compounds contain pseudo-tetrahedrally coordinated cobalt(II) by this criterion, as is also indicated by the magnetic data for two of them. The transition $^4A_2 \rightarrow {}^4T_1(P)$ in tetrahedral symmetry (as of the CoO_4 chromophore) commonly shows some splitting due to spin–orbit coupling.[16] For the chromophore CoO_2Cl_2 of C_{2v} symmetry, the transition becomes $^4A_2 \rightarrow {}^4A_1 + {}^4B_1 + {}^4B_2$, and the "average ligand field" approximation applies. Thus the $Co\{O_2PR_2\}_2$ compounds come at higher energy than the $CoCl_2\{OPR_3\}_2$ compounds, and in all cases the band is structured, with shoulders on the high-energy side. It is interesting that although substituent effects are seen on the P=O vibrational frequency and on its shift upon coordination, the four phosphoryl donors seem to have the same ligand field strengths. The visible spectra of their cobalt(II) chloride complexes are virtually identical.

The complexes of the phosphoryl donors containing ester groups lose all their chloride content on heating to give $Co\{O_2(C_2H_5)_n(OC_2H_5)_{2-n}\}_2$ products. While these could be monomeric, with chelating $O_2PRR'^-$ anionic ligands,[17] their properties suggest association of the type previously found[18] with various polymeric metal phosphinates.

Acknowledgments.—This work was supported by National Science Foundation Grant GP-4185, which is acknowledged with thanks. We also thank the National Science Foundation and the Oregon State University Research Council and General Research Fund for equipment funds and the Ethyl Corp. for a gift of tetraethyllead.

[16] F. A. Cotton, D. M. L. Goodgame, and M. Goodgame, *J. Am. Chem. Soc.*, **83**, 4690 (1961).

[17] V. Gutmann and K. Fenkart, *Monatsh. Chem.*, **99**, 1452 (1968).

[18] G. E. Coates and D. S. Golightly, *J. Chem. Soc.*, 2523 (1962); V. Crescenzi, *et al.*, *J. Am. Chem. Soc.*, **87**, 391 (1965); B. P. Block, *et al.*, *Inorg. Chem.*, **6**, 1439 (1967), and references therein.

CONTRIBUTION FROM THE CENTRAL RESEARCH LABORATORIES, AJINOMOTO COMPANY, INC.,
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Force Constants in the Acetylene Molecule in a Cobalt–Carbonyl Complex and in an Excited Electronic State

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An approximate normal-coordinate treatment has been made as a six-body problem for the $CH\equiv CHCo_2$ part of the $CH\equiv CHCo_2(CO)_6$ molecule. The values of 12 force constants were determined on the basis of 30 observed frequencies of four isotopic molecules (which contain $^{12}CH\equiv{}^{12}CH$, $^{12}CD\equiv{}^{12}CH$, $^{12}CD\equiv{}^{12}CD$, and $^{13}CH\equiv{}^{12}CH$) by the method of least squares. A similar normal-coordinate treatment was made of the acetylene molecule in an excited electronic state (^1A_u). The values of six force constants were estimated on the basis of six observed frequencies. It was found that five of the latter force constant values are nearly equal to the values of the corresponding force constants in the acetylene molecule in the complex.

Introduction

The nature of the coordinate bond has been studied by many investigators and recently some of them have succeeded in elucidating the physical properties of coordination compounds by the use of molecular orbital theory.

As the first approximation, the antibonding and bonding π orbitals of a ligand molecule are taken as the acceptor and donor π orbitals, respectively.[1,2]

The net effect of bond formation on the ligand molecule is assumed to bring the electron of the ligand molecule from the highest bonding π orbital to the lowest antibonding π orbital. That is, the complexed ligand should have an electron configuration analogous to the electronically excited free molecule.

Wilkinson and his coworkers[3] have pointed out that the observed bond lengths and the bond angle in the coordinated CS_2 in $PtCS_2[P(C_6H_5)_3]_2$ are close to the corresponding values in the first excited state of CS_2.

Recently we have demonstrated a similarity of vibrational spectrum of complexed acetylene to that of an excited acetylene[4] and a similarity of the symmetry of a complexed CO_2 with that of an excited carbon dioxide.[5]

In the present work, the author has attempted to determine the force constants of the complexed and excited acetylenes by an approximate normal vibration treatment and to examine the transferability of the force constants between these two states.

Vibrational Frequencies and Their Assignments

Excited Acetylenes.—Ingold and King[6] gave the geometry and totally symmetric vibrational frequencies of the first excited state (^1A_u) of acetylene.

Innes[7] made a refinement of these data. The results

[1] L. E. Orgel, "An Introduction to Transition Metal Chemistry," Methuen and Co. Ltd., London, 1960.

[2] A. C. Blizzard and D. P. Santry, *J. Am. Chem. Soc.*, **90**, 5749 (1968).

[3] M. Baird and G. Wilkinson, *Chem. Commun.*, **18**, 93 (1967).

[4] Y. Iwashita, F. Tamura, and A. Nakamura, *Inorg. Chem.*, **8**, 1179 (1969).

[5] Y. Iwashita and A. Hayata, *J. Am. Chem. Soc.*, **91**, 2525 (1969).

[6] C. K. Ingold and G. W. King, *J. Chem. Soc.*, 2702 (1953).

[7] K. K. Innes, *J. Chem. Phys.*, **22**, 863 (1954).

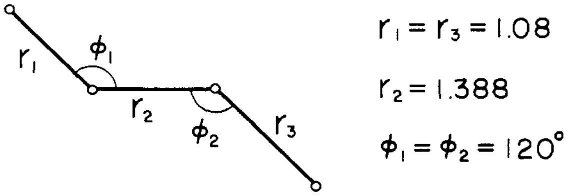

Figure 1.—The molecular model of the excited acetylene.

are given in Figure 1. The assignments of vibrational frequencies can be made by comparing the frequencies of CH≡CH with those of CD≡CD. The assignments are also given in Table I.

TABLE I

VIBRATIONAL FREQUENCIES[a] OF THE EXCITED ACETYLENE

	CH≡CH	CD≡CD
ν_1	3020.0	2215.0
ν_2	1380.0	1310.0
ν_3	1049.0	844.0

[a] These frequencies are quoted from ref 7.

Coordinated Acetylenes.—Iwashita, Tamura, and Nakamura have previously reported the infrared spectra[4] of $CH{\equiv}CHCo_2(CO)_6$, $CD{\equiv}CDCo_2(CO)_6$, $CH{\equiv}CDCo_2(CO)_6$, and $^{13}CH{\equiv}CHCo_2(CO)_6$ from 4000 to 200 cm^{-1}. The observation has now been extended into the far-infrared region by the use of a Hitachi FIS-3 spectrometer. As shown in Figure 2, a few additional absorption bands have been found for $C_2H_2Co_2(CO)_6$ in the 300-60-cm^{-1} region. (The far-infrared spectra, 300-60 cm^{-1}, were measured using a polyethylene cell in a double-beam spectrophotometer. The wave number calibration was made by the known absorptions of water vapor.)

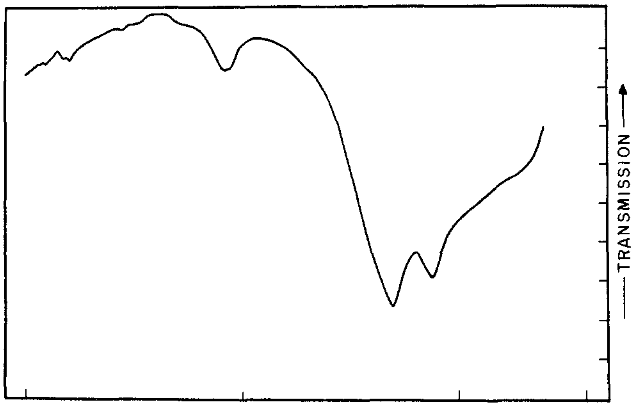

Figure 2.—The far-infrared spectrum of $CH{\equiv}CHCo_2(CO)_6$.

It has been found difficult, however, to make an unequivocal assignment of all observed vibrational frequencies of this complex molecule. As will be described below, the writer made a normal-coordinate treatment of only the $C_2H_2Co_2$ part of the molecule, instead of the whole $C_2H_2Co_2(CO)_6$ molecule. Therefore, the assignments will be given for only the vibrations localized in this part of the molecule.

In our previous paper, we have shown that CH (or CD) stretching, C≡C stretching, CH (or CD) bending, and cobalt–acetylene stretching bands are easily picked up on the basis of the observed H → D and/or $^{12}C \rightarrow {}^{13}C$ isotope effects. It was also shown that the acetylene part of the complex molecule has the C_{2v} form. We shall now assume that the $C_2H_2Co_2$ part of the molecule also has C_{2v} symmetry (see Figure 4). Then, the 12 vibrations should be grouped as follows: $5\ A_1 + 2\ A_2 + 2\ B_1 + 3\ B_2$. The assignments of the observed bands on this grouping will now be given below.

In the CH stretching vibrations, the two bands appear at 3116.0 and 3086.0 cm^{-1}. On ^{13}C substitution, the former shifts by 4 cm^{-1}, while the latter shifts by 5.1 cm^{-1}. On the basis of these isotope shifts, the 3116.0-cm^{-1} band seems to be assigned to the A_1 type of vibration and the 3086.0-cm^{-1} band to the B_2 type of vibration; when the deviation from a linear form is not so large, the ^{13}C isotope shift for the A_1 type of CH stretching frequency should be smaller than that for the B_2 type of CH stretching frequency.

On the basis of the isotope shifts ($^{12}C \rightarrow {}^{13}C$ and H → D) shown in Table II, the band at 1402.5 cm^{-1} can be ascribed to the C≡C stretching vibration.

TABLE II

THE OBSERVED FREQUENCIES AND ASSIGNMENTS OF ACETYLENE–DICOBALT HEXACARBONYLS[a]

	$C_2H_2Co_2(CO)_6$	$C_2D_2Co_2(CO)_6$	$^{13}CHCHCo_2(CO)_6$ (^{13}C shift)		$CH{\equiv}CDCo_2(CO)_6$
		A_1			A′
1	3116.0	2359.0	3112.0 (4.0)	1	3113.0
2	1402.5	1346.5	1379.0 (23.5)	2	2328.0
3	768.0	602.0	766.8 (1.2)	3	1381.0
4	605.0	561.0	597.0 (8.0)	4	861.5
5	207	207	207 (0)	5	657.2
		B_2			
10	3086.0	2297.0	3080.9 (5.1)	6	...
11	894.0	751.4	890.5 (3.5)	7	...
12	551.0	520.0	546.0 (5.0)	8	207

[a] Spectral conditions are given in ref 4.

In *cis*-1,2-dichloroethylene,[8] the symmetric HCCH bending (A_1) mode has a lower frequency than the antisymmetric one. On this basis, the band at 768.0 cm^{-1} of the complex may be attributed to the A_1-type HCCH bending vibration and the band at 894 cm^{-1} to the B_2 type, respectively.

The two acetylene–cobalt stretching vibrations may be assigned to the observed frequencies 605 and 551 cm^{-1}. However, which is of the A_1 type and which is of the B_2 type is not evident.

Of the two cobalt–acetylene stretching bands, the 605-cm^{-1} band is assigned to the A_1 type and the 551-cm^{-1} band to the B_2 type, on the basis of the normal-coordinate analysis.

In the far-infrared region three bands are observed at 207, 130, and 110 cm^{-1} (Figure 2). (The satellite band at about 75 cm^{-1} was due to polyethylene.) The strong bands at 130 and 110 cm^{-1} may be assigned to

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(8) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand and Co., Princeton, N. J., 1945.

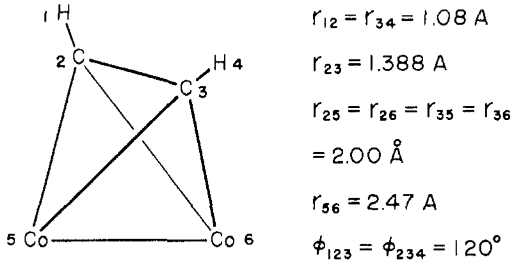

Figure 3.—The assumed model of the complex.

(OC)–Co–(CO) bending modes, based on the study of McDowell and Jones.[9] A weak but sharp band at 207 cm^{-1} is ascribed to the Co–Co stretching mode, on the basis of comparison with other metal–metal stretching vibrations of polynuclear metal carbonyls.[10] Four bending frequencies (ν_6, ν_7, ν_8, and ν_9) remain unassigned. We shall not use these frequencies in estimating the force constants.

Procedure of Calculation

As described before, the assignments are not yet clear for vibrations in the carbonyl part of the complex molecule. In addition, our present interest is rather in the force constant values in the acetylene part of the complex molecule. Therefore, a normal-coordinate treatment of the $C_2H_2Co_2$ system (Figure 3), as a six-body problem, has been carried out. Such a simplification is justified by the fact that no effect can be detected of the deuteration or ^{13}C substitution at the acetylene part of molecule upon the positions and intensities of absorption bands assignable to the C≡O stretching and Co—C≡O bending vibrations.

The normal-coordinate treatment has been carried out by means of Wilson's *GF*-matrices method.[11] Based on the X-ray diffraction studies[12] of $(C_6H_5CCC_6H_5)Co_2(CO)_6$, the Co–C and Co–Co bond distances were taken to be 2.00 and 2.47 Å, respectively. The HCC bond angles of the complexed acetylene are assumed to be 120°, and the C–C and C–H bond lengths are estimated to be identical with those of excited-state acetylene. Small errors in these values may not cause any serious errors in the final results, since the frequency is not very sensitive to the geometry of the molecule.

The assumed model is illustrated in Figure 3 with the assumed values. The 12 symmetry coordinates are shown in Table III. In addition, there are 14 redundant coordinates which are not given here. The *F*-matrix elements were expressed in terms of the Urey–Bradley force field and also in a more general form. The *F* matrices of the excited acetylene and $C_2H_2Co_2$ part of the acetylene complex expressed in terms of the general force field are given in Table IV.

The off-diagonal terms which do not appear in the Urey–Bradley force field are introduced and shown as

Table III

Symmetry Coordinates of the Complex

A_1

SI $= \Delta(r_{12} + r_{34})/\sqrt{2}$
SII $= \Delta r_{23}$
SIII $= \Delta(\phi_{123} + \phi_{234})/\sqrt{2}$
SIV $= \Delta(r_{25} + r_{26} + r_{35} + r_{36})/2$
SV $= \Delta r_{56}$

A_2

SVI $= \Delta(\phi_{125} - \phi_{126} - \phi_{435} + \phi_{436})/2$
SVII $= \Delta(r_{25} - r_{26} - r_{35} + r_{36})/2$

B_1

SVIII $= \Delta(\phi_{125} - \phi_{126} + \phi_{435} - \phi_{436})/2$
SIX $= \Delta(r_{25} - r_{26} + r_{35} - r_{36})/2$

B_2

SX $= \Delta(r_{12} - r_{34})/\sqrt{2}$
SXI $= \Delta(\phi_{123} - \phi_{234})/\sqrt{2}$
SXII $= \Delta(r_{25} + r_{26} - r_{35} - r_{36})/2$

Table IV

The *F* Matrices in Terms of the General Force Field

F Matrix of Excited Acetylene

	Δr_{12}	Δr_{34}	Δr_{23}	$\Delta\phi_{123}$	$\Delta\phi_{234}$
Δr_{12}	$A(AD^a)$				
Δr_{34}	F_1	$A(AD^a)$			
Δr_{23}	P	P	B		
$\Delta\phi_{123}$	Q	F_2	R	C	
$\Delta\phi_{234}$	F_2	Q	R	F_3	C

F Matrix of the $C_2H_2Co_2$ Part of Acetylene–Dicobalt Hexacarbonyl

	Δr_{12}	Δr_{34}	Δr_{23}	Δr_{25}	Δr_{26}	Δr_{35}	Δr_{36}	Δr_{56}	$\Delta\phi_{123}$	$\Delta\phi_{234}$
Δr_{12}	$A(AD^a)$									
Δr_{34}	F_1	$A(AD^a)$								
Δr_{23}	P	P	B							
Δr_{25}	S			D						
Δr_{26}	S				D					
Δr_{35}		S				D				
Δr_{36}		S					D			
Δr_{56}								E		
$\Delta\phi_{123}$	Q	F_2	R						C	
$\Delta\phi_{234}$	F_2	Q	R						F_3	C

[a] In other words, *AD* contains a zero-point energy correction.

F_1, F_2, and F_3, when they express the interactions between the coordinates of the coordinated acetylene only. Since all 13 force constants are not independent, some of them were fixed at one value and the independent set of force constants were selected in order to determine the force constants by the least-squares method. For example, the values of the force constants *P* were fixed arbitrarily at -0.2 mdyn/Å in the calculation of the complexed and the excited acetylenes, because the force constants *P* and *Q* were not independent in these two states. To obtain a reasonable value of the arbitrarily fixed force constant, this fixed value was changed from one to another value, point by point, and then for each value the adjustment of the other force constants was made by the least-squares method. The final set of the force constants gave the closest values of the calculated frequencies to the observed ones (Table V).

At the start, the force constants of the acetylene moiety were transferred from those of benzene.[13] For

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[9] R. S. McDowell and J. H. Jones, *J. Chem. Phys.*, **36**, 3321 (1962).

[10] H. M. Gager, J. Lewis, and M. J. Ware, *Chem. Commun.*, **17**, 616 (1966).

[11] E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill Book Co., Inc., New York, N. Y., 1955.

[12] W. G. Sly, *J. Am. Chem. Soc.*, **81**, 18 (1959).

[13] S. Mizushima and T. Shimanouchi, "Infrared Spectra and Raman Effect," Kyoritsu Printing Co., Inc., Tokyo, Japan, 1958.

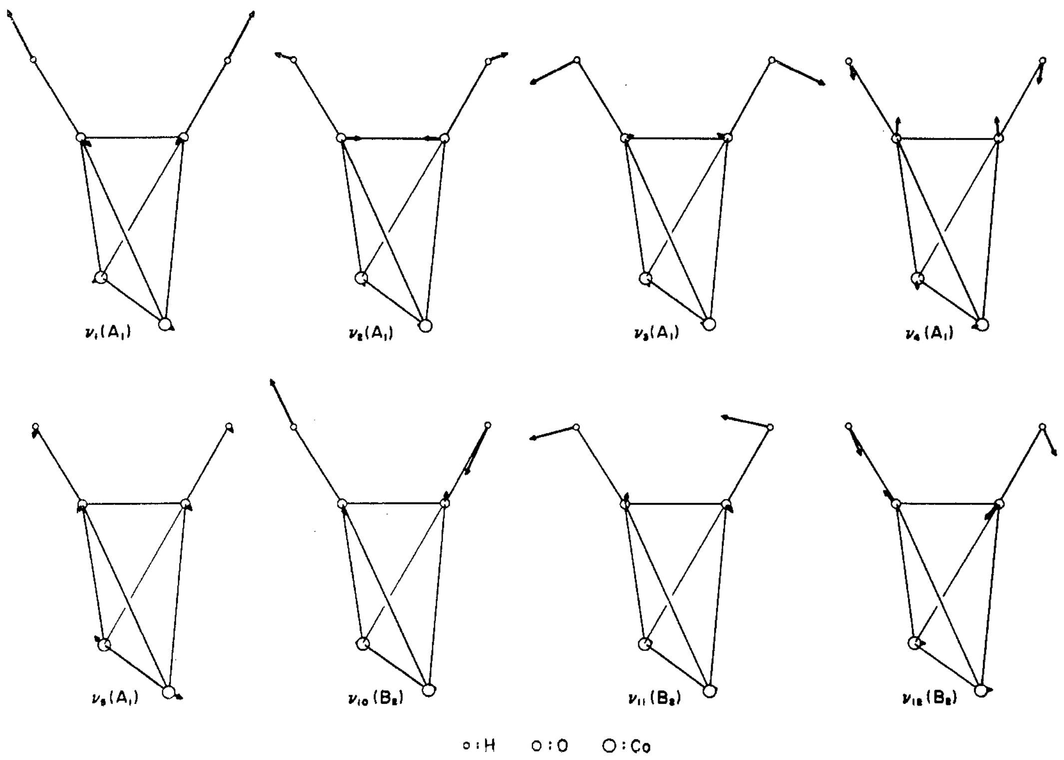

Figure 4.—Normal vibrations of the complex.

TABLE V

THE COMPARISON OF THE FORCE CONSTANTS BETWEEN THE EXCITED AND COORDINATED ACETYLENES

Urey–Bradley Force Field

State	K_{CH}	K_{CC}	K_{CCo}	K_{CoCo}	H_{HCC}	F_{CH}	F_{HCo}
Excited	4.69	5.93	...	...	0.20	0.61	...
Coordinated I[a]	4.96	6.18	2.12	0.86	0.10	0.49	0.05

General Force Field

State	A	AD	B	C	D	E	P
Excited[b]	4.96	4.81	7.26	0.64	...	...	−0.20
Coordinated I[b]	4.95	4.79	7.32	0.41	2.41	0.86	−0.40
Coordinated II	5.02	4.94	7.48	0.45	2.21	0.86	−0.20

State	Q	R	S	F_1	F_2
Excited[b]	0.29	0.76	...	0	0
Coordinated I[b]	−0.24	0.13	−0.70	0	0
Coordinated II	−0.23	0.51	−0.46	0.11	0.21

[a] $F_{H\cdots Co}$ = 0.05 arbitrarily fixed. [b] F_1, F_2 = 0 arbitrarily fixed.

the Co–C and Co–Co stretching vibrations, Pt–C[14] and Mn–Mn[10] stretching force constants were transferred at the start of the least-squares minimization. In the calculation by the use of the Urey–Bradley force field (UBFF), the repulsive force constant between cobalt and hydrogen is assumed arbitrarily to be 0.05 mdyn/Å. In the general force field (GFF) treatment, the long-range interaction terms F_1 and F_2 were determined by the least-squares method, but the value of F_3, which expresses the interaction between two HCC bending vibrations, was not obtainable because of the divergence of the calculated frequencies. Perhaps this comes from neglect of the mixing of HCC bending vibrations with Co—(C≡O) stretching and Co—C≡O bending vibrations. The calculation has been made by the use of a CDC 3600 computer and programs BGLZ and LSMA.[15]

Results and Discussion

Table V shows the final sets of the force constants of the excited and coordinated acetylenes. The deviation of the calculated frequencies of the coordinated acetylene was 1.5% (Table VI) by the use of the Urey–Bradley force field but it was lessened to 0.6% on the average when the force constants of the general force field, set II, were used as shown in Table VII. The normal mode of vibrations calculated are shown in Figure 4.

TABLE VI

THE CALCULATED FREQUENCIES OF THE EXCITED AND COORDINATED ACETYLENES FROM THE UREY–BRADLEY FORCE FIELD SHOWN IN TABLE V

Excited Acetylenes

CH≡CH		CD≡CD	
ν_{obsd}	ν_{calcd}	ν_{obsd}	ν_{calcd}
3020.0	3022.3	2215.0	2211.9
1380.0	1352.1	1310.0	1338.5
1049.0	1058.7	844.0	831.9

Coordinated Acetylenes

	$CH{\equiv}CHCo_2(CO)_6$		$CD{\equiv}CDCo_2(CO)_6$		^{13}C isotope shifts		$CD{\equiv}CHCo_2(CO)_6$	
	ν_{obsd}	ν_{calcd}	ν_{obsd}	ν_{calcd}	$\Delta\nu_{obsd}$	$\Delta\nu_{calcd}$	ν_{obsd}	ν_{calcd}
ν_1	3116.0	3118.2	2359.0	2298.6	4.0	0	3113.0	3118.0
ν_2	1402.5	1392.4	1346.5	1371.4	23.5	26.3	2328.0	2294.4
ν_3	768.0	747.5	602.0	627.1	1.2	1.4	1381.0	1382.0
ν_4	605.0	611.7	561.0	508.7	8.0	6.7	861.5	870.5
ν_5	207.0	207.3	207.0	206.2	~0	0.5	657.2	651.2
ν_{10}	3086.0	3118.3	2297.0	2290.1	5.0	9.3	...	594.0
ν_{11}	894.0	913.6	751.4	775.9	3.5	7.2	...	488.0
ν_{12}	551.0	544.0	520.0	478.3	5.0	7.4	207	206.8

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(14) M. J. Grogan and K. Nakamoto, *J. Am. Chem. Soc.*, **88**, 5454 (1966).

(15) H. Schachtschneider and R. G. Snyder, *Spectrochim. Acta*, **19**, 117 (1963).

TABLE VII

THE CALCULATED FREQUENCIES AND POTENTIAL ENERGY DISTRIBUTION[a] OF THE EXCITED AND COORDINATED ACETYLENES FROM THE GENERAL FORCE FIELD SHOWN IN TABLE V (SET II)

Excited Acetylenes

CH≡CH					CD≡CD				
		PED, %					PED, %		
ν_{obsd}	ν_{calcd}	SI	SII	SIII	ν_{obsd}	ν_{calcd}	SI	SII	SIII
3020.0	3020.0	98.4	0.6	0.3	2215.0	2215.0	94.2	3.3	0.8
1380.0	1380.0	1.1	79.4	4.4	1310.0	1310.0	3.6	100.8	0.5
1049.0	1049.0	1.1	39.6	115.4	844.0	844.0	2.8	15.5	118.8

Coordinated Acetylenes

	$C_2H_2Co_2(CO)_6$		PED, %							
	ν_{obsd}	ν_{calcd}	SI	SII	SIII	SIV	SV	SX	SXI	SXII
ν_1	3116.0	3125.4	94.7	1.1	0	0.5	0			
ν_2	1402.5	1404.0	4.0	95.7	0	4.4	0			
ν_3	768.0	771.4	0	18.7	118.0	0.3	0			
ν_4	605.0	608.3	5.2	3.2	0.4	96.5	2.1			
ν_5	207.0	207.2	0.1	0.1	0	2.1	97.9			
ν_{10}	3086.0	3086.6						92.4	0.5	0.5
ν_{11}	894.0	907.5						19.0	104.8	7.5
ν_{12}	551.0	547.9						3.2	5.0	96.4

	^{13}C isotope shifts		$C_2D_2Co_2(CO)_6$		$CHCDCo_2(CO)_6$	
	$\Delta\nu_{obsd}$	$\Delta\nu_{calcd}$	ν_{obsd}	ν_{calcd}	ν_{obsd}	ν_{calcd}
ν_1	4.0	6.4	2359.0	2350.0	3113.0	3105.2
ν_2	23.5	24.4	1346.5	1345.3	2328.0	2331.0
ν_3	1.2	1.3	602.0	608.1	1381.0	1377.0
ν_4	8.0	7.0	561.0	538.1	861.5	856.4
ν_5	~0	0.5	207.0	206.1	657.2	641.8
ν_{10}	5.1	9.2	2297.0	2309.6	...	599.0
ν_{11}	3.5	5.4	751.4	733.2	...	504.1
ν_{12}	5.0	8.4	520.0	492.3	207.0	206.7

[a] PED is the set of coefficients in the linear combination of symmetry coordinates in the normal coordinates.

As given in Table V, the C–C stretching force constant on the basis of the Urey–Bradley force field is 5.9 mdyn/Å in the excited (^1A_u) acetylene molecule and 6.2 mdyn/Å in the coordinated acetylene molecule. On the basis of the general force field, this (*B* in Table V) is 7.3 mdyn/Å for the ^1A_u acetylene and 7.3–7.5 mdyn/Å for the coordinated acetylene molecule. In any case, the C–C stretching force constant in the coordinated acetylene is quite close to the excited (^1A_u) acetylene and is different from that (15.8 mdyn/Å[8]) of ground-state acetylene.

Likewise, the C–H stretching force constant K_{CH} (Urey–Bradley force field) or *A* or *AD* (general force field) of the coordinated acetylene, 4.69–5.02 mdyn/Å, is close to that of excited (^1A_u) acetylene and different from that (5.92–5.99 mdyn/Å[8]) of ground-state acetylene. This is the case also for the force constant *P* which represents the coupling between the two C–H stretching motions. There is significant difference between the coordinated acetylene and the excited acetylene (^1A_u) in the force constants H_{HCC} or *C* and *Q*. These force constants are concerned with the HCC bending motion; the deviation must therefore be due to the interaction between hydrogen and cobalt atoms and to a change in molecular shape from the *trans* to the *cis* form.

Because we neglected the cobalt–carbonyl bonds, the values of other force constants are not very significant. It is interesting, however, that the value obtained (2.2 mdyn/Å for both UBFF and GFF) for the cobalt–acetylene stretching force constant is very close to the reported value of the force constant of $Co(CN)_6^{3-}$ (2.33 mdyn/Å[13]). The Co–Co stretching force constant (0.86 mdyn/Å) is smaller than the value in $Mn_2(CO)_{10}$ (1.4 mdyn/Å[10]) but is comparable with 0.8 mdyn/Å of $Re_2(CO)_{10}$.[16]

By the present examination, the similarity of the force constants of the acetylenes in the excited and the coordinated states has been established. This result suggests something about the electronic state of acetylene in the complex. Just one electron is completely subtracted from the lowest bonding π orbital and just one d electron is added to the high antibonding π orbital; that is, the resultant electron configuration is analogous to that of an excited acetylene. Blizzard and Santry[2] have derived the relation between electron distribution and the bond angle of acetylene on the basis of the molecular orbital theory. The assumed bond angle of 120° of CCH and the electron configuration of the coordinated acetylene are in agreement with what is expected from their relation. As to why the complexed acetylene has the *cis* form rather than the *trans*, the following two factors can be taken into account. One is the unfavorable repulsion of CH σ-bond electrons and C–Co σ-bond electrons. The other is that the *cis* form has almost the same stability as the *trans* form in the free molecule of the excited state.[17]

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