# Microwave Spectra for $(C_6H_5D)Cr(CO)_3$, $(C_6D_6)Cr(CO)_3$, and $(C_6H_5F)Cr(CO)_3$ and the Structure of (Benzene)chromium Tricarbonyl

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Microwave spectra for the $D_1$ and $D_6$ isotopomers of (benzene)chromium tricarbonyl and (fluorobenzene)chromium tricarbonyl were measured using a Flygare-Balle type microwave spectrometer system. The new rotational constants for the deuterium-substituted isotopomers are used with previous data which include $^{13}C$ isotopomers to obtain a gas-phase structure for (benzene)chromium tricarbonyl. The new rotational constant for the $C_6D_6$, symmetric-top, isotopomer is $B(\text{bz-}d_6) = 698.6934(1)$ MHz. Asymmetric-top structure were observed for a single deuterium substitution on benzene, giving $B(\text{bz-}d_1) = 730.0491(4)$ MHz and $C(\text{bz-}d_1) = 723.6641(4)$ MHz. Rotational constants obtained for (fluorobenzene)chromium tricarbonyl are $A = 814.1491(2)$ MHz, $B = 641.1594(2)$ MHz, and $C = 586.5866(1)$ MHz. The centrifugal distortion constants are small, with $D_J \cong 0.05$ kHz. Structural parameters determined are center of the benzene carbon plane to chromium distance $r(\text{Cr–bz}) = 1.66(2)$ Å, the chromium to carbonyl carbon bond length $r(\text{Cr–CO}) = 1.876(7)$ Å, the benzene carbon to hydrogen bond length $r(\text{C–H}) = 1.080(3)$ Å, and the carbonyl carbon to oxygen bond length $r(\text{C–O}) = 1.148(7)$ Å. The OC–Cr–CO interbond angle is $\alpha = 87.4(6)°$. The average benzene C–C bond length is 1.413(4) Å. A small isotopic shift in the $^{53}Cr$ quadrupole coupling strength was observed for the $C_6D_6$ isotopomer relative to the normal isotopomer. The hydrogen atoms are displaced out of the benzene carbon plane toward the Cr atom with the C–H bond axis at an angle $\gamma = 2.8(2)°$ with respect to the benzene carbon plane.

## Introduction

The chemistry of ($\eta^6$-arene)$Cr(CO)_3$-type complexes has been extensively studied.[1] The motivation for much of the research in this area has been due, in part, to the utility of the arene–$Cr(CO)_3$ complexes in organic synthesis.[2,3] Complex formation causes a withdrawal of electrons from the arene by the $Cr(CO)_3$, thereby activating the benzene for nucleophilic attack. Some of the reactions involving these complexes are stereospecific, further increasing their usefulness in organic synthesis. There has been considerable previous interest in the structure of (benzene)chromium tricarbonyl since it was found[4] that there is an alteration of approximately 0.02 Å in the C–C bond lengths in the complexed benzene. It appears that the carbonyl ligands interact with benzene, slightly modifying the aromatic character. An electron diffraction study of this complex[5] indicated relatively free rotation of benzene relative to $Cr(CO)_3$, but no evidence for this effect was found in the previous microwave work[6] or in the present results. The upper limit for the $V_6$ potential barrier to internal rotation from the microwave work is 4 THz (1.6 kJ/mol). This would be considered a low barrier, and a value close to this could cause the electron diffraction data to be compatible with nearly free internal rotation.

The new data for the deuterium-substituted isotopomers allow us to determine the structure from the microwave measurements. The basic structure obtained for (benzene)chromium tricarbonyl also provides a good fit to the (fluorobenzene)chromium tricarbonyl spectrum, indicating that the fluorine substitution on benzene does not appear to cause significant changes in the structure.

## Experimental Section

The samples containing the substituted benzenes, $C_6H_5D$, $C_6D_6$, and $C_6H_5F$, were synthesized by refluxing a solution of $Cr(CO)_6$ and the substituted benzene in diglyme according to general method of Strohmeier.[7] In a typical preparation 3 g of $Cr(CO)_6$ and 4 mL of $C_6D_6$ in 70 mL of diglyme were refluxed under 1 atm of $N_2$ for 15 h. The solvents were distilled off under vacuum, and the product was purified by sublimation at 100 °C and $10^{-2}$ Torr pressure. Rotational transitions in the 4–17 GHz frequency range were measured using a Flygare-Balle type spectrometer described earlier.[8] The samples and pulse valve were maintained at 85–100 °C to obtain sufficient sample vapor pressure. The carrier gas was "first-run" neon at 0.6–1.0 atm.

## Results and Data Analysis

A strong, symmetric-top spectrum was observed for $(C_6D_6)$-$Cr(CO)_3$, and the measured transition frequencies are listed in Table 1. The transitions for different $K$ values were unresolved due to the small $D_{JK}$ centrifugal distortion constant. A least-squares fit to the measured transition frequencies yielded the rotational constant $B = 698.6394(1)$ MHz and $D_J = 0.0431(1)$ kHz with a standard deviation for the fit of 0.8 kHz.

The $C_6H_5D$ isotopomer is a near-prolate asymmetric top with the largest dipole moment component along the $a$ axis. The 41 $a$-dipole measured transitions used in the fit to determine molecular parameters are listed in Table 2. A five-parameter fit was used to determine $A = 909.68$ MHz, $B = 730.0491(2)$ MHz, $C = 723.6641(2)$ MHz, $\Delta_J = 0.052(3)$ kHz, and $\Delta_{JK} = -0.07(1)$ kHz with a standard deviation for the fit of $\sigma = 3.4$

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**Table 1.** Results of Measurements and Least-Squares-Fit Calculations for $(C_6D_6)^{52}Cr(CO)_3$ Transitions[a]

| $J$ | $J'$ | measd | calcd | measd − calcd |
|---|---|---|---|---|
| 2 | 3 | 4191.832 | 4191.832 | 0.0001 |
| 3 | 4 | 5589.104 | 5589.104 | −0.0006 |
| 4 | 5 | 6986.372 | 6986.373 | −0.0010 |
| 5 | 6 | 8383.635 | 8383.636 | −0.0013 |
| 6 | 7 | 9780.894 | 9780.893 | 0.0009 |
| 7 | 8 | 11178.143 | 11178.143 | 0.0005 |
| 8 | 9 | 12575.387 | 12575.385 | 0.0015 |
| 9 | 10 | 13972.618 | 13972.618 | 0.0002 |
| 10 | 11 | 15369.840 | 15369.841 | 0.0003 |

[a] The best fit parameters are $B$ = 698.6394(1) MHz and $D_J$ = 0.043(1) kHz. Frequencies are in MHz. The standard deviation for the fit is 0.0008 MHz.

**Table 2.** Results of Measurements and a Least-Squares Fit for the Single Subsituation of Deuterium on the Benzene Ring, $(C_6H_5D)^{52}Cr(CO)_3$[a]

| $J$ | $K_p$ | $K_o$ | $J'$ | $K_p'$ | $K_o'$ | measd | calcd | measd − calcd |
|---|---|---|---|---|---|---|---|---|
| 2 | 1 | 2 | 3 | 1 | 3 | 4351.450 | 4351.454 | −0.0037 |
| 2 | 0 | 2 | 3 | 0 | 3 | 4360.465 | 4360.466 | −0.0010 |
| 2 | 2 | 1 | 3 | 2 | 2 | 4361.142 | 4361.136 | 0.0063 |
| 2 | 1 | 1 | 3 | 1 | 2 | 4370.604 | 4370.606 | −0.0021 |
| 3 | 1 | 3 | 4 | 1 | 4 | 5801.740 | 5801.744 | −0.0037 |
| 3 | 0 | 3 | 4 | 0 | 4 | 5813.171 | 5813.174 | −0.0035 |
| 3 | 2 | 2 | 4 | 2 | 3 | 5814.711 | 5814.712 | −0.0007 |
| 3 | 3 | 0 | 4 | 3 | 1 | 5815.191 | 5815.187 | 0.0038 |
| 3 | 2 | 1 | 4 | 2 | 2 | 5816.384 | 5816.377 | 0.0072 |
| 3 | 1 | 2 | 4 | 1 | 3 | 5827.263 | 5827.267 | −0.0045 |
| 4 | 1 | 4 | 5 | 1 | 5 | 7251.873 | 7251.875 | −0.0019 |
| 4 | 0 | 4 | 5 | 0 | 5 | 7265.229 | 7265.230 | −0.0013 |
| 4 | 2 | 3 | 5 | 2 | 4 | 7268.169 | 7268.171 | −0.0024 |
| 4 | 3 | 1 | 5 | 3 | 2 | 7269.156 | 7269.150 | 0.0058 |
| 4 | 2 | 2 | 5 | 2 | 3 | 7271.479 | 7271.481 | −0.0019 |
| 4 | 1 | 3 | 5 | 1 | 4 | 7283.741 | 7283.743 | −0.0018 |
| 5 | 1 | 5 | 6 | 1 | 6 | 8701.816 | 8701.818 | −0.0011 |
| 5 | 0 | 5 | 6 | 0 | 6 | 8716.504 | 8716.505 | −0.0015 |
| 5 | 2 | 4 | 6 | 2 | 5 | 8721.485 | 8721.486 | −0.0012 |
| 5 | 5 | 1 | 6 | 5 | 2 | 8722.681 | 8722.673 | 0.0083 |
| 5 | 4 | 2 | 6 | 4 | 3 | 8722.816 | 8722.816 | 0.0009 |
| 5 | 3 | 3 | 6 | 3 | 4 | 8723.086 | 8723.086 | −0.0002 |
| 5 | 3 | 2 | 6 | 3 | 3 | 8723.239 | 8723.239 | −0.0003 |
| 5 | 2 | 3 | 6 | 2 | 4 | 8727.213 | 8727.214 | −0.0010 |
| 5 | 1 | 4 | 6 | 1 | 5 | 8739.975 | 8739.975 | −0.0004 |
| 6 | 1 | 6 | 7 | 1 | 7 | 10151.549 | 10151.548 | 0.0014 |
| 6 | 0 | 6 | 7 | 0 | 7 | 10166.914 | 10166.913 | 0.0013 |
| 6 | 2 | 5 | 7 | 2 | 6 | 10174.625 | 10174.626 | −0.0014 |
| 6 | 5 | 1 | 7 | 5 | 2 | 10176.534 | 10176.539 | −0.0047 |
| 6 | 4 | 3 | 7 | 4 | 4 | 10176.768 | 10176.767 | 0.0008 |
| 6 | 4 | 2 | 7 | 4 | 3 | 10176.774 | 10176.772 | 0.0023 |
| 6 | 2 | 4 | 7 | 2 | 5 | 10183.635 | 10183.631 | 0.0043 |
| 6 | 1 | 5 | 7 | 1 | 6 | 10195.900 | 10195.900 | 0.0000 |
| 7 | 1 | 7 | 8 | 1 | 8 | 11601.049 | 11601.048 | 0.0010 |
| 7 | 0 | 7 | 8 | 0 | 8 | 11616.429 | 11616.426 | 0.0033 |
| 7 | 2 | 6 | 8 | 2 | 7 | 11627.565 | 11627.565 | −0.0002 |
| 7 | 5 | 2 | 8 | 5 | 3 | 11630.442 | 11630.445 | −0.0026 |
| 7 | 4 | 3 | 8 | 4 | 4 | 11630.792 | 11630.798 | −0.0064 |
| 7 | 3 | 5 | 8 | 3 | 6 | 11631.284 | 11631.284 | 0.0000 |
| 7 | 2 | 5 | 8 | 2 | 6 | 11640.727 | 11640.727 | 0.0000 |
| 7 | 1 | 6 | 8 | 1 | 7 | 11651.447 | 11651.445 | 0.0016 |

[a] Parameter values are $A$ = 909.685(2) MHz, $B$ = 730.0491(4) MHz, $C$ = 723.6641(4) MHz, $\Delta_J$ = 0.052(2) kHz, and $\Delta_{JK}$ = −0.07(1) kHz. The standard deviation for the fit is 0.0034 MHz. Values are in MHz.

kHz. The above error limits on the parameters are 2$\sigma$. The value of $A$ is less reliable since this is a near-prolate symmetric top, and $A$ is likely to be highly correlated with $\Delta_K$, which was not determined. Therefore, only $B$ and $C$ rotational constants for the $C_6H_5D$ and the $^{13}C$ isotopomers were used in the fit to determine the structural parameters.

**Table 3.** Results of Measurements and a Least-squares Fit for the (Fluorobenzene)chromium Tricarbonyl complex, $(C_6H_5F)^{52}Cr(CO)_3$[a]

| $J$ | $K_p$ | $K_o$ | $J'$ | $K_p'$ | $K_o'$ | measd | calcd | measd − calcd |
|---|---|---|---|---|---|---|---|---|
| 3 | 2 | 1 | 4 | 3 | 2 | 5884.693 | 5884.693 | −0.0002 |
| 3 | 2 | 2 | 4 | 3 | 1 | 5946.745 | 5946.746 | −0.0009 |
| 4 | 1 | 4 | 5 | 1 | 5 | 5966.417 | 5966.416 | 0.0009 |
| 4 | 0 | 4 | 5 | 0 | 5 | 5989.445 | 5989.444 | 0.0009 |
| 4 | 0 | 4 | 5 | 1 | 5 | 6012.046 | 6012.045 | 0.0006 |
| 4 | 2 | 3 | 5 | 2 | 4 | 6114.345 | 6114.345 | −0.0003 |
| 4 | 4 | 1 | 5 | 4 | 2 | 6163.066 | 6163.065 | 0.0012 |
| 4 | 3 | 2 | 5 | 3 | 3 | 6164.069 | 6164.069 | −0.0001 |
| 4 | 4 | 0 | 5 | 4 | 1 | 6164.255 | 6164.256 | −0.0010 |
| 4 | 2 | 2 | 5 | 3 | 3 | 7056.015 | 7056.015 | 0.0001 |
| 5 | 1 | 5 | 6 | 0 | 6 | 7134.848 | 7134.849 | −0.0015 |
| 5 | 1 | 5 | 6 | 1 | 6 | 7145.246 | 7145.246 | −0.0003 |
| 5 | 2 | 4 | 6 | 1 | 5 | 7152.139 | 7152.139 | −0.0002 |
| 5 | 0 | 5 | 6 | 0 | 6 | 7157.450 | 7157.451 | −0.0008 |
| 5 | 0 | 5 | 6 | 1 | 6 | 7167.847 | 7167.848 | −0.0006 |
| 4 | 2 | 3 | 5 | 3 | 2 | 7235.716 | 7235.716 | 0.0005 |
| 5 | 2 | 4 | 6 | 2 | 5 | 7318.281 | 7318.282 | −0.0005 |
| 6 | 1 | 6 | 7 | 0 | 7 | 8316.811 | 8316.811 | −0.0004 |
| 6 | 1 | 6 | 7 | 1 | 7 | 8321.362 | 8321.361 | 0.0007 |
| 6 | 0 | 6 | 7 | 0 | 7 | 8327.209 | 8327.208 | 0.0008 |
| 6 | 0 | 6 | 7 | 1 | 7 | 8331.757 | 8331.758 | −0.0011 |
| 7 | 4 | 3 | 8 | 3 | 6 | 8406.156 | 8406.155 | 0.0001 |
| 6 | 2 | 5 | 7 | 1 | 6 | 8417.338 | 8417.337 | 0.0006 |
| 6 | 2 | 5 | 7 | 2 | 6 | 8513.983 | 8513.983 | 0.0001 |
| 6 | 1 | 5 | 7 | 1 | 6 | 8583.480 | 8583.480 | 0.0002 |
| 6 | 5 | 2 | 7 | 5 | 3 | 8633.686 | 8633.683 | 0.0034 |
| 6 | 5 | 1 | 7 | 5 | 2 | 8634.455 | 8634.457 | −0.0022 |
| 6 | 4 | 3 | 7 | 4 | 4 | 8642.956 | 8642.956 | 0.0003 |
| 6 | 4 | 2 | 7 | 4 | 3 | 8659.259 | 8659.262 | −0.0028 |
| 6 | 1 | 5 | 7 | 2 | 6 | 8680.125 | 8680.125 | −0.0001 |
| 6 | 3 | 3 | 7 | 3 | 4 | 8741.403 | 8741.403 | 0.0005 |
| 5 | 3 | 2 | 6 | 4 | 3 | 8750.205 | 8750.204 | 0.0007 |
| 6 | 2 | 4 | 7 | 2 | 5 | 8764.644 | 8764.643 | 0.0008 |
| 7 | 1 | 7 | 8 | 0 | 8 | 9494.000 | 9494.000 | 0.0004 |
| 7 | 1 | 7 | 8 | 1 | 8 | 9495.922 | 9495.922 | 0.0002 |
| 7 | 0 | 7 | 8 | 0 | 8 | 9498.549 | 9498.549 | −0.0005 |
| 7 | 0 | 7 | 8 | 1 | 8 | 9500.473 | 9500.472 | 0.0013 |
| 5 | 5 | 1 | 6 | 6 | 0 | 9571.274 | 9571.274 | −0.0001 |
| 7 | 2 | 6 | 8 | 1 | 7 | 9651.007 | 9651.007 | 0.0004 |
| 7 | 2 | 6 | 8 | 2 | 7 | 9702.250 | 9702.251 | −0.0007 |
| 7 | 1 | 6 | 8 | 1 | 7 | 9747.652 | 9747.652 | 0.0000 |
| 7 | 1 | 6 | 8 | 2 | 7 | 9798.896 | 9798.896 | −0.0001 |
| 7 | 3 | 5 | 8 | 3 | 6 | 9840.861 | 9840.861 | 0.0001 |
| 8 | 1 | 8 | 9 | 0 | 9 | 10668.891 | 10668.891 | −0.0004 |
| 8 | 1 | 8 | 9 | 1 | 9 | 10669.682 | 10669.683 | −0.0006 |
| 8 | 0 | 8 | 9 | 0 | 9 | 10670.813 | 10670.814 | −0.0007 |
| 8 | 0 | 8 | 9 | 1 | 9 | 10671.606 | 10671.605 | 0.0012 |
| 8 | 2 | 7 | 9 | 2 | 8 | 10884.612 | 10884.611 | 0.0011 |
| 8 | 1 | 7 | 9 | 1 | 8 | 10910.513 | 10910.514 | −0.0010 |
| 8 | 2 | 6 | 9 | 2 | 7 | 11179.332 | 11179.332 | −0.0004 |

[a] The best fit parameters are listed in Table 4. The frequencies are in MHz.

The measured and best fit, calculated transition frequencies for $(C_6H_5F)Cr(CO)_3$ are listed in Table 3. Since the $a$ principal axis for this complex is rotated by 33° away from the benzene $C_6$ axis due to the added fluorine mass, this complex is not a near-symmetric rotor. Also, both the $a$ and $b$ components of the dipole moment are reasonably large. Of the 50 transitions listed in Table 3, 21 are $b$-dipole transitions and 29 are $a$-dipole transitions, so accurate values can be obtained for all three rotational constants and five centrifugal distortion constants. The molecular parameters obtained from fitting the (fluorobenzene)chromium tricarbonyl data are listed in Table 4. The standard deviation for the fit is 1 kHz, so the fractional uncertainties in the rotational constants are less than $3 \times 10^{-7}$ (2$\sigma$).

## Molecular Structure Parameters

The $B$ and $C$ rotational constants for the $C_6H_5D$ isotopomer and two $^{13}C$ isotopomers measured previously[6] and $B$ rotational constants for the $C_6D_6$ isotopomer, the $^{53}Cr$ isotopomer,[6] and normal isotopomer[6] were used in a least-squares fit to determine

**Table 4.** Results of Measurements and a Least-Squares Fit for (Fluorobenzene)chromium Tricarbonyl, $(C_6H_5F)^{52}Cr(CO)_3$[a]

| mol param | value | mol param | value |
|---|---|---|---|
| $A$ | 814.1491(3) MHz | $\Delta_{JK}$ | 0.134(6) kHz |
| $B$ | 641.1593(2) MHz | $\Delta_K$ | −0.076(7) kHz |
| $C$ | 586.5866(1) MHz | $\delta_J$ | −0.0021(8) kHz |
| $\Delta_J$ | 0.023(2) kHz | $\delta_K$ | −0.15(1) kHz |

[a] The indicated uncertainties are two standard deviations. The standard deviation for the fit is 0.0010 MHz. The data are located in Table 3.

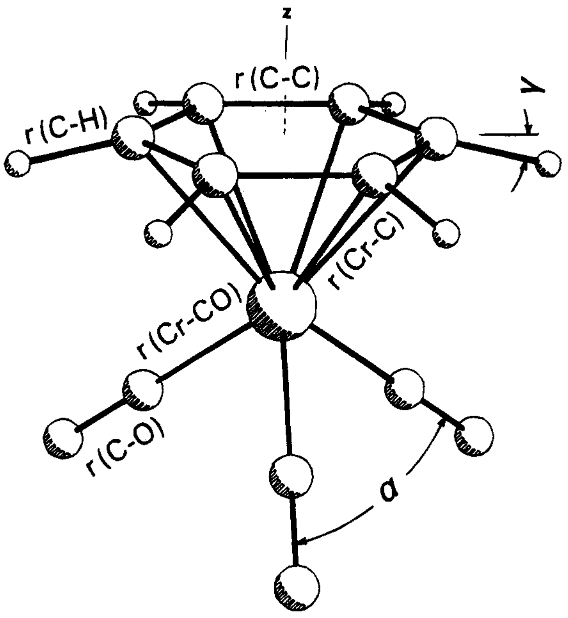

**Figure 1.** Basic structure of the (benzene)chromium tricarbonyl complex identifying the structural parameters used in the fitting procedure. The magnitude of γ has been increased to 20° for illustration purposes. The rest of the structure is nearly to scale.

**Table 5.** Results of Fitting the Measured Rotational Constants for the Various Isotopomers To Determine Structural Parameters[a]

| param | exptl | calcd | exptl − calcd |
|---|---|---|---|
| $B(^{52}Cr)$ | 732.8886 | 732.8907 | −0.0021 |
| $B(^{53}Cr)$ | 732.8966 | 732.8907 | 0.0059 |
| $B(^{13}CO)$ | 731.5036 | 731.5048 | −0.0012 |
| $C(^{13}CO)$ | 729.1657 | 729.1653 | 0.0004 |
| $B(bz\text{-}^{13}C)$ | 729.9606 | 729.9630 | −0.0024 |
| $C(bz\text{-}^{13}C)$ | 727.9024 | 727.8999 | 0.0025 |
| $B(D_1)$ | 730.0491 | 730.0532 | −0.0041 |
| $C(D_1)$ | 723.6641 | 723.6685 | −0.0044 |
| $B(D_6)$ | 698.6394 | 698.6386 | 0.0008 |

[a] The best fit parameters are given in Table 6. Values are in MHz. The standard deviation for the fit is 5 kHz.

structural parameters. $C_{6v}$ symmetry was assumed for the benzene ring since the previously observed[4] C−C bond length alteration would not have an observable effect on rotational constants for any of the above isotopomers. The seven adjustable parameters were as follows: *r*(Cr−bz), the distance between the chromium atom and the center of the benzene ring; *r*(Cr−CO), the Cr−C bond length from chromium to the carbonyl carbon; *r*(C−O), the bond length from the carbonyl carbon to the oxygen; α, the OC−Cr−CO interbond angle; *r*(C−H), the bond length from the benzene carbons to hydrogen atoms; *r*(C−C), the benzene C−C bond distance; and γ, the angle between the C−H bonds and the benzene carbon plane. These parameters are shown in Figure 1. The results of this fit are shown in Tables 5 and 6. We were able to fit the nine measured rotational constants using the above seven parameters to obtain a standard deviation for the fit of 5 kHz. The standard deviation is only slightly larger with the C−O bond length fixed at 1.15 Å and slightly smaller with *r*(C−C) fixed at 1.415 Å, the averaged value from the neutron diffraction work.[4] Values for the additional parameter, which was not a "fit" parameter, *r*(Cr−C(benzene)) are listed in Table 6 for comparison with the diffraction results.

**Table 6.** Structural Parameters for (Benzene)chromium Tricarbonyl Obtained by Fitting the Experimental Rotational Constants for Six Isotopomers[a]

| interatomic dist | microwave value (2σ) | ND value | ED value |
|---|---|---|---|
| *r*(C−H)(benzene), Å | 1.080(3) | 1.086 | 1.10 |
| *r*(C−C)(benzene), Å | 1.413(4) | 1.415 | 1.417 |
| *r*(Cr−C(benzene)), Å | 2.178(18) | 2.230 | 2.208 |
| *r*(Cr−Bz(benzene carbon plane)), Å | 1.658(13) | 1.726 | 1.693 |
| *r*(Cr−CO), Å | 1.876(7) | 1.842 | 1.863 |
| *r*(C−O), Å | 1.148(7) | 1.156 | 1.153 |

| interbond angle | designation | microwave value (2σ) | ND value | ED value |
|---|---|---|---|---|
| H−C−(benzene plane), deg | γ | 2.8(2) | 1.6 | |
| OC−Cr−CO, deg | α | 87.4(7) | 87 | 88.5 |

[a] Results from the neutron diffraction work (ND values) and the electron work[5] (ED values) are also listed for comparison. The *r*(Cr−C(benzene)) parameter was not a "fit" parameter, since it is directly related to *r*(Cr−bz), but is listed here to facilitate comparison to the diffraction results.

Bond lengths and interbond angles obtained from the fit results are listed in Table 6. We have also listed the neutron diffraction[4] and electron diffraction values[5] for comparison. We note that the agreement is reasonably good between the three sets of results. Most of the present microwave bond lengths are slightly shorter than the electron diffraction or neutron diffraction values. The value of $\gamma = 2.8°$ indicates a displacement of the benzene hydrogen atoms out of the plane of the benzene carbon atoms in a direction toward the Cr atom and the center of the complex. The same direction of H atom displacement was obtained in the neutron diffraction work. The chromium atom coordinates are not as accurately determined as those of other substituted atoms since it is so close to the center of mass of the complex. Values in Table 6 indicate that *r*(Cr−bz) is in better agreement with the electron diffraction value than with the neutron diffraction value, but this could be an indication of increased uncertainty in the microwave coordinates for the Cr atom.

In these experiments we observe only ground state, gas-phase molecules cooled to ~20 K, a temperature which would not significantly populate exicted torsional states if $V_6 \cong 4$ THz (see above). The temperature of molecules in the electron diffraction experiment, however, was 400 K, a temperature which could partially populate the excited torsional states and give indications of internal rotation in the electron diffraction data. Also, the excitation and averaging over vibrational modes could be partially responsible for the electron diffraction interatomic distances being a few hundredths of an angstrom longer. We obtain a slightly lower standard deviation for the fit when the benzene C−C bond length is fixed to the ND (neutron diffraction) value, and all three methods agree very well on this bond length. There was considerable uncertainty in the angle α from the crystal studies,[4] with a range of 86−89°; this is apparently due to crystal packing effects. Intermolecular interactions within the crystal may be partly responsible for the slightly lower ND bond lengths compared with microwave values. We note that the benzene C−C bond lengths are all about 0.02 Å longer than the value of 1.397 Å for free

**Table 7.** Cartesian Coordinates for (Benzene)chromium Tricarbonyl (in Å) Obtained from Microwave Measurements on Six Isotopomers[a]

| atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| C1 | −1.413 | 0.000 | 1.658 |
| C2 | −0.707 | 1.224 | 1.658 |
| C3 | 0.707 | 1.224 | 1.658 |
| C4 | 1.413 | 0.000 | 1.658 |
| C5 | 0.707 | −1.224 | 1.658 |
| C6 | −0.707 | −1.224 | 1.658 |
| H1 | −2.492 | 0.000 | 1.606 |
| H2 | −1.246 | 2.158 | 1.606 |
| H3 | 1.246 | 2.158 | 1.606 |
| H4 | 2.492 | 0.000 | 1.606 |
| H5 | 1.246 | −2.158 | 1.606 |
| H6 | −1.246 | −2.158 | 1.606 |
| Cr | 0.000 | 0.000 | 0.000 |
| C7 | 0.000 | 1.496 | −1.131 |
| C8 | −1.296 | −0.748 | −1.131 |
| C9 | 1.296 | −0.748 | −1.131 |
| O1 | 0.000 | 2.412 | −1.823 |
| O1 | −2.088 | −1.206 | −1.823 |
| O3 | 2.088 | −1.206 | −1.823 |

[a] The benzene ring was constrained to $C_{6v}$ symmetry. The $z$ axis is coincident with the $a$ inertial axis of the normal isotopomer. The origin is the Cr atom.

benzene.[9,10] The Cartesian coordinates for the atoms are given in Table 7. The microwave C−H bond length, 1.080 Å, is in excellent agreement with the free benzene value[10] of 1.0815 Å.

## Isotope Effect on Chromium Quadrupole Coupling

Seven transitions for $(C_6D_6)^{53}Cr(CO)_3$ were measured with sufficiently high signal-to-noise ratio to obtain $B$ and $eqQ$($^{53}$Cr) for this isotopomer. The observed transitions for this isotopomer were weak, due to the 4% abundance of $^{53}$Cr, and broadened, presumably due to unresolved deuterium hyperfine structure, so the measured data set was quite limited. All molecular parameters except the rotational constant $B$ and $^{53}$Cr quadrupole coupling were fixed at values obtained for other isotopomers, and the data were fit to obtain $B = 698.642(1)$ MHz and $eqQ(^{53}\mathrm{Cr}) = -11.9(1)$ MHz. The above indicated uncertainties are $3\sigma$, since the data set was so small. The above value for $eqQ$($^{53}$Cr) is smaller, by $6\sigma$, than the value −12.11(1) MHz obtained earlier[6] for $(C_6H_6)^{53}Cr(CO)_3$. This appears to be a secondary isotope effect of about 1% due to the deuterium substitution on the benzene moiety. This is significantly larger than the 0.2% reduction of chlorine quadrupole coupling observed earlier[11] in methyl chloride when the methyl group was fully deuterated. In both of these cases, we believe that this quadrupole coupling reduction is due to a secondary isotope effect resulting from the vibrational averaging over the C−H stretching vibrational coordinates. This vibrational averaging effect has been known for about 30 years; it causes $r_0$ values for C−D bonds to be about 0.004 Å shorter than those for corresponding C−H bonds and is due to anharmonicity in the C−H potential. The effect of this "bond shortening" is to reduce the electron-withdrawing character of benzene, as it does with the methyl group, and modify the electric field gradient at the $^{53}$Cr nucleus. This secondary effect is much larger than direct effects due to benzene−Cr vibrational motion because for C−H vibration the reduced mass is changed by nearly a factor of 2, on deuterium substitution, whereas the reduced mass for benzene−Cr motion is only changed by 3% on deuterium substitution. We believe that the effect is larger for this complex than for $CH_3Cl$ because six H atoms are substituted, rather than three, and that there is a relatively small net field gradient at $^{53}$Cr due to the nearly symmetrical charge distribution and the near cancellation of the effects of nuclear charges by the electronic charge distribution. The proposed secondary isotope effect would primarily affect the contributions to the field gradient from the electronic charge distribution.

We were able to fit the rotational constants for (fluorobenzene)chromium tricarbonyl with a standard deviation by 15 kHz by adjusting only the C−F bond length and fixing all other bond lengths and angles at values obtained for (benzene)chromium tricarbonyl. The fluorine atom was located in the same plane as the benzene carbon atoms. It appears that there is very little change in the geometery of this complex on fluorine substitution. This is not unreasonable since the geometry of free fluorobenzene[9,12] is very similar to that of free benzene,[9,10] with only differences of ±0.003 Å or less for carbon−carbon distances and even smaller differences for C−H distances. The C−F bond length obtained as 1.33(3) Å, in good agreement with the value of 1.35 Å for free fluorobenzene.[9,12] Attempts to tilt the fluorobenzene plane relative to the $Cr(CO)_3$ symmetry axis did not improve the fit to the data.

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