allowed to operate. A column approximately 100 cm long and 5 cm wide will contain 1 kg of alumina, sufficient for the purification of about 10 l of DMF. With this column a drop rate of approximately one drop per five seconds has been found to give a pure product.

After passing the column, the DMF smells strongly of amine. The amine is eliminated by bubbling pure nitrogen through the DMF for several hours. The resultant product shows two peaks in gas-liquid chromatography, the smaller of which is 100 ppm of the bigger one (90°C, stationary phase: polypropylene glycol). Polarography shows no defined wave, but a residual current of approximately 0.02 μA. The water content has been measured by Karl Fischer titration. Up to about 100 ppm of water has been found.

Acetonitrile. Acetonitrile is obtained as a byproduct in the manufacture of acrylonitrile, which is the main impurity in commercial acetonitrile. The difference in boiling points of these two compounds is only 4.2°C, so the complete separation by normal fractional distillation is practically impossible. The author has found, however, that separation is possible by distillation of the ternary and secondary azeotropes the two liquids form with ethanol and water.

In a typical run 300 ml of 96 % ethanol was added to 3.5 l of commercial acetonitrile and the mixture was distilled on a Stedman column using an automatic take-off head. The column is 110 cm long, with inner diameter 2.5 cm and equals 60—65 theoretical plates. With a reflux ratio of 80, the distillate was pure after nine days of distillation. Total yield of pure acetonitrile: approximately 1.5 l. The purity was measured by gas-liquid chromatography and by polarography. Gas chromatography shows two peaks, the smaller of which is 60 ppm of the bigger one. (65°C, stationary phase: polypropylene glycol). Polarography shows a residual current of about 0.01 μA.

Provided the joints by which the receiver is connected to the column are not greased the pure acetonitrile is also well suited for ultra-violet spectroscopy.[2]

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Spectroscopic Studies on Metal Carbonyls

VI. Mean Amplitudes of Vibration and Shrinkage Effects for Iron Pentacarbonyl

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This paper continues the series on metal carbonyls wherein the previous papers[1-3] have given spectroscopic calculations for the chromiun and molybdenum hexacarbonyls, and for nickel tetracarbonyl.

The trigonal bipyramidal symmetry of the iron pentacarbonyl molecule is in accordance with electron diffraction studies,[4,5] X-ray crystallographic calculations,[6] and the numbers of infrared and Raman fundamentals.[7] Fateley and Lippincott,[8] and Kawai and Murata[9] have carried out normal coordinate analyses, and given symmetry force constants[8] and Urey-Bradley force constants.[9] In this paper fundamental frequencies given by Edgell et al.[7] were adopted. Two fundamentals, the A_2' frequency (ν_5) and one of the A_2'' frequencies (ν_9), not given by Edgell et al. were taken from Fateley and Lippincott's paper.[8] Symmetry force constants were computed, with the assumption of zero values for all the off-diagonal elements. By means of this force field the mean amplitudes of vibration (Table 1) and Bastiansen-Morino shrinkage effects (Table 2) were computed. In the tables "(eq)" and "(ax)" refer to "equatorial" and "axial" distances, respectively. The equilibrium distances used are given in parentheses. Both types of C=O bond distances, equatorial and axial, were given the same equilibrium

Table 1. Mean amplitudes of vibration (Å units) for iron pentacarbonyl.

Distance (equil.)		$T = 0$	298°K
Fe$-$C(eq)	(1.800)	0.0446	0.0484
Fe$-$C(ax)	(1.800)	0.0464	0.0506
C(eq)$-$O(eq)	(1.136)	0.0348	0.0348
C(ax)$-$O(ax)	(1.136)	0.0353	0.0353
Fe$\cdots$O(eq)	(2.936)	0.0459	0.0503
Fe$\cdots$O(ax)	(2.936)	0.0474	0.0525
C(eq)$\cdots$C(eq)	(3.118)	0.0733	0.1053
C(eq)$\cdots$C(ax)	(2.546)	0.0848	0.1490
C(eq)$\cdots$O(eq)	(4.141)	0.0797	0.1284
C(eq)$\cdots$O(ax)	(3.444)	0.0949	0.1795
C(ax)$\cdots$O(eq)	(3.444)	0.0946	0.1818
O(eq)$\cdots$O(eq)	(5.085)	0.0928	0.1718
O(eq)$\cdots$O(ax)	(4.152)	0.1163	0.2451
C(ax)$\cdots$C(ax)	(3.600)	0.0585	0.0649
C(ax)$\cdots$O(ax)	(4.736)	0.0591	0.0663
O(ax)$\cdots$O(ax)	(5.872)	0.0599	0.0677

Table 2. Bastiansen-Morino shrinkage effects (Å units) for iron pentacarbonyl.

Distance (equil.)		$T = 0$	298°K
Fe$\cdots$O(eq)	(2.936)	0.0056	0.0074
Fe$\cdots$O(ax)	(2.936)	0.0039	0.0044
C(eq)$\cdots$C(eq)	(3.118)	0.0025	0.0070
C(eq)$\cdots$C(ax)	(2.546)	0.0011	0.0036
C(eq)$\cdots$O(eq)	(4.141)	0.0080	0.0161
C(eq)$\cdots$O(ax)	(3.444)	0.0046	0.0079
C(ax)$\cdots$O(eq)	(3.444)	0.0060	0.0106
O(eq)$\cdots$O(eq)	(5.085)	0.0130	0.0263
O(eq)$\cdots$O(ax)	(4.152)	0.0084	0.0151
C(ax)$\cdots$C(ax)	(3.600)	0.0045	0.0193
C(ax)$\cdots$O(ax)	(4.736)	0.0089	0.0286
O(ax)$\cdots$O(ax)	(5.872)	0.0138	0.0414

value, and put equal to r_g of Ref. 6. The results for the Fe$-$C bond distances of that paper [6] have been commented on by Donohue and Caron.[10] Here the value of this distance was taken to be 1.80 Å both for the equatorial and the axial bonds. The shrinkage effects given are the so called "practical" shrinkage effects.[11]

For the previously investigated metal carbonyls the mean amplitude of vibration of the M$\cdots$O distance (M = central atom) is suprisingly small,[2,3] and of the same magnitude as the bonded M$-$C amplitude. The same result is found for iron pentacarbonyl. The mean amplitudes of vibration for the equatorial bond distances are smaller than the values for the analogous axial bond distances.

According to Edgell *et al.*[7] the normal vibration associated with the frequency 431 cm^{-1} is mainly connected with Fe$-$C$_{eq}$ stretching, and the 544 cm^{-1} with Fe$-$C$_{eq}$ $=$O$_{eq}$ linear bending. Calculations on the potential energy distribution [12] using the present force field gave the contributions of 0.09 and 0.73 from the Fe$-$C$_{eq}$ stretching and the Fe$-$C$_{eq}$$=O_{eq}$ bending, respectively, for the 431 cm^{-1} normal vibration. For the 544 cm^{-1} normal vibration on the other hand one obtained the contributions of 0.55, 0.04, and 0.34 from the Fe$-$C$_{eq}$ stretching, the Fe$-$C$_{eq}$$=O_{eq}$ bending, and the Fe$-$C$_{ax}$$=O_{ax}$ bending, respectively.

This force field therefore rather leads to an assignment of the 544 cm^{-1} normal vibration to the Fe$-$C$_{eq}$ stretching symmetry coordinate of species E'. The writer does not maintain this to be the right conclusion, however, because of the approximate nature of the force field.

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