Analysis of vibrational spectra of naphthalene, deuterionaphthalenes, and chromium (η^6-naphthalene)tricarbonyl based on density functional calculations

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The vibrational frequencies and force constants for naphthalene ($C_{10}H_8$), 1,4,5,8- and 2,3,6,7-tetradeuterionaphthalenes ($C_{10}H_4D_4$), octadeuterionaphthalene ($C_{10}D_8$), and chromium (η^6-naphthalene)tricarbonyl were calculated by the DFT method using the PBE approximation in extended and split bases. The results calculated without the use of scaling factors are in good agreement with the IR and Raman experimental data. All vibrational frequencies for the free ligand and π-complex molecules were assigned. The influence of coordination to the transition metal on the frequencies and force field of the naphthalene molecule (both for the free ring and the ring coordinated to the transition metal) was discussed.

Key words: density functional theory, vibrational spectra, calculation of vibrational spectra, IR spectroscopy, Raman spectroscopy, naphthalene, deuterionaphthalenes, chromium (η^6-naphthalene)tricarbonyl, π-complexes.

Ab initio calculations of the geometric parameters and force fields and, hence, vibrational spectra of complex molecules are among the most important achievements of the computer chemistry in the last two decades. The most part of *ab initio* calculations of vibrational spectra until the late 1980s were performed by the Hartree—Fock method, which gave, as a rule, overestimated values for most frequencies. Therefore, to obtain the better agreement with experiment, the "scaling" procedure was carried out, *i.e.*, the force constants obtained were multiplied by empirical coefficients. The use of many (often more than ten) scaling factors decreases sharply the reliability of the results. Since calculations are cumbersome and time-consuming even when modern computers are used, they are very expensive. Therefore, such multielectronic systems as, for example, transition metal complexes cannot be calculated.

Another method of calculation of the molecular properties based on the density functional theory (DFT) is being rapidly developed in the recent years. This method is a good alternative to the Hartree—Fock *ab initio* calculations and allows successful calculations of complicated molecular systems with much smaller time expenses and lower cost. The recent calculations of vibrational spectra of many different molecules showed that the DFT method often gave a good correlation of the calculated and experimental frequencies without the scaling procedure. In particular, the first calculations of the transition metal complexes $Ni(CO)_4$ and $Cr(CO)_6$,[1—5] ferrocene,[6] chromium (η^6-benzene)tricarbonyl (η^6-C_6H_6)$Cr(CO)_3$, and dibenzenechromium (η^6-C_6H_6)$_2$Cr [7] showed the applicability of the DFT method to calculations of transition metal compounds and estimated the factors influencing the quality of calculation. It has been shown[7] that the quality of the optimized geometric parameters (bond lengths and bond angles) obtained by the calculation affects strongly the calculation of force fields, frequencies, and intensities in the IR spectra. When geometric parameters are well reproduced, vibrational spectra, as a rule, are also reproduced well. Therefore, for the optimization of the geometric parameters approximations of a higher level should be used for the density functional (nonlocal DFT approximation), and a lower-level approximation (local DFT approximation) can be used for the calculation of vibrational spectra without a substantial decrease in accuracy, which simplifies and accelerates the calculation of the force field and frequencies.

Ab initio DFT calculations of the vibrational spectra and force fields of transition metal π-complexes make it

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 9, pp. 1521—1530, September, 2002.

possible to return at a new level to the study of the influence of the formation of the coordination π-bond on the vibrational frequencies and force constants of the coordinated ligand molecule. The published data on the vibrational spectra of the transition metal π-complexes with cyclic ligands, *viz.*, cyclopentadienyl, arene, and heterocyclic ligands, revealed some regularities in changing the vibrational frequencies of the ligand molecule when it forms a coordination bond with the metal atom.[8,9] However, the available material is based on the empirical assignment of vibrational frequencies. Reliable data on the force fields of the complexes are lacking because the force field calculation by the classical methods is ambiguous. *Ab initio* methods allow direct calculation of the force field of a molecule without any initial assumptions and simplifications and hence, evaluation of the influence of complex formation on the frequencies and also on the force fields of coordinated ligands.

In this work we calculated by the DFT method the vibrational frequencies of naphthalene ($C_{10}H_8$), 1,4,5,8- and 2,3,6,7-tetradeuterionaphthalenes (α- and β-$C_{10}H_4D_4$), octadeuterionaphthalene ($C_{10}D_8$), and the chromium π-(η^6-naphthalene)tricarbonyl complex (η^6-$C_{10}H_8$)Cr(CO)$_3$ and performed the complete normal mode analysis. The calculated frequencies were compared with experiment, and the assignment of the frequencies was compared with that made previously from the experimental data and normal mode analysis.

Procedure of calculations

Quantum-chemical calculations were performed by the PRIRODA program developed by D. N. Laikov.[10] The generalized gradient approximation was used to approximate the exchange-correlation energy.[11] For the expansion of one-electron functions we used the extended atomic basis sets of grouped functions of the Gauss type {311/1} for the H atom, {611111/411/11} for the C, N, and O atoms, and {711111111111/511111111/5111} for the Cr atom (figures in braces show the example of arrangement of the Gauss functions for the s-, p-, and d-symmetries). According to the algorithm,[10] the matrix elements of the Coulomb and exchange-correlation potentials are performed by the electron density expansion in the auxiliary basis, which consists of sets centered on atoms of the non-grouped functions of the Gauss type. In this work we used the auxiliary basis sets of the size (5s1p) for H, (10s3p3d1f) for C, N, and O, and (18s6p6d5f5g) for Cr. The errors introduced to the calculated properties of the molecules from the application of the bases listed should be rather small, according to the estimations, namely, ~0.001 Å in the bond lengths and $\leq$2 kcal mol^{-1} in the relative energies of the structures under study.[10] The vibrational frequencies and intensities in the IR spectra were calculated in the framework of the same program. The vibrations were calculated in the Cartesian coordinates. The NCA99 [12] and DISP [13] program packages were used to transform the data obtained into the system of internal coordinates.

Results and Discussion

From the point of view of the stated problem, chromium (η^6-naphthalene)tricarbonyl (η^6-$C_{10}H_8$)Cr(CO)$_3$ (CNT) is an interesting object.

1. In this molecule the bicyclic ligand (naphthalene) is coordinated to the Cr atom only by one of its aromatic cycles. The Cr atom is arranged above the center of one of the naphthalene cycles and bound to six C atoms (Cr—C distances 2.19—2.33 Å).[14,15] Four other C atoms are remote from the Cr atom at distances, which do not allow the formation of a chemical bond. Therefore, it seems possible to monitor the influence of coordination on the vibrational characteristics of both the π-coordinated and free aromatic rings.

2. The spectrum of the free naphthalene molecule is well studied, and its complete interpretation based on the calculation of normal modes of both the deuterated and non-deuterated molecules is available in the literature.[16]

3. The spectrum of the CNT complex is also studied in detail.[17] Its IR spectra in the medium and long-wave IR regions in the solid state and in solutions and Raman spectra were studied. The detailed interpretation of the spectra is based on a comparison of the IR and Raman spectra of the complex and ligand. Thus, all necessary data for the comparison of the calculated and experimental spectra of CNT are available. This allows not only their new interpretation but also evaluation of the applicability of DFT calculations to complicated transition metal π-complexes.

Naphthalene and deuterionaphthalenes. *Geometric parameters of the naphthalene molecule.* The designations of bonds and angles in the naphthalene molecule are given in Fig. 1. The optimized geometric parameters of the naphthalene molecule are presented in Table 1. It is seen that the published X-ray diffraction[18—21] and electron diffraction[22] data on the bond lengths in the naphtha-

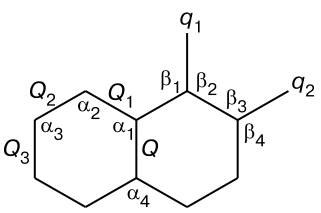

Fig. 1. Designations of symmetrically equivalent bonds and angles in the naphthalene molecule.

Table 1. Calculated by DFT and experimental bond lengths (d/Å) in the naphthalene molecule $C_{10}H_8$

Bond[a]	Calculation	Experiment				
		XRD				ED[b]
		I[c]	II[d]	III[e]	IV[f]	
Q	1.4373	1.426	1.421(3)	—	1.418	1.420
Q_1	1.4211	1.426	1.424(2)	1.420	1.421	1.422
Q_2	1.3800	1.378	1.377(2)	1.357	1.364	1.371
Q_3	1.4163	1.415	1.411(2)	1.416	1.415	1.412
q_1	1.0916	0.95 [g]	0.96(3)	—	—	—
q_2	1.0905	0.93 [g]	0.99(3)	—	—	—

[a] Designations of symmetrically equivalent bonds are shown in Fig. 1.

[b] Electron diffraction in the gas phase.[22]

[c] See Ref. 18.

[d] $T = -150$ °C.[19]

[e] See Ref. 20.

[f] See Ref. 21.

[g] The mean value without a thermal correction to the libration motion.

lene molecule diverge considerably. Probably, the results[18,19] obtained using the modern technique are more correct because both the C—C and C—H bond lengths were determined (it was impossible in earlier works because the H atoms were difficult to localize). The electron diffraction data[22] also agree better with the results of the later works.[18,19] For the Q_1, Q_2, and Q_3 bonds the discrepancies between the calculation and experiment are at most 0.005 Å. For the central Q bond the discrepancy is somewhat greater and equals 0.012—0.016 Å. The calculation gives the substantially overestimated values (by 0.10—0.16 Å) for the C—H bond lengths.

The alternation of the carbon—carbon bond lengths in both benzene rings found by the calculation is in good accordance with experiment. The Q_2 bond is much shorter than the Q_1 and Q_3 bonds. The structural data give close values for the Q and Q_1 bond lengths. However, the length of the Q bond, which is common for two rings, is somewhat increased, according to the calculation, over the other carbon—carbon bonds. The same result was obtained[23] by the calculation of the naphthalene molecule by both the MP2 and DFT methods in the BP*/6-31G**, BLYP/JMW, and LYP/B88 basis sets and by the *ab initio* calculation[24] during refinement of the geometric parameters for the better agreement of the calculated and experimental vibrational frequencies. Based on the results of independent calculations, we assumed that the elongation of the central Q bond is not a calculated effect but is a real property of the system. This assumption is favored by the good accordance of the vibrational spectra calculated with these geometric parameters and experimental data (see below).

Vibrational spectra of naphthalene. Table 2 contains the vibrational frequencies of naphthalene classified by symmetry and their assignment to the bond and angle vibrations based on the calculated modes of vibrations and potential energy distribution (PED) over the internal vibrational coordinates (see Fig. 1).

It can be seen that the calculation reproduces well the experimental frequencies of all IR- and Raman-active vibrations without the use of scaling factors and the assignment of the vibrational frequencies agrees well with the previous assignments based on the experimental data and normal mode analysis.[16,17] The exception are the frequencies of stretching vibrations of C—H, whose calculated values are overestimated by 30—90 cm^{-1} be-

Table 2. Calculated and experimental vibrational spectra[a] of naphthalene $C_{10}H_8$ (symmetry D_{2h}) and assignment of bands in the spectra

Symmetry of vibration (activity)	Vibration[c]	DFT calculation	Experiment[12]		Assignment	PED[b]
			IR	Raman		
A_{1g}, in-plane	1	3121	—	3055	ν(CH)	100q
(Raman)	2	3096	—	3006	ν(CH)	100q
	3	1569	—	1575	ν(ring)	70.5Q + 11.5α + 9.2β
	4	1444	—	1462	β(CH) + ν(ring)	65.1β + 31.3Q
	5	1380	—	1380	ν(ring)	87.3Q
	6	1145	—	1145	β(CH)	88.0β
	7	1022	—	1020	ν(ring) + β(CH)	65.6Q + 21.5β
	8	755	—	762	ν(ring)	71.6Q + 16.4α + 8.3β
	9	509	—	512	δ(ring)	53.9α + 35.5Q + 6.1β
A_{1u}, out-of-plane	25	922	975	—	ρ(CH)	66.0ρ + 31.3χ
(inactive)	26	809	841?	—	ρ(CH)	63.0ρ + 37.0χ
	27	614	581	—	γ(ring)	64.8χ + 35.2ρ
	28	176	195	—	γ(ring)	79.0χ + 21.0ρ

(*to be continued*)

Table 2 (*continued*)

Symmetry of vibration (activity)	Vibration[c]	DFT calculation	Experiment[12]		Assignment	PED[b]
			IR	Raman		
B_{1g}, in-plane (Raman)	10	3107	—	3029	ν(CH)	$100q$
	11	3090	—	3018	ν(CH)	$100q$
	12	1622	—	1626	ν(ring)	$70.4Q + 12.9\beta + 9.4\alpha$
	13	1447	—	1442	β(CH) + ν(ring)	$46.5\beta + 42.3Q + 5.8\alpha$
	14	1236	—	1243	β(CH) + ν(ring)	$45.2\beta + 25.1Q + 14.1\alpha$
	15	1136	—	1158	β(CH) + ν(ring)	$66.52\beta + 31.9Q$
	16	941	—	938	δ(ring)	$8.1Q + 47.0\alpha + 16.2\beta$
	17	507	—	510	δ(ring	$13.5Q + 74.1\alpha + 6.7\beta$
B_{1u}, out-of-plane (IR)	29	909	958	—	ρ(CH)	$73.1\rho + 26.9\chi$
	30	769	753	—	ρ(CH)	$63.0\rho + 37.0\chi$
	31	468	476	—	γ(ring)	$56.7\chi + 43.0\rho$
	32	165	176	—	γ(ring)	$79.5\chi + 22.0\rho$
B_{2g}, out-of-plane (Raman)	18	897	—	876	ρ(CH)	$70.6\rho + 26.1\chi$
	19	696	—	717	ρ(CH)	$78.6\rho + 17.8\chi$
	20	380	—	386	γ(ring)	$16.9\rho + 84.4\chi$
B_{2u}, in-plane (IR)	33	3108	3066	—	ν(CH)	$100q$
	34	3090	3090	—	ν(CH)	$100q$
	35	1593	1600	—	ν(ring)	$71.2Q + 19.5\beta$
	36	1375	1392	—	β(CH)	$73.1\beta + 20.2Q$
	37	1255	1270	—	β(CH) + ν(ring)	$54.3\beta + 25.1Q + 14.1\alpha$
	38	1124	1128	—	β(CH) + ν(ring)	$49.2\beta + 22.6Q + 16.3\alpha$
	39	793	782	—	δ(ring)	$53.6\alpha + 27.9Q + 14.0\beta$
	40	355	357	—	δ(ring)	$79.8\alpha + 17.0Q$
B_{3g}, out-of-plane (Raman)	21	930	—	948	ρCH	$62.7\rho + 37.3\gamma$
	22	863	—	846	ρ(CH)	$78.0\rho + 22.0\chi$
	23	759	—	780	γ(ring)	$92.0\chi + 7.9\rho$
	24	459	—	463	γ(ring)	$86.2\chi + 10.2\rho$
B_{3u}, in-plane (IR)	41	3121	3090	—	ν(CH)	$100q$
	42	3093	3032	—	ν(CH)	$100q$
	43	1503	1506	—	ν(ring)	$54.3Q + 37.9\beta$
	44	1378	1361	—	ν(ring) + β(CH)	$74.3Q + 22.3\beta$
	45	1209	1210	—	ν(ring) + β(CH)	$60.5Q + 38.1\beta$
	46	1142	1138	—	β(CH)ν	$80.3\beta + 19.8Q$
	47	1014	1011	—	(ring) + β(CH)	$74.8Q + 16.9\beta$
	48	618	618	—	δ(ring)	$79.6\alpha + 16.0\beta$

[a] The following designations were used: Q and q are the stretching vibrations of C—C and C—H, respectively; α and β are the bendings of the C—C—C and C—C—H angles, respectively; ρ is the out-of-plane mode of C—H; and χ is the out-of-plane ring deformation.

[b] Only the PED values exceeding 5% are presented.

[c] Vibrations are numerated according to the previously published work.[12]

cause anharmonicity was ignored. The deviation of the calculated frequencies of the in-plane modes of the A_{1g}, B_{1g}, B_{2u}, and B_{3u} classes from the experimental values is ≤2%. Some changes compared to the previous data were introduced into the assignment for the forbidden A_{1u} vibrations and the weak bands of B_{3g} out-of-plane modes of the ρ and χ types, which are active only in the Raman spectra. The changes in the assignment provide a better agreement with the calculation and do not create basic contradictions with the experimental data. For the out-of-plane modes the discrepancy between the calculation and experiment is somewhat greater and reaches 2.8%. The exception is the IR-active C—H band of the B_{1u} out-of-plane mode. For this band the calculated value is 909 cm^{-1}, while the single appropriate band, which is intense in the IR spectrum, was found at 958 cm^{-1}, *i.e.*, the deviation is >5%. As a whole, the data in Table 2 indicate that the DFT calculation of naphthalene without using the scaling procedure reproduces well the experimental vibrational spectra.

To verify the quality of the calculated force field, we calculated the vibrational spectra of deuterated naphthalenes: 1,4,5,8-tetradeuterionaphthalene (α-naphthalene-d_4), 2,3,6,7-tetradeuterionaphthalene (β-naphthalene-d_4), and octadeuterionaphthalene (naphthalene-d_8).

The calculated and experimental[16] frequencies for the deuterionaphthalenes are presented in Table 3. Although the experimental data on the spectra of the deuterio-

Table 3. Calculated and experimental frequencies in the vibrational spectra of deuterionaphthalenes*

Vibration	Symmetry of vibration	α-Naphthalene-d_4			β-Naphthalene-d_4			Naphthalene-d_8		
		Calculation	Experiment[12]		Calculation	Experiment[12]		Calculation	Experiment[12]	
			IR	Raman		IR	Raman		IR	Raman
41	B_{3u}	3115	3076	—	3096	3046	—	2307	2284	—
10	B_{1g}	3115	—	3063	3099	—	(3070)	2320	—	2302
33	B_{2u}	3099	3046	—	3097	3046	—	2308	2284	—
1	A_{1g}	3099	—	3045	3098	—	3048	2320	—	2293
34	B_{2u}	2297	2278	—	2295	2263	—	2288	2266	—
11	B_{1g}	2297	—	2276	2296	—	2274	2290	—	2275
42	B_{3u}	2295	2260	—	2314	2278	—	2283	2248	—
2	A_{1g}	2293	—	2252	2314	—	2294	2285	—	2263
12	B_{1g}	1607	—	(1610)	1613	—	(1628)	1597	—	1604
35	B_{2u}	1578	1581	—	1561	1564	—	1551	1562	—
3	A_{1g}	1554	—	1569	1566	—	1565	1545	—	1550
43	B_{3u}	1475	1480	—	1473	1486	—	1444	1466	—
13	B_{1g}	1434	—	1410	1380	—	1398	1360	—	1330
4	A_{1g}	1399	—	1392	1403	—	1413	1385	—	1383
36	B_{2u}	1350	1362	—	1281	1278	—	1253	1268	—
5	A_{1u}	1350	—	1355	1375	—	1380	1283	—	1290
44	B_{3u}	1334	1318	—	1373	1359	—	1348	1320	—
45	B_{3u}	1189	1199	—	1186	1173	—	1092	1087	—
37	B_{2u}	1185	1178	—	1254	1256	—	1031	1040	—
14	B_{1g}	1154	—	1140	1213	—	1230	1014	—	1030
46	B_{3u}	1102	1098	—	946	998	—	819	831	—
6	A_{1g}	1056	—	1095	1026	—	1130	828	—	864
25	A_{1u}	954	(966)	—	852	(873)	—	756	797	—
15	B_{1g}	925	—	958	1020	—	1008	877	—	927
21	B_{3g}	904	—	958	888	—	(908)	858	—	875
38	B_{2u}	896	942	—	941	974	—	873	881	—
29	B_{1u}	857	874	—	889	921	—	751	791	—
18	B_{2g}	835	—	871	882	—	(905)	733	—	777
22	B_{3g}	834	—	871	831	—	853	732	—	760
7	A_{1g}	833	—	864	843	—	853	822	—	833
16	B_{1g}	823	—	844	855	—	(904)	820	—	833
47	B_{3u}	820	823	—	770	846	—	819	819	—
39	B_{2u}	791	(740)	—	723	(732)	—	720	723	—
30	B_{1u}	712	729	—	618	(635)	—	616	626	—
8	A_{1g}	699	—	710	726	—	738	685	—	693
26	A_{1u}	668	(682)	—	741	(768)	—	625	655	—
23	B_{3g}	625	—	673	725	—	732	636	—	671
19	B_{2g}	601	—	639	568	—	(590)	534	—	540
48	B_{3u}	599	602	—	608	(595)	—	593	593	—
27	A_{1u}	577	557	—	554	(531)	—	527	(507)	—
9	A_{1g}	503	—	505	499	—	503	491	—	495
17	B_{1g}	498	—	(500)	494	—	(480)	489	—	(490)
24	B_{3g}	459	—	467	407	—	415	406	—	408
31	B_{1u}	400	407	—	466	(470)	—	398	404	—
20	B_{2g}	340	—	350	371	—	381	335	—	339
40	B_{2u}	333	338	—	342	(316)	—	323	328	—
28	A_{1u}	167	—	183	169	(181)	—	160	—	180
32	B_{1u}	164	(172)	—	153	(165)	—	152	(163)	—

* Numeration of vibrations and designations of symmetry classes are presented in Table 2.

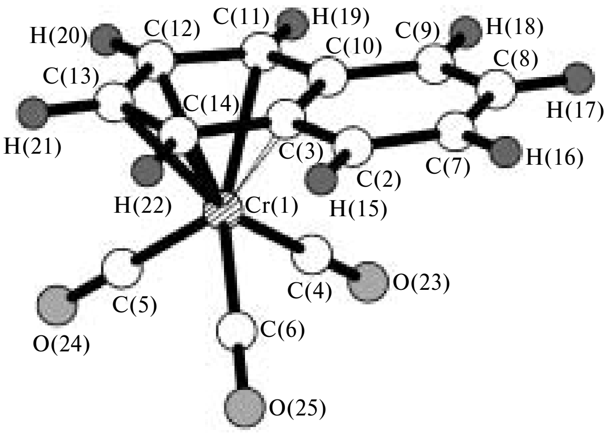

Fig. 2. Crystal structure of chromium (η^6-naphthalene)tricarbonyl.

naphthalenes are incomplete, the calculated and experimental spectra correlate well, except for the frequencies of stretching C—H and C—D vibrations, which were overestimated in the calculation because ignoring the anharmonicity. The assignment of the vibrations by symmetry based on the quantum-chemical DFT calculation agrees well with the assignment based on the experiment and normal mode analysis by the classical method.[16]

Chromium (η^6-naphthalene)tricarbonyl. *Geometric parameters of chromium (η^6-naphthalene)tricarbonyl.* The numeration of atoms in the chromium (η^6-naphthalene)tricarbonyl molecule is shown in Fig. 2. The optimized geometric parameters of the (η^6-$C_{10}H_8$)Cr(CO)$_3$ molecule are presented in Table 4 along with the XRD data for the CNT single crystal.[25] Comparing these data, one should take into account that the calculation gives the perfect structure of an isolated molecule for CNT, while the symmetry of the molecule can be decreased in the crystalline state due to the interaction with the environment. The calculated structure has a symmetry close to C_s. The calculation discrepancies in lengths of symmetrically equivalent bonds are within the fifth decimal place. The symmetry plane passes through the Cr atom, one of the C—O bonds (Cr—C(5)—O(24)), and the middle of the C(3)—C(10), C(12)—C(13), and C(7)—C(8) bonds. All bond angles in the naphthalene ring are close to 120°, the Cr—C—O angles are close to 180°, and the OC—Cr—CO angles are close to 90°. The Cr atom is slightly shifted from the center of the coordinated benzene ring to the side of the molecule: the bonds of the Cr atom with the C(11), C(12), C(13), and C(14) atoms are by ~0.12 Å shorter than the bonds with the C(3) and C(10) atoms forming the central bond of the naphthalene molecule. The X-ray diffraction data indicate that the molecule in crystal is somewhat distorted, which impedes the comparison of the calculated and experimental bond lengths. The average experimental bond lengths differ from the calculated values within 0.2 Å. The comparison with the data in Table 1 shows that the coordination with the metal elongates all carbon—carbon bonds in the coordinated ring by 0.1—0.2 Å. For the "free" naphthalene ring the changes in bond lengths are much smaller. As in the naphthalene molecule, the carbon—carbon bond lengths in the rings of the complex differ noticeably, and the Q_2 bonds alter-

Table 4. Calculated by DFT and experimentally measured bond lengths (*d*) and bond angles (ω) in the (η^6-$C_{10}H_8$)Cr(CO)$_3$ molecule*

Parameter	Calculation	Experiment[25]
Bond	*d*/Å	
C(3)—C(10)	1.4427	1.439
C(10)—C(11) (C(3)—C(14))	1.4409	1.404, 1.447
C(11)—C(12) (C(13)—C(14))	1.4044	1.389, 1.383
C(12)—C(13)	1.4263	1.375
C(10)—C(9) (C(3)—C(1))	1.4255	1.438, 1.406
C(9)—C(8) (C(2)—C(7))	1.3764	1.375, 1.415
C(7)—C(8)	1.4184	1.392
C(11)—H(19)	1.0888	—
C(12)—H(20)	1.0879	—
C(9)—H(18)	1.0905	—
C(8)—H(17)	1.0898	—
Cr—C(5)	1.8299	1.830
Cr—C(4) (Cr—C(6))	1.8480	1.818, 1.815
Cr—C(3)	2.3361	2.213
Cr—C(13)	2.2134	2.191
Cr—C(11)	2.2169	2.214
Cr—C(12)	2.2114	2.186
Cr—C(14)	2.2169	2.306
Cr—C(10)	2.3366	2.337
C(4)—O(23) (Cr(6)—O(25))	1.1655	1.167, 1.147
C(5)—O(24)	1.1683	1.137
Angle	ω/deg	
C(2)—C(3)—C(10)	118.773	120.0, 120.6
C(2)—C(7)—C(8)	120.728	116.0, 118.5
C(7)—C(8)—C(9)	120.483	119.6, 124.9
C(3)—C(10)—C(11)	118.765	118.0, 118.2
C(10)—C(11)—C(12)	121.028	120.8, 121.6
C(7)—C(8)—C(9)	119.948	118.5, 122.5
Cr—C(5)—O(24)	179.418	—
Cr—C(6)—O(25)	179.667	—
(OC)—Cr—(CO)	87.587, 87.619, 89.413	87.0, 90.7, 90.1

* Numeration of atoms is given in Fig. 2.

Table 5. Comparison of vibrational frequencies (ν) of the (η^6-$C_{10}H_8$)Cr(CO)$_3$ complex and free naphthalene molecule $C_{10}H_8$

Symmetry	ν/cm^{-1}		Assignment	PED	Symmetry	ν/cm^{-1}		Assignment	PED
	Calculation	Experiment[17]				Calculation	Experiment[17]		
			(π-$C_{10}H_8$)Cr(CO)$_3$					$C_{10}H_8$	
A'	3145.0	3078	ν(CH)*	$99.4q^*$	A_{1g}	3121.0	3055	ν(CH)	$100q$
A''	3136.2	3100	ν(CH)*	$99.6q^*$	B_{2u}	3108.3	3066	ν(CH)	$100q$
A'	3130.1	3063	ν(CH)	$99.3q$	B_{3u}	3120.6	3052	ν(CH)	$100q$
A'	3124.3	3056	ν(CH)*	$99.7q^*$	A_{1g}	3095.6	3006	ν(CH)	$100q$
A''	3123.4	3060	ν(CH)*	$97.3q^*$	B_{1g}	3107.2	3029	ν(CH)	$100q$
A''	3119.8	—	ν(CH)	$97.1q$	B_{2u}	3090.2	3090	ν(CH)	$100q$
A'	3108.5	3049	ν(CH)	$99.8q$	B_{3u}	3093.4	3032	ν(CH)	$100q$
A''	3103.8	—	ν(CH)	$99.8q$	B_{1g}	3089.6	3018	ν(CH)	$100q$
A'	1978.2	1971	ν(CO)	$95.8r$	—	—	—	—	—
A''	1928.3	1908	ν(CO)	$96.3r$	—	—	—	—	—
A'	1917.6	1893	ν(CO)	$96.0r$	—	—	—	—	—
A''	1605.5	1625	ν(ring)	$67.4Q + 6.5\alpha + 22.3\beta$	B_{1g}	1622.3	1626	ν(ring)	$70.4Q + 9.4\alpha + 12.9\beta$
A'	1535.7	1550	ν(ring)	$61.2Q + 9.4\beta + 4.9\beta^* + 9.1Q^* + 10.7\alpha$	A_{1g}	1568.6	1575	ν(ring)	$70.5Q + 11.5\alpha + 9.2\beta$
A''	1519.5	1540	ν(ring*) + β(CH)*	$53.0Q^* + 26.6\beta^* + 4.2\beta + 6.9Q + 5.4\alpha^*$	B_{2u}	1592.6	1600	ν(ring)	$71Q + 19.5\beta$
A'	1468.3	1480	ν(ring*) + β(CH)	$34.0Q^* + 19.4Q + 24.5\beta + 12.0\beta^* + 6.1\alpha^*$	B_{3u}	1503.2	1513	ν(ring)	$54.3Q + 37.9\beta$
A'	1431.4	1441	ν(ring) + β(CH)	$21.29Q + 20.0Q^* + 30.3\beta + 21.7\beta^*$	A_{1g}	1443.7	1462	β(CH) + ν(ring)	$61.5\beta + 31.3Q$
A''	1423.7	1402 (IR)	ν(ring) + β(CH)	$17.8Q + 13.3Q^* + 31.6\beta + 28.6\beta^*$	B_{1g}	1446.9	1442	β(CH) + ν(ring)	$46.5\beta + 42.3Q + 5.8\alpha$
A'	1407.3	1402 (Raman)	ν(ring*) + β(CH)*	$56.0Q^* + 12.9Q + 26.6\beta^* + 2.2\beta$	B_{3u}	1377.9	1361	ν(ring) + β(CH)	$74.3Q + 22.3\beta$
A'	1359.3	1379	ν(ring)	$64.7Q + 18.3Q^* + 4.5\beta^*$	A_{1g}	1380.4	1380	ν(ring)	$87.3Q$
A''	1356.5	1372	β(CH)	$42.7\beta^* + 29.6\beta + 4.5Q + 10.6Q^* + 6.9\alpha$	B_{2u}	1374.7	1392	β(CH)	$71.3\beta + 20.2Q$
A''	1237.5	1253	β(CH) + ν(ring)	$49.6\beta + 6.3\beta^* + 19.7Q + 8.5Q^* + 11.5\alpha^*$	B_{2u}	1255.2	1270	β(CH) + ν(ring)	$54.3\beta + 25.1Q + 14.1\alpha$
A''	1216.1	1230	β(CH) + ν(ring)	$45.3\beta^* + 18.9\alpha + 15.9Q^* + 8.0\beta + {} + 5.6Q + 5.1\alpha^*$	B_{1g}	1235.6	1243	β(CH) + ν(ring)	$45.2\beta + 25.1Q + 14.1\alpha$
A'	1195.2	1199	β(CH) + ν(ring)	$32.5Q + 18.3\beta + 17.1\beta^*$	B_{3u}	1208.8	1210	ν(ring) + β(CH)	$60.5Q + 38.1\beta$
A'	1159.9	1167	β(CH)	$69.9\beta + 17.6\beta^* + 9.1Q$	A_{1g}	1145.1	1145	β(CH)	88.0β
A'	1138.1	1152	β(CH)	$67.9\beta^* + 15.5\beta + 6.1Q + 9.3Q^*$	B_{3u}	1142.0	1137	β(CH)	$80.3\beta + 19.8Q$
A''	1133.1	1145	β(CH) + ν(ring)	$47.9\beta + 6.6\beta^* + 28.7Q + 5.9Q^*$	B_{1g}	1136.2	1168	β(CH) + ν(ring)	$66.5\beta + 39.9Q$
A''	1101.3	1110	β(CH) + ν(ring)	$38.2\beta^* + 2.2\beta + 33.2Q^* + 14.0\alpha + 9.2\alpha^*$	B_{2u}	1124.3	1128	β(CH) + ν(ring)	$49.2\beta + 22.6Q + 16.3\alpha$
A'	1017.9	1018	ν(ring) + β(CH)	$66.7Q + 23.4\beta + 1.5\beta^* + 5.4\alpha$	A_{1g}	1022.0	1020	ν(ring) + β(CH)	$65.6Q + 21.5\beta$
A'	1003.3	1004	ν(ring*) + β(CH)	$66.8Q^* + 21.0\beta^*$	B_{3u}	1014.4	1012	ν(ring) + β(CH)	$74.8Q + 16.9\beta$
A''	936.2	960	ρ(CH) + δ(ring)	$37.1\rho^* + 20.8\rho + 17.8\alpha^* + 16.5\alpha + 7.7\chi^*$	B_{1g}	940.7	938	δ(ring)	$47.0\alpha + 16.2\beta + 8.1Q$
A''	931.6	942	ρ(CH)	$76.4\rho + 14.2\chi + 4.0\alpha + 5.4\alpha^*$	B_{3g}	930.1	948	ρ(CH)	$62.7\rho + 37.3\chi$
A'	914.4	933	ρ(CH)	$73.2\rho + 17.0\rho^* + 9.8\chi$	B_{1u}	909.0	957	ρ(CH)	$73.1\rho + 26.9\chi$
A''	912.8	902	ρ(CH)*	$56.3\rho^* + 21.7\rho + 10.4\alpha + 3.3\chi + 8.2\chi^*$	A_{1u}	921.5	970?	ρ(CH)	$66.0\rho + 31.3\chi$
A'	892.6	887	ρ(CH)*	$86.7\rho^* + 2.9\rho + 2.8\chi + 6.4\chi^*$	B_{2g}	897.0	876	ρ(CH)	$70.6\rho + 26.1\chi$
A''	846.4	846	ρ(CH)*	$73.4\rho^* + 26.6\rho$	B_{3g}	862.6	846	ρ(CH)	$78.3\rho + 22.0\chi$
A''	823.4	836	ρ(CH)	$57.6\rho + 29.8\rho^*$	A_{1u}	808.9	841?	ρ(CH)	$63.0\rho + 37.0\chi$
A'	801.8	827	ρ(CH)*	$88.2\rho^* + 4.9\rho$	B_{1u}	768.9	780	ρ(CH)	$63.0\rho + 37.0\chi$

A''	782.7	787	δ(ring)	$35.7\alpha + 26.3\alpha^* + 13.5Q + 15.6Q^* + 10.1\mathrm{L}$	B_{2u}	793.0	753	δ(ring)	$53.6\alpha + 27.9Q + 14.0\beta$
A'	745.4	755	ν(ring)	$50.1Q + 16.9Q^* + 9.2\alpha + 6.4\alpha^*$	A_{1g}	755.2	762	ν(ring)	$71.6Q + 16.4\alpha + 8.3\beta$
A'	729.9	750	ρ(CH)	$79.8\rho + 4.0\rho^* + 7.5\chi^*$	B_{2g}	695.6	724	ρ(CH)	$78.6\rho + 17.8\chi$
A''	726.2	740	γ(ring)	$77.0\chi + 18.3\chi^*\text{-}2.2(\rho + \rho^*) + 5.4\mathrm{L} + 1.5\omega$	B_{3g}	758.7	780	γ(ring)	$92.0\chi + 8.0\rho$
A'	674.8	665	δCr(CO)	$63.4\varphi + 21\rho + 3.7\rho^* + 15.9R + 2.7\mathrm{L} + 9.9\omega$	—	—	—	—	—
A''	636.0	630	δCr(CO)	$40.5\varphi + 21.3R + 19.8\eta + 8.2\omega$	—	—	—	—	—
A'	632	615	δCr(CO)	$31.3\varphi + 24.4R + 12.9\eta + 8.8\mathrm{L} + 7.5\omega + 5.5\beta^*$	—	—	—	—	—
A'	614.7	—	δ(ring)	$45.0\alpha + 26.7\alpha^* + 12.7\mathrm{L}$	B_{3u}	618.3	616	δ(ring)	$79.6\alpha + 16.0\beta$
A''	586.1	600	γ(ring)	$32.9\chi + 45.8\chi^* + 5.2\rho + 10.6\rho^* + 5.5\mathrm{L}$	A_{1u}	614.1	581?	γ(ring) + ρ(CH)	$64.8\chi + 35.2\rho$
A'	544.6	540	δCr(CO)	$45.1\varphi + 9.1\alpha + 6.8R + 12.0\chi + 7.0\mathrm{L} + 8.8\omega$	—	—	—	—	—
A''	536.8	530	δCr(CO)	$52.8\varphi + 18.0R + 19.0\omega$	—	—	—	—	—
A'	512.7	513	νCr(CO) + δ(ring)	$36.6R + 14.2\alpha + 9.1\alpha^* + 10.0\varphi$	A_{1g}	508.7	512	δ(ring)	$53.9\alpha + 35.5Q + 6.1\beta$
A''	509.9	512	δ(ring)	$33.6\alpha + 21.1\alpha^* + 5.8Q + 5.9Q^* + 6.6\chi + + 8.1R + 19.9\mathrm{L}$	B_{1g}	506.8	510	δ(ring)	$74.1\alpha + 13.5Q + 6.7\beta$
A'	488.1	487	νCr(CO) + δCr(CO)	$52.6R + 18.5\varphi + 5.8\alpha + 3.4\alpha^*$	—	—	—	—	—
A'	478.0	479	δCr(CO) + νCr(CO)	$50.8\varphi + 30.9R + 6.0\omega$	—	—	—	—	—
A''	476.1	475	δCr(CO) + νCr(CO)	$40.8\varphi + 27.2R + 8.9\chi + 7.8\chi^* + 7.3\omega$	—	—	—	—	—
A''	467.0	462	γ(ring)	$46.4\chi + 32.2\chi^* + 14.8R + 8.0\varphi + 5.4\mathrm{L}$	B_{3g}	459.4	463	γ(ring)	$86.2\chi + 10.2\rho$
A'	465.8	462?	γ(ring)	$53.1\chi^* + 35.7\chi + 7.7R$	B_{1u}	468.1	476	γ(ring)	$56.7\chi + 43.0\rho$
A''	417.2	—	δCr(CO)	94.1φ	—	—	—	—	—
A'	393.5	397	γ(ring)	$45.7\chi + 20.0\chi^* + 12.3\mathrm{L} + 5.7\alpha^* + 8.6\rho^*$	B_{2g}	380.0	392	γ(ring)	$83.3\chi + 16.6\rho$
A''	354.0	357	δCC(ring)	$32.3\alpha + 28.5\alpha^* + 13.8\mathrm{L} + 9.4Q + 7.3Q^*$	B_{2u}	354.7	357	—	$79.8\alpha + 17.0Q$
A''	312.1	316	νCrL	$74.3\mathrm{L} + 6.8(\alpha + \alpha^*) + 8\ 0\chi$	—	—	—	—	—
A'	311.3	300	νCrL	$77.1\mathrm{L} + 5.2(Q + Q^*) + 5.7R$	—	—	—	—	—
A'	262.9	270	νCrL	$55.0\mathrm{L} + 32.8\chi + 8.6\chi^*$	—	—	—	—	—
A''	161.9	—	γCCC	$28.2\chi + 47.1\chi^* + 9.7\eta + 8.7\mathrm{L} + 5.8\omega$	A_{1u}	176.4	195	γ(ring)	$79.0\chi + 21.0\rho$
A'	150.8	—	δLCrC + γCCC	$33.5\omega + 11.7\mathrm{L} + 9.0\chi + 27.9\chi^* + 14.6\varphi$	B_{1u}	164.8	176	γ(ring)	$79.5\chi + 22.0\rho$
A'	101.5	—	δCCrC	$37.0\eta + 31.5\varphi + 24.6\omega + 1.5\chi + 3.2\mathrm{L}$	—	—	—	—	—
A''	101.4	—	δLCrC + δCC*r*C	$45.7\omega + 19.5\varphi + 17.3\eta + 7.6\mathrm{L} + 6.0\chi$	—	—	—	—	—
A''	86.2	—	δLCrC + δCC*r*C	$41.0\omega + 30.9\varphi + 27.6\eta$	—	—	—	—	—
A'	82.9	—	δCCrC	$56.1\eta + 30.3\varphi + 10.3\omega$	—	—	—	—	—
A'	65.8	—	δLCrC	$42.9\omega + 23.8\chi^* + 10.4\mathrm{L} + 8.7\varphi$	—	—	—	—	—
A''	37.8	—	δLCrC	96.0ω	—	—	—	—	—

Note. The following designations were used: *R*, *r*, and *L* are the stretching vibrations of Cr—(CO), C—O, and C(ring)—Cr, respectively; φ and η are the bendings of Cr—C—O and (OC)—Cr—(CO) angles, respectively; and ω is the bending of C(ring)—Cr—C angle (rocking vibration of Cr(CO)$_3$). For other designations, see Table 1. The coordinates marked with asterisk are attributed to the metal-coordinated benzene ring.

nating from the longest central C(3)—C(10) bond (Q) are shortened in both rings. However, unlike the experimental data, the calculated Q_3 bond is longer than Q_2, while the structural data give close values for them. The distinctions can be related to both the influence of the environment and different orientations of the $Cr(CO)_3$ group relatively to the benzene ring.

Vibrational spectra of chromium (η^6-naphthalene)tricarbonyl. The calculated optimized geometry of the molecule was used for the calculations of the vibrational spectra of CNT. The calculated vibrational frequencies of CNT compared to the vibrations of the naphthalene molecule are presented in Table 5. This table also demonstrates the assignment of vibrations by symmetry, taking the D_{2h} symmetry for naphthalene and C_s for CNT, and the assignment of vibrations and PED over internal coordinates. For convenience the bond vibrations of the same type are united in the column containing the potential energy distribution on the normal coordinates, *i.e.*, for example, the coefficient at the Q^* coordinate implies the contribution of all C—C bonds in the metal-coordinated ring to the vibration, and the coefficient at the ρ coordinate means the contribution of out-of-plane modes of the C—H bonds of the "free" ring. The frequencies in the table are arranged in such a manner that vibrations of the free and coordinated naphthalene could conveniently be compared according to the correlation of representations of the D_{2h} and C_s symmetry groups.

Analysis of the data in Table 5 shows that the DFT calculation using the optimized geometry of the CNT molecule gives a good agreement of the calculated spectrum with experiment. The assignment of vibrations coincides completely with that proposed by us earlier[17] from the detailed analysis of the experimental data (frequencies, intensities of bands, polarization of lines in Raman spectra, comparison with the spectrum of the ligand and the spectra of the related chromium tricarbonyl complexes). The deviation of the calculated frequencies from the experimental values is ≤2.5%. As for naphthalene, the maximum difference between the calculation and experiment was observed for the frequencies of C—H stretching vibrations, which is associated with their strong anharmonicity. As a whole, the results of calculation confirm that the DFT method can be used without the scaling procedure for the calculation of vibrational spectra of transition metal π-complexes with rather large ligands.

The obtained complete and reliable assignment of bands in the IR and Raman spectra (based on both the experimental data and quantum-chemical calculation) allows us to inspect the influence of the formation of a π-complex with the metal on the spectrum of the coordinated ligand. In particular, the calculation performed makes it possible to differentiate vibrations of naphthalene localized mainly on the metal-coordinated and "free" rings.

Some empirical regularities concerning the effect of a metal on vibrations of the benzene rings have previously been found by the analysis of experimental assignments of bands for the metal π-benzene complexes.[8] The ν(CC) frequencies of in-plane modes of the benzene rings undergo the strongest low-frequency shifts, up to 70—100 cm^{-1}, upon complex formation. On the contrary, the ρ(CH) frequencies of out-of-plane modes are strongly, up to 100 cm^{-1}, shifted to the high-frequency region. The β(CH) in-plane bending vibrations in complexes change slightly. Since the in-plane modes of the ligand are poorly kinematically coupled with the metal—ligand vibrations, their shifts were mainly ascribed to changes in the electronic structure of the ligand. The out-of-plane modes of the ligand, for which the atoms shift in parallel to the direction of the metal—ligand bond, can strongly interact with the skeletal modes of the complex, and their change can be related not only to a change in the electronic structure. For the naphthalene ligand the situation is more complicated due to two types of the benzene rings. Let us consider in more detail the main types of vibrations.

Stretching ring vibrations. It is seen from the data in Table 5 that the coordinates of the Q type contribute mainly to six vibrations in the 1380—1620 cm^{-1} region and to two vibrations at ~1000 cm^{-1} for both free and coordinated naphthalenes. Indeed, for the seven of the indicated vibrations the calculation predicts the low-frequency shift from 5 to 72 cm^{-1}. However, one of the vibrations increases the frequency from 1378 to 1407 cm^{-1}, and this vibration is mainly localized on the coordinated ring. In fact, as it is seen from the PED, in some cases the β(CH) in-plane bending vibrations contribute noticeably, along with the coordinates of the Q type, to the so-called ring vibrations. Some vibrations are localized on one of the rings, and some vibrations involve, to a great extent, the vibrations of the carbon—carbon bonds of both rings. In addition, the coordination changes substantially the modes of vibrations of the naphthalene molecule and the contribution of particular coordinates to the PED. Therefore, the comparison of frequencies is formal to a great extent, although the general tendency to decrease the frequencies of in-plane modes during coordination, in fact, takes place. It is more correct to compare changes in force constants of the C—C bonds. This problem could not be solved earlier because of uncertainty of the force field calculation. *Ab initio* calculations of the force field of the molecule allow this solution. Some diagonal force constants for the naphthalene and CNT molecules are compared in Table 6. It is seen that for the coordinates of the Q type all force constants of the carbon—carbon bonds decrease upon coordination. The force constants of the coordinated ring decrease more strongly (by 10—15%) than those for the free ring (by 6—10%).

Table 6. Comparison of the force constants (K*) of the free and η^6-coordinated naphthalene ligands

Internal coordinate	$C_{10}H_8$	(η^6-$C_{10}H_8$)Cr(CO)$_3$	
		Free ring	Bound ring
Q	5.0373	4.2805	4.2805
Q_1	5.7647	5.4045	5.0836
Q_2	7.0808	6.9307	5.9961
Q_3	5.8357	5.4779	5.2870
q_1	5.2680	5.3144	5.3597
q_2	5.3073	5.3396	5.3981
α_1	0.9180	0.8551	0.5280
α_2	1.0476	0.8664	0.5318
α_3	0.9624	0.8038	0.4832
β_1	0.5054	1.0061	0.9815
β_4	0.5013	1.0077	0.9915
ρ_1	0.4571	1.6152	1.7378
ρ_2	0.3470	1.6337	1.8748

* For bond stretches of the Q and q types the force constants have a dimensionality of 10^2 N m^{-1}, and for the angular coordinates α, β, ρ the dimensionality is 10^{-18} N m rad.

C—H stretching vibrations. The calculation predicts an increase in the frequencies of C—H stretching vibrations in the complex by 10—30 cm^{-1} compared to the ligand, which corresponds well to the spectral data. The same increase has previously been observed for coordinated benzene and thiophene.[8,26,27] The ν(CH) vibrations are highly characteristic, and their increase can be related only to an increase in the force constants of the C—H bonds. In fact, as can be seen from the data in Table 6, some increase in the K_q values occurs for all C—H bonds, and the coordinated ring exhibits a more considerable increase.

In-plane stretching vibrations. The eigenvectors of in-plane stretching vibrations are complicated. Changes in both the α and β angles and the C—H bond lengths (q coordinates) contribute to these vibrations. Therefore, it is difficult to distinguish any regularities for a change in the corresponding frequencies in the complex. The assignment (see Table 5) is conventional to a considerable extent because is takes into account the coordinates, whose contribution to the vibration is maximum. However, the total contribution of other coordinates is sometimes comparable with this value.

Since in calculations of the free ligand and complex the internal coordinates for vibrations of the β, ρ, and χ types were introduced by different methods, the direct comparison of the force constants of these coordinates presented in Table 6 is incorrect. We can only mention the distinction of the force constants for the free and coordinated rings of CNT. The K_α values in the coordinated ring is strongly decreased compared to those in the free ring, and some decrease is observed for K_β.

Out-of-plane bending vibrations. Out-of-plane ρ(CH) modes are characteristic to a great extent and are slightly mixed with other modes. Unlike the coordinated benzene molecule, whose complex exhibits a strong increase in the frequencies of the out-of-plane ρ(CH) modes, no sharp changes in these frequencies are observed in the case of CNT. The K_ρ force constants of the coordinated ring is somewhat increased over those for the free ring, which agrees with the concepts about an increase in the ρ(CH) frequency upon coordination.

Metal—ligand vibrations. Three rather characteristic frequencies at 260—320 cm^{-1} are referred to the chromium—ring stretching vibrations. For these frequencies the Cr—C coordinates (L) contribute mainly to the PED. The calculated and experimental values of these frequencies are in good accordance. The coordinates of the L type contribute noticeably to other low-frequency vibrations at 350—470 cm^{-1}, which are described as out-of-plane bending vibrations of the rings. The difference in the Cr—C bond lengths (see Table 4) is manifested in the difference in the force constants (K) for these bonds presented below. For the longer Cr—C(3) and Cr—C(10) bonds the force constants have lower values.

Bond	$K \cdot 10^{-2}$/N m^{-1}
Cr—C(3), Cr—C(10)	0.7597
Cr—C(14), Cr—C(11)	0.9856
Cr—C(13), Cr—C(12)	0.9788
Cr—C(5)	3.1845
Cr—C(4), Cr—C(6)	2.9748
C(5)—O(24)	14.9894
C(4)—O(23), C(6)—O(25)	15.2047

Vibrations of the Cr(CO)$_3$ fragment. The Cr—CO vibrations are noticeably mixed with the Cr—C—O anglular bendings. The coordinates of the R type (changes in the Cr—CO bond lengths) make the maximum contribution to vibrations, whose frequencies lie in the 450—520 cm^{-1} region, which agrees with the previous assignments.[17] Since all these vibrations are mixed, their frequencies provide a few information on the structure of the Cr(CO)$_3$ fragment. However, the K_R force constants presented above indicate a distinction of the Cr—C bond, which lies in the symmetry plane of the molecule, from two other bonds. The force constants for the latter are somewhat lower.

On the contrary, the ν(CO) stretching vibrations are highly characteristic. Their frequencies are close to the ν(CO) frequencies of other chromium tricarbonyl complexes.[8,26,27] The K_{CO} force constant of the bond, which lies in the symmetry plane, is slightly higher than two others.

* * *

The data obtained show that the DFT method is promising for the analysis of vibrational spectra of transition metal π-complexes. In the case of chromium (η^6-naphthalene)tricarbonyl (for both the complex and organic aromatic ligand), a good agreement of the calculated frequencies with experiment (except frequencies of stretching vibrations of C—H) is achieved without using the scaling procedure. This allowed us to interpret completely the vibrational spectra of the naphthalene and CNT molecules, compare the geometric parameters and force fields of the ligand and complex, and inspect the effect of coordination with the metal on the properties of the ligand, particularly for the metal-coordinated and free benzene rings.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 01-03-32212-a).

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Received January 22, 2002;
in revised form March 29, 2002