829	829
	36	603	3.8	598	594
b_{3g}	37	2348	54	2267	2276
	38	2324	11	2248	2261
	39	1630	6.3	1592	1603
	40	1385	4.1	1357	1359
	41	1037	0.66	1023	1025
	42	892	2.3	880	881
	43	840	4.4	830	828
	44	498	9.3	492	492
b_{3u}	45	807	5.7	794	792
	46	639	48	629	629
	47	408	27	401	401
	48	157	2.7	153	153

[a] Infrared intensities are in km/mol, and Raman scattering activities are in $Å^4$/amu.

3.3. Naphthalene-d_8. The computed harmonic and fundamental frequencies of $C_{10}D_8$ are reported in Table 3 with the corresponding experimental ones obtained from infrared high-resolution gas-phase[7] and Ar matrix spectra[11] and from Raman spectra.[28] Only one different assignment compared to those which were previously presented[7] is proposed for fundamentals not involving the CD stretching modes: the ν_{32} mode has been assigned[11] at 1312 cm^{-1} instead of 1332 cm^{-1}. As found in $C_{10}H_8$, the largest deviation from the experimental frequency

TABLE 4: Computed and Observed Fundamental Frequencies, Computed Harmonic and Deperturbed Fundamentals (cm^{-1}) of the CD Stretching Mode of Naphthalene-d_8, and Indexing of $v_n = v_m = 1$ States Involved in Fermi Resonances

		calculated			experiment	
	mode	harmonic	deperturbed	fundamental	fundamental	$v_n = v_m = 1$ states in Fermi resonance
a_g	1	2361	2291	2282	2292	20,21 19,23 31,34 31,35
	2	2333	2256	2251	2273	20,21 19,23 31,34 31,35
b_{1u}	17	2349	2271	2264	2279	8,19 4,22 3,23 31,42 31,43 34,40
	18	2326	2248	2250	2255	8,19 4,22 3,23 31,42 31,43 34,40
b_{2u}	29	2361	2285	2291	2301	6,31 7,31 22,40 20,41
	30	2330	2254	2250	2260	6,31 7,31 22,40 20,41
b_{3g}	37	2348	2271	2267	2276	4,42 8,39 6,40 5,41
	38	2324	2248	2248	2261	4,42 8,39 6,40 5,41

TABLE 5: Experimental and Computed Harmonic Infrared Band Intensities[a] of Naphthalene

$C_{10}H_8$			$C_{10}D_8$		
mode	experiment	B9-71/TZ2P	mode	experiment	B9-71/TZ2P
ν_{47}	33	23	ν_{36}	0.70	0.52
ν_{36}	3.3	3.6	ν_{46}	6.80	6.60
ν_{46}	126	124	ν_{23}	0.04	0.03
ν_{45}	3.9	4.0	ν_{45}	1.10	0.78
ν_{35}	6.0	8.0	ν_{35} ν_{34}	1.0	0.94
ν_{22} ν_{34}	4.4	5.8	ν_{22}	1.0	1.00
ν_{33}	0.77	0.74	ν_{21}	0.06	0.001
ν_{21}	4.6	6.8	ν_{33}	0.02	0.04
ν_{20}	3.5	4.6	ν_{20}	0.50	0.47
ν_{31}	7.5	8.8	ν_{32}	0.10	0.02
ν_{19}	2.9	3.8	ν_{31}	0.64	0.47
ν_{17} ν_{18} ν_{29} ν_{30}	96	72	ν_{19}	0.18	0.04
			ν_{17} ν_{18} ν_{29} ν_{30}	8.1	5.42

[a] Intensities of $C_{10}H_8$ bands are in km/mol; for $C_{10}D_8$ the intensity values are relative to that of ν_{22}.

is quoted for ν_5 (23 cm^{-1}). The computed fundamentals of the a_u modes can be considered the best estimate of the experimental unknown ones.

3.4. CD Stretching Modes of Naphthalene-*d*$_8$. As pointed out for the hydrogenated species, the most difficult assignments concern the CD stretching vibrations. The proposed assignments together with the list of singly excited states affected by Fermi resonances are collected in Table 4. Only one of the assignments of the gerade modes has been modified:[28] ν_1 is now assigned at 2292 cm^{-1} instead of 2308 cm^{-1}. This choice is based on our calculations and agrees also with the suggestion of Stenman et al.[28] that indicated 2292 cm^{-1} as a plausible choice. Among the infrared active modes, ν_{18}, not measured so far, is now assigned to the band observed[7] at 2255 cm^{-1}, while the other assignments are unchanged.

The MAD evaluated from the 44 assigned modes is 6 cm^{-1}, 50% larger than that of naphthalene-*h*$_8$. The larger deviation derives mainly from ν_5 and the CD stretching modes, underestimated by 12 cm^{-1} on average. After excluding the CD stretches, the MAD becomes 5 cm^{-1}, nearer that of $C_{10}H_8$.

The overall performance of the present calculation seems to be better than that obtained with the same or similar density functional and basis set in azabenzenes.[3] The calculations presented by Barone[4] have been characterized by a MAD equal to 10 cm^{-1} while those from Martin[3] have been characterized by a MAD of 6 cm^{-1}, excluding the CH stretching modes since they were underestimated by about 20−30 cm^{-1}.

3.5. Band Intensities. The harmonic oscillator band intensities computed with the same DFT and basis set which were employed for the calculation of the frequencies are reported in Tables 1 and 3 for $C_{10}H_8$ and $C_{10}D_8$, respectively. In Table 5 the theoretical intensities of several infrared active fundamentals are compared to the corresponding experimental data from the infrared gas-phase spectra.[7] The results are very good, with the mean deviation being 15% for $C_{10}H_8$ and 20% for $C_{10}D_8$. The largest deviations are found for the CH and CD stretching modes, in which the computed intensities are calculated to be lower by 25−35% than the measured ones. The discrepancy between the calculated and the experimental data affecting the CH and CD stretchings can be explained, noting that the measured intensities include the contribution from a large number of combination bands, strongly overlapped with the CH fundamental bands in the gas-phase spectra, as can be seen from the Ar matrix spectra.[11,23]

3.6. Scale Factors. So far, the calculated vibrational spectrum of naphthalene relied on the applications of scale factors to the computed harmonic frequencies. The results were very good, with a MAD of 8−10 cm^{-1},[7−9] considering the low cost of such calculations. The scaling procedure can be empirical or more sophisticated, involving the transfer of corrective coefficients derived from the fit of the experimental spectrum of a parent molecule, such as benzene in the case of naphthalene. From the ratio of the computed fundamentals to the computed harmonic frequencies, two scale factors for naphthalene-*h*$_8$ have been derived, 0.982 and 0.960. The first resulted from non CH stretching modes; the second resulted from the CH stretching modes. These can be used to calculate the naphthalene-*d*$_8$ fundamentals from the harmonic data. The scale factor to be applied to the CD stretching modes has been modified from 0.960 to 0.971, taking into account the lower anharmonic character of CD stretching respect to the CH one. Thus the MAD results as 5 cm^{-1} for all fundamentals of $C_{10}D_8$, apart from the four a_u modes, better than that for the fundamentals calculated from the anharmonic force field. From these results we can conclude that scale factors can be reasonably employed to calculate the fundamentals of molecules belonging to the same

TABLE 6: Bond Lengths (pm) of Naphthalene[a]

	$r_{1,2}$	$r_{1,3}$	$r_{3,5}$	$r_{5,7}$	$r_{3,11}$	$r_{5,13}$
B9-71/TZ2P computed equilibrium	143.1	142.0	137.4	141.6	108.5	108.4
B9-71/cc-pVQZ computed equilibrium	143.0	141.9	137.3	141.5	108.4	108.3
B3LYP/cc-pVQZ computed equilibrium	142.8	141.6	137.0	141.1	108.2	108.1
B9-71/TZ2P vibration averaged	143.6	142.5	137.8	142.0	108.8	108.7
GED[b] experimental averaged	141.2(8)	142.2(3)	138.1(2)	141.7(4)	109.2	109.2

[a] For atom indexing, see Figure 1. [b] In parentheses are reported the quoted uncertainties.

family (for example, the PAHs), rather than the more computationally demanding ab initio anharmonic corrections, which are too expensive at the present state of the art for such large molecules.

3.7. Geometry. The B9-71/TZ2P equilibrium and vibrationally averaged bond distances of naphthalene used in these calculations are listed in Table 6. They agree within 5 pm with the geometry of Martin et al.[9] obtained at the B3LYP/cc-pVTZ level and empirically corrected. In the same table the equilibrium geometry obtained with the B9-71/cc-pVQZ and B3LYP/cc-pVQZ methods is also reported. The B9-71/TZ2P vibrationally averaged data are in good agreement with the gas-phase electron diffraction (GED) geometry,[29] except for the $C_1{=}C_2$ bond length, which is longer by 2.4 ± 0.8 pm in the computed geometry.

4. Conclusions

The ab initio B9-71/TZ2P anharmonic force field has proved to be very valuable in the analysis of the vibrational spectrum of a molecule as large as naphthalene, for which the difference between the calculated and observed fundamentals was calculated to be 5 cm^{-1}, on average; we should point out that the agreement is remarkable considering the complexity of the system and that no empirical corrections were employed. Few systematic deviations regarding the "Kekulé" mode and some of the CH stretching modes have been pointed out. The effect of Fermi interactions on the frequencies of the complex band structure, observed in the CH stretching region in both the infrared and Raman spectra, has been found to be of limited importance. Up to 15 interactions are believed to be affecting each stretching mode, but the overall average effect of this complex set of interactions seems to be responsible for frequency shifts as large as a few wavenumbers. The agreement between the harmonic calculated infrared band intensities and the experimental ones is good.

Acknowledgment. E.C. and A.T. thank the Ministero della Università e Ricerca for financial support.

Supporting Information Available: Provided are the harmonic, the $x_{i,j}$ constants, the cubic and the quartic anharmonic constants, together with the calculated spectra of both $C_{10}H_8$ and $C_{10}D_8$. The two files are in doc format. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Miani, A.; Cané, E.; Palmieri, P.; Trombetti, A.; Handy, N. C. *J. Chem. Phys.* **2000**, *112*, 248.

(2) Martin, J. M. L.; Lee, T. J.; Taylor, P. R.; François, J. P. *J. Chem. Phys.* **1995**, *103*, 2589.

(3) Boese, A. D.; Martin, J. M. L. *J. Phys. Chem. A* **2004**, *108*, 3085.

(4) Barone, V. *J. Phys. Chem. A* **2004**, *108*, 4146.

(5) Burcl, R.; Handy, N. C.; Carter, S. *Spectrochim. Acta, Part A* **2003**, *59*, 1881.

(6) Carbonniere, P.; Lucca, T.; Pouchan, C.; Rega, N.; Barone, V. *J. Comput. Chem.* **2005**, *26*, 384.

(7) Cané, E.; Palmieri, P.; Tarroni, R.; Trombetti, A.; Handy, N. C. *Gazz. Chim. Ital.* **1996**, *126*, 289.

(8) Sellers, H.; Pulay, P.; Boggs, J. E. *J. Am. Chem. Soc.* **1985**, *107*, 6487.

(9) Martin, J. M. L.; El-Yazal, J.; François, J. P. *J. Phys. Chem.* **1996**, *100*, 15358.

(10) Langhoff, S. R. *J. Phys. Chem.* **1996**, *100*, 2819.

(11) Bauschlicher, C. W., Jr.; Langhoff, S. R.; Sanford, S. A.; Hudgins, D. H. *J. Phys. Chem. A* **1997**, *101*, 2414.

(12) Lokshin, B. V.; Borisova, N. E.; Senyavin, B. M.; Reshetova, M. D. *Russ. Chem. Bull. Int. Ed.* **2002**, *9*, 1656.

(13) A preliminary report of these results has been presented at the 17th Colloquium on High Resolution Molecular Spectroscopy, Groningen, 2001, as poster contribution D13.

(14) Léger, A.; Puget, J. *Astron. Astrophys.* **1984**, *137*, 45.

(15) Allamandola, L. J.; Hudgins, D. M.; Sandford, S. A. *Astrophys. J.* **1999**, *511*, 115.

(16) Gillett, F. C.; Forrest, W. J.; Merrill, K. M. *Astrophys. J.* **1973**, *183*, 87.

(17) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision B.05; Gaussian, Inc.: Pittsburgh PA, 2003.

(18) Hamprecht, F. A.; Cohen, A. J.; Tozer, D. J.; Handy, N. C. *J. Chem. Phys.* **1998**, *109*, 6264.

(19) Dunning, T. H. *J. Chem. Phys.* **1971**, *55*, 716.

(20) Carbonniere, P.; Barone, V. *Chem. Phys. Lett.* **2004**, *399*, 226.

(21) Boese, A. D.; Koppler, W.; Martin, J. M. L. *Int. J. Quantum Chem.* **2005**, *104*, 830.

(22) Barone, V. *J. Chem. Phys.* **2005**, *122*, 14108.

(23) Hudgins, D. H.; Sanford, S. A. *J. Phys. Chem. A* **1998**, *102*, 329.

(24) Broude, V. L.; Umarov, L. M. *Opt. Spectosc.* **1975**, *39*, 39.

(25) Stenman, F. *J. Chem. Phys.* **1971**, *54*, 4217.

(26) Hanson, D. M.; Gee, A. R. *J. Chem. Phys.* **1969**, *51*, 5052.

(27) Pietilä, L.-O.; Stenman, F. *Commun. Phys.-Math.* **1978**, *48*, 145.

(28) Karonen, A.; Räsänen, J.; Stenman, F. *Commun. Phys.-Math.* **1976**, *46*, 69.

(29) Ketkar, S. N.; Fink, M. *J. Mol. Struct.* **1981**, *77*, 139.