Articles

Gas-Phase Iron Tricarbonyl Cyclooctatetraene Exhibits a “Rigid-Rotor” Microwave Spectrum

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The microwave rotational spectrum of (η^4-C_8H_8) $Fe(CO)_3$ was measured in the 4−12 GHz range using a pulsed-beam, Fourier transform spectrometer system. Nearly all strong transitions can be fit using a near-rigid-rotor model with very small centrifugal distortion terms. These results indicate that this complex has a fairly rigid structure in the gas phase, with no observed evidence for fluxional behavior or internal rotation on the microwave time scale ($\tau < 10^{-4}$ s). These gas-phase observations initially appeared to be in sharp contrast to the solution NMR studies, where this complex is observed to be a “ring whizzer” with cyclic 1,2 carbon shifts. Further analysis indicates these two sets of measurements are compatible since, with an intermediate level barrier to internal motion ($V > 500$ cm^{-1}), the structure would appear rigid on the microwave time scale, yet could appear quite fluxional on the much longer NMR time scale. The rotational constants are $A = 825.2559(2)$, $B = 510.5149(1)$, and $C = 462.5246(1)$ MHz. Centrifugal distortion constants are $\Delta_J = 0.0146(5)$, $\Delta_{JK} = 0.015(3)$, $\Delta_K = 0.049(4)$, $\delta_J = 0.0034(3)$, and $\delta_K = -0.092(6)$ kHz. The measured rotational constants all agree with those calculated from the X-ray structure to within 0.3%. The excellent agreement between the rotational constants makes it very likely that the solid-state and gas-phase structures are nearly identical.

Introduction

The iron tricarbonyl cyclooctatetraene complex is one of the earliest reported examples of fluxional molecules.[1] Only a single proton resonance was observed[1,2] for the solution NMR spectrum, indicating a fairly rapid exchange of cyclooctatetraene (COT) protons. This work was preceded by similar observations of single lines for the proton spectrum[3] of (η^5-C_5H_5) $Fe(CO)_2$-(η^2-C_5H_5) and the ^{13}C spectrum[4] of $Fe(CO)_5$. These results were all interpreted as indications of “fluxional behavior” of the complexes.[1] For the COT complex, the motion was described[5,6] as sequential, cyclic 1,2 shifts of the ring carbon atoms relative to the $Fe(CO)_3$ group, and this complex was called[5] a “ring whizzer”. For the proton spectrum of the (COT)$Fe(CO)_3$ complex, the limiting spectrum (with the internal motion frozen out) was not obtained[1] by lowering the temperature of the solution. For the (COT)$Ru(CO)_3$ complex, however, at low temperatures, a well-resolved limiting spectrum was obtained.[7] In subsequent work,[6] limiting ^{13}C spectra were obtained for the (COT)$Fe(CO)_3$ and (COT)$Ru(CO)_3$ complexes.

Olefin transition metal complexes are important because they may be used as models for olefin−metal interactions, which are important in catalysis. Changes in the conformation of the olefin on complexation can have significant effects on the energetics and kinetics of subsequent reactions.

For benzene, the high-stability equal carbon−carbon bond lengths and other interesting properties are attributed to the resonance stabilization and aromatic character of this important molecule. Cyclooctatetraene, on the other hand, is predicted to lack sufficient resonance stabilization, and the free molecule is nonplanar. Free cyclooctatetraene adopts a “tub” structure[8,9] and has the chemical properties of a nonaromatic polyolefin. The crystal structure for the iron tricarbonyl cyclooctatetraene complex was reported in 1962 by Dickens and Lipscomb.[10] The COT ligand is asymmetrically bound to $Fe(CO)_3$. The $Fe(CO)_3$ is apparently η^4-bonded to a butadiene-like portion of the COT ring. The two ethylene like regions which are not complexed to the iron atom are distorted from the “tub” conformation to form a near-planar structure for that portion of the COT ligand. The X-ray structure is shown in Figure 1.

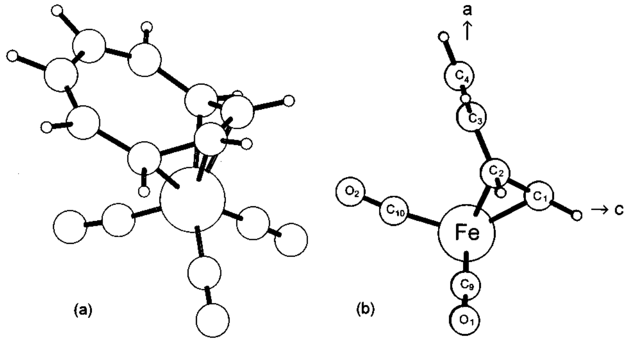

Figure 1. Molecular structure for iron tricarbonyl cyclooctatetraene: (a) arbitrary-axis view; (b) view down the *b* principal axis, with numbering of carbon atoms indicated. Coordinates are from the X-ray work.[10]

The microwave spectroscopy study was initiated with the expectation that effects of nonrigid behavior, similar to internal

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Table 1. Transition Frequencies for Iron Tricarbonyl Cyclooctatetraene Which Can Be Fit to a Rigid-Rotor Model with Small Centrifugal Distortion Terms[a]

J'	K_p'	K_o'	J	K_p	K_o	measd	calcd	dev
3	2	2	2	1	2	4007.310	4007.310	0.0004
3	3	0	2	2	0	4611.075	4611.075	0.0001
3	3	1	2	2	1	4615.817	4615.816	0.0006
5	1	5	4	1	4	4726.237	4726.237	0.0003
5	0	5	4	0	4	4777.200	4777.201	−0.0006
4	2	2	3	1	2	4836.513	4836.512	0.0003
5	2	4	4	2	3	4853.910	4853.909	0.0005
5	4	2	4	4	1	4876.467	4876.467	−0.0006
5	4	1	4	4	0	4876.615	4876.616	−0.0009
5	3	3	4	3	2	4879.380	4879.379	0.0004
6	0	6	5	1	4	4882.511	4882.511	−0.0002
5	3	2	4	3	1	4886.324	4886.322	0.0013
5	2	3	4	2	2	4941.750	4941.750	0.0008
5	1	4	4	1	3	4959.244	4959.242	0.0020
4	2	3	3	1	3	5051.393	5051.393	0.0005
6	1	5	5	2	3	5089.854	5089.852	0.0017
5	1	4	4	0	4	5596.072	5596.072	0.0003
4	3	2	3	2	2	5598.076	5598.076	−0.0001
6	1	6	5	1	5	5662.019	5662.018	0.0014
6	0	6	5	0	5	5701.383	5701.382	0.0002
9	4	6	8	5	4	5781.526	5781.525	0.0008
5	2	3	4	1	3	5801.366	5801.366	−0.0001
9	4	5	8	5	3	5803.729	5803.730	−0.0012
6	2	5	5	2	4	5815.532	5815.538	−0.0063
6	5	2	5	5	1	5850.990	5850.986	0.0046
6	4	3	5	4	2	5855.287	5855.288	−0.0007
6	4	2	5	4	1	5855.951	5855.952	−0.0008
6	3	4	5	3	3	5857.694	5857.693	0.0002
6	3	3	5	3	2	5875.665	5875.664	0.0008
8	2	7	7	3	5	5884.053	5884.053	0.0000
6	1	5	5	1	4	5931.976	5931.976	−0.0002
6	2	4	5	2	3	5951.716	5951.716	0.0002
7	1	6	6	2	4	6030.295	6030.294	0.0007
5	2	4	4	1	4	6118.352	6118.352	0.0002
8	0	8	7	1	6	6222.645	6222.645	0.0006
4	4	0	3	3	0	6263.920	6263.915	0.0049
4	4	1	3	3	1	6264.232	6264.235	−0.0033
9	3	7	8	4	5	6418.746	6418.745	0.0013
5	3	2	4	2	2	6525.838	6525.838	0.0000
9	1	9	8	2	7	6530.226	6530.227	−0.0005
8	2	6	7	3	4	6538.349	6538.348	0.0003
5	3	3	4	2	3	6589.264	6589.265	−0.0008
7	1	7	6	1	6	6594.692	6594.692	0.0002
7	0	7	6	0	6	6621.965	6621.964	0.0009
9	2	8	8	3	6	6744.220	6744.219	0.0010
6	1	5	5	0	5	6750.847	6750.847	−0.0002
7	2	6	6	2	5	6772.482	6772.483	−0.0005
6	2	4	5	1	4	6793.840	6793.840	−0.0001
7	5	2	6	5	1	6829.411	6829.414	−0.0033
7	3	5	6	3	4	6835.286	6835.286	0.0000
7	4	4	6	4	3	6835.722	6835.722	0.0001
7	4	3	6	4	2	6837.905	6837.902	0.0031
7	3	4	6	3	3	6873.693	6873.694	−0.0012
7	1	6	6	1	5	6892.157	6892.158	−0.0015
8	1	7	7	2	5	6908.504	6908.505	−0.0003
6	2	5	5	1	5	7207.654	7207.653	0.0006
5	4	1	4	3	1	7237.139	7237.140	−0.0006
5	4	2	4	3	2	7239.331	7239.326	0.0052
6	3	3	5	2	3	7459.752	7459.752	−0.0004
6	3	4	5	2	4	7593.050	7593.049	0.0008
9	1	8	8	2	6	7717.451	7717.449	0.0016
8	2	7	7	2	6	7724.368	7724.368	−0.0002
8	6	3	7	6	2	7803.547	7803.546	0.0010
8	5	3	7	5	2	7809.403	7809.404	−0.0013
8	3	6	7	3	5	7810.936	7810.937	−0.0016
8	4	5	7	4	4	7817.629	7817.630	−0.0009
7	2	5	6	1	5	7821.456	7821.458	−0.0017
8	4	4	7	4	3	7823.491	7823.492	0.0000
8	1	7	7	1	6	7837.804	7837.804	−0.0003
8	3	5	7	3	4	7881.699	7881.701	−0.0025
5	5	0	4	4	0	7914.595	7914.598	−0.0028
5	5	1	4	4	1	7914.616	7914.616	0.0003
7	1	6	6	0	6	7941.623	7941.623	0.0001
8	2	6	7	2	5	7960.485	7960.485	−0.0003
6	4	2	5	3	2	8206.769	8206.769	0.0005
6	4	3	5	3	3	8215.235	8215.235	−0.0003
7	3	4	6	2	4	8381.729	8381.731	−0.0015
9	1	9	8	1	8	8453.162	8453.163	−0.0008
10	1	9	9	2	7	8457.046	8457.046	0.0001
9	0	9	8	0	8	8463.710	8463.710	−0.0004
8	3	5	7	2	5	9303.836	9303.838	−0.0021
10	0	10	9	0	9	9386.311	9386.308	0.0034
8	2	7	7	1	7	9447.795	9447.794	0.0006
6	6	0	5	5	0	9565.110	9565.108	0.0018
9	2	7	8	1	7	10003.074	10003.075	−0.0011
9	3	6	8	2	6	10241.751	10241.752	−0.0016
11	1	11	10	1	10	10306.363	10306.365	−0.0019
11	0	11	10	0	10	10309.821	10309.821	−0.0003
9	1	8	8	0	8	10384.586	10384.589	−0.0023
7	6	2	6	5	2	10539.669	10539.675	−0.0059
11	2	10	10	2	9	10550.312	10550.311	0.0008
9	2	8	8	1	8	10594.039	10594.039	0.0004
11	1	10	10	1	9	10606.876	10606.876	−0.0003
8	5	4	7	4	4	10836.692	10836.691	0.0011
11	3	8	10	3	7	10937.765	10937.766	−0.0015
9	4	5	8	3	5	11051.283	11051.284	−0.0013
10	2	8	9	1	8	11162.523	11162.518	0.0047
9	4	6	8	3	6	11165.256	11165.256	−0.0006
7	7	0	6	6	0	11215.593	11215.592	0.0007
7	7	1	6	6	1	11215.593	11215.592	0.0006
10	1	9	9	0	9	11611.568	11611.570	−0.0017
10	2	9	9	1	9	11753.790	11753.789	0.0010
10	3	8	9	2	8	11790.828	11790.826	0.0023
9	5	4	8	4	4	11801.757	11801.755	0.0015
9	5	5	8	4	5	11809.723	11809.720	0.0022

[a] The calculated values were obtained from a least-squares fit with parameters given in Table 2. All frequencies are in megahertz. "dev" (MHz) is the measured minus the calculated frequency. The standard deviation for the fit was 1.8 kHz.

rotation, would be observed in the spectrum. The observed spectrum was that of a rigid rotor.

Experimental Section

The sample was purchased from Strem (No. 26-0875) and used without further purification. Microwave transitions were measured in the 4−12 GHz range using a Flygare-Balle type pulsed-beam spectrometer system.[11] The sample and pulse valve (General Valve 9-181) were maintained at 70−80 °C to obtain sufficient vapor pressure of the complex. The sample was mixed with neon at 0.6−1.0 atm and pulsed into the Fabry Perot microwave cavity for measurements of the spectrum. The statistical uncertainty in the line center measurements ranged from 0.1 to 3 kHz. There are over 250 transitions for the normal isotopomer in the 4−12 GHz range which should be observable. The 105 measured transition frequencies, which were used to obtain the molecular parameters, are given in Table 1. Many other, weaker, transitions were observed, and we believe that these transitions are most likely due to the ^{54}Fe and ^{13}C isotopomers.

Data Analysis

Two views of the structure of the iron tricarbonyl cyclooctatraene complex, as determined from the X-ray data,[10] are shown in Figure 1. Hydrogen atom coordinates were not obtained from the X-ray data but were estimated by using a C−H bond length of 1.08 Å and placing the C−H bonds near the plane of the local carbon atoms. We note from Figure 1b, which shows a view down the *b* principal axis, that this complex would

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Table 2. Molecular Constants for Iron Tricarbonyl Cyclooctatetraene Obtained from the Least-Squares Fit to Transition Frequencies Listed in Table 1[a]

param	value	param	value	param	value
A (MHz)	825.2559(2)	Δ_J (kHz)	0.0146(5)	δ_J (kHz)	0.0034(3)
B (MHz)	510.5149(1)	Δ_{JK} (kHz)	0.015(3)	δ_K (kHz)	−0.092(6)
C (MHz)	462.5246(1)	Δ_K (kHz)	0.049(4)		

[a] Error limits are 2σ, and the standard deviation for the fit was 1.8 kHz.

be expected to have both a-axis and c-axis dipole moment components. We therefore assigned observed transitions to quantum numbers appropriate for a-dipole and c-dipole selection rules.

The measured transition frequencies listed in Table 1 were fit using a distortable rigid-rotor Hamiltonian with seven adjustable parameters. The A-reduced Hamiltonian in the I^r representation,[12] with rotational constants A, B, and C, and the five quartic distortion parameters Δ_J, Δ_{JK}, Δ_K, δ_J, and δ_K were used in a nonlinear least-squares fit to determine parameter values. The "best fit" parameter values, with 2σ error limits, are listed in Table 2. The centrifugal distortion terms are quite small, consistent with a fairly rigid complex. The rotational constants, calculated using the X-ray structure[10] with hydrogen atoms added, are $A = 827.22$, $B = 512.03$, and $C = 463.20$ MHz. These values are in excellent agreement with observed rotational constants. This agreement can be interpreted as an indication that the gas-phase and solid-state structures are almost identical. We would not expect significant changes in bond lengths, and it is quite unlikely that the angles would be distorted in the solid in such a way that effects on the moments of inertia of two or more such distortions would cancel. The standard deviation for the fit of 1.8 kHz is close to estimated experimental errors for the measurements. The relative error limits (2σ) for the parameters listed in Table 2 are extremely small, and this is also consistent with a rigid-rotor spectrum.

Discussion

The gas-phase rotational spectrum of iron tricarbonyl cyclooctatetraene can be fit very precisely using a rigid-rotor model. None of the microwave measurements, in our opinion, show evidence for hindered internal rotation or more complex internal motions. In retrospect, these results are quite compatible with the solution NMR work, since Cotton and Hunter[6] obtained a barrier height of 8.1 kcal for the "ring-whizzing" motion. A barrier as high as this (2800 cm^{-1}) would cause line splittings due to internal rotation which would be much too small to observe since typical microwave line widths are 10−20 kHz (fwhm) for the Flygare-Balle spectrometer. In the NMR experiments the "sampling time" during which the transition is observed is in the range of seconds to minutes. If the internal motion (1,2 shifts or "ring whizzing") takes place more rapidly than this, one sees a "single-line" spectrum with a chemical shift which is an average over the chemical shifts for the various proton or ^{13}C sites in the complex. If the barrier to the internal motion were approximately 4000 cm^{-1}, or greater, the steps in the internal motion would take place much slower than the "sampling time", and a resolved or nearly-resolved spectrum would be obtained.

Summary

A near-rigid-rotor spectrum was observed for iron tricarbonyl cyclooctatetraene, and accurate and precise values for the rotational constants and centrifugal constants were obtained. The experimental A, B, and C values are in excellent agreement with those calculated for the X-ray structure, indicating that the gas-phase and solid-state structures are nearly the same. The presence of a barrier to internal motion of 500 cm^{-1} or higher would cause splittings too small to be resolved, resulting in a "rigid-rotor" type microwave spectrum. This "low barrier" however would still allow sufficiently rapid internal motion to observe a "single-line" NMR spectrum, since the NMR time scale is 4 or more orders of magnitude longer than the microwave time scale. We propose that this "intermediate-barrier" behavior is fairly common and should apply to many "fluxional" organometallic complexes, where the barriers are between 500 and 4000 cm^{-1}.

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