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BENZENECHROMIUM TRICARBONYL
II. SYMMETRY COORDINATES OF MOLECULAR VIBRATIONS

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SUMMARY

A complete set of symmetry coordinates based on conventional valence coordinates is constructed for a C_{3v} model of benzenechromium tricarbonyl. Another set is described, which preserves the identity of the benzene ligand as far as possible, and which is supposed to be useful in a forthcoming normal coordinate analysis.

INTRODUCTION

The first part[1] of this article series is a report on the Raman spectrum of benzenechromium tricarbonyl, $C_6H_6Cr(CO)_3$. This study is a continuation of a series of total vibrational analyses of π-arene–transition metal compounds[2-4]. In these studies we analyze the vibrational spectra of such complexes employing two essentially different types of symmetry coordinates. One type is constructed so that it preserves as far as possible the identity of the complexed ligands. As in the case of bis(benzene)chromium[2], this type of coordinates can be expected to be a reasonable basis for the development of a harmonic force field for the inspected molecule. It is then intended to transform this force field, as was done for bis(benzene)chromium[3], to another set of symmetry coordinates of a more conventional type. In the following discussion the two types of symmetry coordinates will be referred to as "physical"[2] and "conventional"[3], respectively. It is believed that the conventional set may form a convenient standard basis of reference to the force constants of molecules of this class of compounds. It should also be useful in further calculations with a given force field.

The purpose of the present article is to give a detailed specification of conventional symmetry coordinates for a molecular model of benzenechromium tricarbonyl. Also, a short description of physical symmetry coordinates is given. It is more difficult to construct a proper set of physical coordinates in the present case than for bis(benzene)chromium because of the lack of a horizontal symmetry plane in benzenechromium tricarbonyl.

In future work it is intended to develop a harmonic force field for $C_6H_6Cr(CO)_3$ with the aid of experimental frequencies from infrared[5] and Raman[1] spectral data.

MOLECULAR MODEL

Fig. 1 shows the adopted molecular model of $C_6H_6Cr(CO)_3$. The benzene ligand was assumed to be planar. In the $Cr(CO)_3$ part the Cr–C–O chains were taken to be linear, and the group was assumed to be staggered with respect to the benzene ligand; see Figs. 2 and 3. Consequently, the six CC benzene distances split into two sets of symmetrically equivalent distances with three members in each. Nevertheless all the six CCC valence angles, CH distances and CrC distances are each symmetrically equivalent. The overall symmetry is C_{3v}.

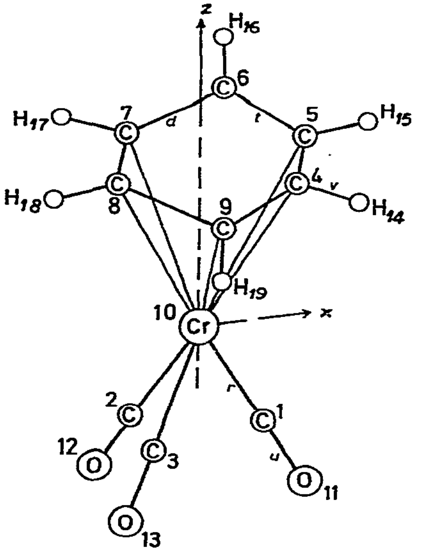

Fig. 1. The benzenechromium tricarbonyl molecular model. Equilibrium interatomic distances are identified with capital letters.

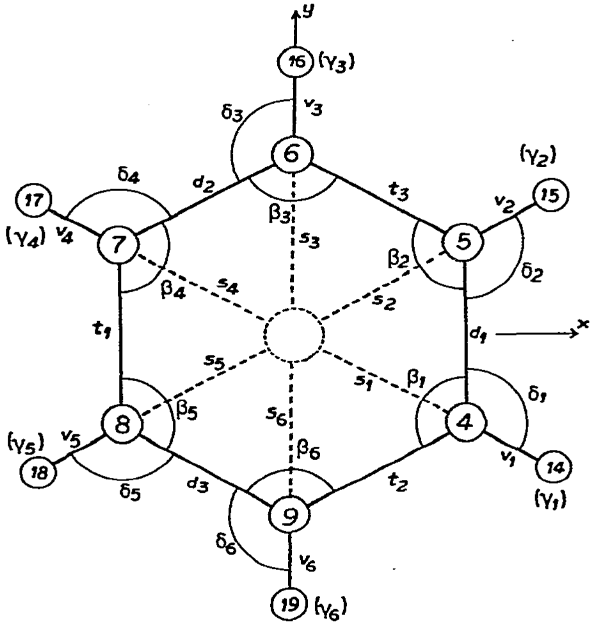

Fig. 2. Valence coordinates for the benzene ligand part of the benzenechromium tricarbonyl model. The symbols $s_1, \ldots, s_6$ denote Cr–C stretchings, and $\gamma_1, \ldots, \gamma_6$ are CH out-of-plane bendings. All the other definitions of stretchings and bendings are obvious.

CONVENTIONAL SYMMETRY COORDINATES

The normal modes of vibration are distributed among the symmetry species of the C_{3v} point group according to

$$\Gamma = 10\,A_1 + 7\,A_2 + 17\,E$$

The valence coordinates defined in Figs. 2 and 3 all belong to the conventional types. They were used to construct a complete set of symmetry coordinates as specified in the following:

Species A_1

$S_1(A_1) = 3^{-\frac{1}{2}}(r_1+r_2+r_3)$

$S_2(A_1) = 3^{-\frac{1}{2}} R\cdot(\alpha_1+\alpha_2+\alpha_3)$

$S_3(A_1) = 6^{-\frac{1}{2}}(s_1+s_2+s_3+s_4+s_5+s_6)$

$S_4(A_1) = 3^{-\frac{1}{2}}(d_1+d_2+d_3)$

$S_5(A_1) = 3^{-\frac{1}{2}}(t_1+t_2+t_3)$

$S_6(A_1) = 3^{-\frac{1}{2}}(u_1+u_2+u_3)$

$S_7(A_1) = (RU/3)^{\frac{1}{2}}\cdot(\xi_1+\xi_2+\xi_3)$

$S_8(A_1) = 6^{-\frac{1}{2}}(v_1+v_2+v_3+v_4+v_5+v_6)$

$S_9(A_1) = [V(DT^{\frac{1}{2}})^{\frac{1}{2}}/6]^{\frac{1}{2}}\cdot(\gamma_1+\gamma_2+\gamma_3+\gamma_4+\gamma_5+\gamma_6)$

$S_{10}(A_1) = (DV/6)^{\frac{1}{2}}\cdot(\delta_1+\delta_2+\delta_3+\delta_4+\delta_5+\delta_6)$

Species A_2

$S_1(A_2) = 6^{-\frac{1}{2}}(s_1-s_2+s_3-s_4+s_5-s_6)$

$S_2(A_2) = (RS/6)^{\frac{1}{2}}\cdot(\phi_1-\phi_2+\phi_3-\phi_4+\phi_5-\phi_6)$

$S_3(A_2) = (DT/6)^{\frac{1}{2}}\cdot(\beta_1-\beta_2+\beta_3-\beta_4+\beta_5-\beta_6)$

$S_4(A_2) = (RU/3)^{\frac{1}{2}}\cdot(\eta_1+\eta_2+\eta_3)$

$S_5(A_2) = 6^{-\frac{1}{2}}(v_1-v_2+v_3-v_4+v_5-v_6)$

$S_6(A_2) = [V(DT)^{\frac{1}{2}}/6]^{\frac{1}{2}}\cdot(\gamma_1-\gamma_2+\gamma_3-\gamma_4+\gamma_5-\gamma_6)$

$S_7(A_2) = (DV/6)^{\frac{1}{2}}\cdot(\delta_1-\delta_2+\delta_3-\delta_4+\delta_5-\delta_6)$

Species E(a)

$S_{1a}(E) = 6^{-\frac{1}{2}}(2r_1-r_2-r_3)$

$S_{2a}(E) = 6^{-\frac{1}{2}} R\cdot(2\alpha_1-\alpha_2-\alpha_3)$

$S_{3a}(E) = 12^{-\frac{1}{2}}(2s_1+2s_2-s_3-s_4-s_5-s_6)$

$S_{4a}(E) = \frac{1}{2}(s_3-s_4-s_5+s_6)$

$S_{5a}(E) = (RS/12)^{\frac{1}{2}}\cdot(2\phi_1+2\phi_2-\phi_3-\phi_4-\phi_5-\phi_6)$

$S_{6a}(E) = \frac{1}{2}(RS)^{\frac{1}{2}}\cdot(\phi_3-\phi_4-\phi_5+\phi_6)$

$S_{7a}(E) = 6^{-\frac{1}{2}}(2d_1-d_2-d_3)$

$S_{8a}(E) = 6^{-\frac{1}{2}}(2t_1-t_2-t_3)$

$S_{9a}(E) = 6^{-\frac{1}{2}}(2u_1-u_2-u_3)$

$S_{10a}(E) = (RU/6)^{\frac{1}{2}}\cdot(2\xi_1-\xi_2-\xi_3)$

$S_{11a}(E) = (RU/2)^{\frac{1}{2}}\cdot(-\eta_2+\eta_3)$

$S_{12a}(E) = 12^{-\frac{1}{2}}(2v_1+2v_2-v_3-v_4-v_5-v_6)$

$S_{13a}(E) = \frac{1}{2}(v_3-v_4-v_5+v_6)$

$S_{14a}(E) = [V(DT)^{\frac{1}{2}}/12]^{\frac{1}{2}}\cdot(2\gamma_1+2\gamma_2-\gamma_3-\gamma_4-\gamma_5-\gamma_6)$

$S_{15a}(E) = \frac{1}{2}[V(DT)^{\frac{1}{2}}]^{\frac{1}{2}}\cdot(\gamma_3-\gamma_4-\gamma_5+\gamma_6)$

$S_{16a}(E) = (DV/12)^{\frac{1}{2}}\cdot(2\delta_1+2\delta_2-\delta_3-\delta_4-\delta_5-\delta_6)$

$S_{17a}(E) = \frac{1}{2}(DV)^{\frac{1}{2}}\cdot(\delta_3-\delta_4-\delta_5+\delta_6)$

Species E(b)

$S_{1b}(E) = 2^{-\frac{1}{2}}(r_2-r_3)$

$S_{2b}(E) = 2^{-\frac{1}{2}} R\cdot(\alpha_2-\alpha_3)$

$S_{3b}(E) = \frac{1}{2}(s_3+s_4-s_5-s_6)$

$S_{4b}(E) = 12^{-\frac{1}{2}}(-2s_1+2s_2+s_3-s_4+s_5-s_6)$

$S_{5b}(E) = \frac{1}{2}(RS)^{\frac{1}{2}}\cdot(\phi_3+\phi_4-\phi_5-\phi_6)$

$S_{6b}(E) = (RS/12)^{\frac{1}{2}}\cdot(-2\phi_1+2\phi_2+\phi_3-\phi_4+\phi_5-\phi_6)$

$S_{7b}(E) = 2^{-\frac{1}{2}}(d_2-d_3)$

$S_{8b}(E) = 2^{-\frac{1}{2}}(t_2-t_3)$

$S_{9b}(E) = 2^{-\frac{1}{2}}(u_2-u_3)$

$S_{10b}(E) = (RU/2)^{\frac{1}{2}}\cdot(\xi_2-\xi_3)$

$S_{11b}(E) = (RU/6)^{\frac{1}{2}}\cdot(2\eta_1-\eta_2-\eta_3)$

$S_{12b}(E) = \frac{1}{2}(v_3+v_4-v_5-v_6)$

$S_{13b}(E) = 12^{-\frac{1}{2}}(-2v_1+2v_2+v_3-v_4+v_5-v_6)$

$S_{14b}(E) = \frac{1}{2}[V(DT)^{\frac{1}{2}}]^{\frac{1}{2}}\cdot(\gamma_3+\gamma_4-\gamma_5-\gamma_6)$

$S_{15b}(E) = [V(DT)^{\frac{1}{2}}/12]^{\frac{1}{2}}\cdot(-2\gamma_1+2\gamma_2+\gamma_3-\gamma_4+\gamma_5-\gamma_6)$

$S_{16b}(E) = \frac{1}{2}(DV)^{\frac{1}{2}}\cdot(\delta_3+\delta_4-\delta_5-\delta_6)$

$S_{17b}(E) = (DV/12)^{\frac{1}{2}}\cdot(-2\delta_1+2\delta_2+\delta_3-\delta_4+\delta_5-\delta_6)$

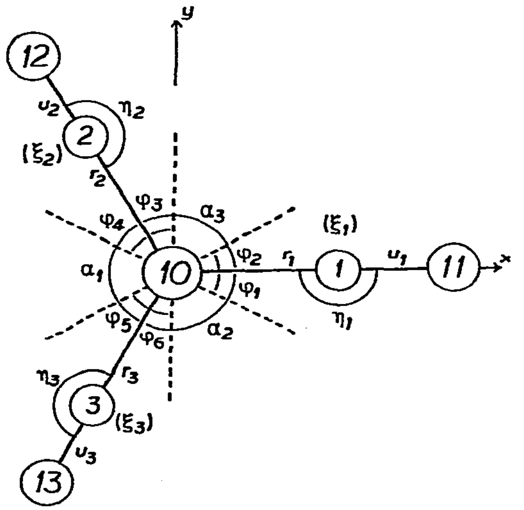

Fig. 3. Valence coordinates for the Cr–CO part of the benzenechromium tricarbonyl model. In particular $\phi_1, \ldots, \phi_6$ denote six symmetrically equivalent $C_{carbonyl}$–Cr–$C_{benzene}$ bendings; ξ_1, ξ_2 and ξ_3 are Cr–C–O linear bendings in planes through the Z axis.

It was stated that this set of symmetry coordinates is complete, which implies that all the given coordinates are independent. It does not mean, however, that many important valence angle bendings and other types of valence coordinates have not been omitted when choosing the basis for the set. Also, the totally symmetric combination of the ϕ coordinates was omitted, whereby a redundancy in species A_1 was avoided. Furthermore, only one out of the six possible independent β combinations was used.

All these features result in the conclusion that this symmetry coordinate set should not be used when setting up an initial force field. There are expected to be many significant interaction force constants, and even the diagonal constants may hardly be estimated *a priori*. Therefore, an alternative set of symmetry coordinates was constructed. It is described in the next section.

PHYSICAL SYMMETRY COORDINATES

The alternative set of symmetry coordinates are basically of the same types as those of the corresponding set applied to bis(benzene)chromium[2]. In contrast, however, the distinction between in-phase and out-of-phase ligand motions disappears in the present case because of the lack of a horizontal symmetry plane. For the same reason it was more difficult to construct the appropriate coordinates in the case of benzenechromium tricarbonyl so as to make them fulfill the general requirements for an internal coordinate. Altogether the following coordinates were used:

(A). Fifteen coordinates for the $Cr(CO)_3$ fragment constructed as formally identical to the symmetry coordinates of a pyramidal $X(YZ)_3$ model with linear XYZ chains[6]. These coordinates have also been applied to the phosphorus and arsenic tricyanide molecules[6].

(B). Thirty coordinates for the C_6H_6 ligand taken from the benzene model[7].

(C). Additional six coordinates involving the motions of both groups, $Cr(CO)_3$ and C_6H_6.

These different types of coordinates are distributed among the symmetry species of C_{3v} in the following way:

Species A_1

4 A_1 coordinates of type (A); 2 $A_{1g}+A_{2u}+2\,B_{2u}$ of type (B); one (C) type describing compensated translations of the two groups $Cr(CO)_3$ and C_6H_6in the Z direction.

Species A_2

One A_2 coordinate of type (A); $A_{2g}+2\,B_{2g}+2\,B_{1u}$ from (B); one (C) type describing internal rotation of the two groups.

Species E

5 E coordinates of type (A); $E_{1g}+4\,E_{2g}+3\,E_{1u}+2\,E_{2u}$ from (B); two degenerate pairs of complicated motion classified under (C), containing librations and translations with some deformation of the two groups.

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