

# Microwave measurements of rhenium quadrupole coupling in cyclopentadienyl rhenium tricarbonyl

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Microwave measurements of rotational transitions for cyclopentadienyl rhenium tricarbonyl were performed in the gas phase using pulsed beam Fourier transform microwave spectroscopy. One hundred and sixty five transitions were assigned to two isotopomers of rhenium. The location of the rhenium atom near the center of mass produced significant overlap between the spectra of the two isotopomers. The data were accurately fit using a symmetric top, rigid rotor Hamiltonian that included nuclear quadrupole coupling and centrifugal distortion constants. The rotational constants obtained were  $B(^{187}\text{Re}) = 724.9794(2)$ ,  $B(^{185}\text{Re}) = 724.9795(2)$ . The quadrupole coupling constants obtained were  $eQq(^{187}\text{Re}) = 614.464(12)$  and  $eQq(^{185}\text{Re}) = 649.273(14)$  MHz. The successful fitting of the measured spectra to a symmetric top Hamiltonian indicates that the cyclopentadienyl group retains  $C_{5v}$  symmetry, and the  $\text{Re}(\text{CO})_3$  group  $C_{3v}$  symmetry in the gas phase. The measured rotational constants are in reasonable agreement with those calculated from the structural parameters obtained in the earlier x-ray work. The Re quadrupole coupling constants obtained are compared with values for other complexes. © 1998 American Institute of Physics. [S0021-9606(98)00921-0]

## I. INTRODUCTION

The structures of the isoelectronic compounds  $\text{CpMn}(\text{CO})_3$  and  $\text{CpRe}(\text{CO})_3$  have been extensively studied by a wide variety of techniques.<sup>1-5</sup> Several of these techniques<sup>1-4</sup> have indicated that the Cp group interacts with the  $C_{3v}$  symmetry, carbonyl portion of the molecule and exhibits a reduction in symmetry to  $C_{2v}$ . For these examples, the molecule would no longer be a symmetric top. Analysis of the microwave spectrum<sup>5</sup> of  $\text{CpMn}(\text{CO})_3$  showed that this molecule is a prolate symmetric top in the gas phase. Presented here is a similar analysis of  $\text{CpRe}(\text{CO})_3$  indicating that it is also a prolate symmetric top in the gas phase.

Nuclear quadrupole coupling in molecules can produce large splittings in the microwave spectrum, and therefore, accurate values for this coupling can often be obtained from the spectra. The magnitude of this coupling reflects anisotropy in the electric field gradient surrounding the quadrupolar nucleus. Gas phase quadrupole coupling in rhenium compounds has only been studied for a few cases such as  $\text{HRe}(\text{CO})_5$  and  $\text{CH}_3\text{ReO}_3$  and results in very large splitting patterns. The electric field gradients obtained from the measured coupling constants can be useful for describing bonding between related molecules and for comparison with calculated electronic properties.

## II. EXPERIMENT

Microwave measurements in the 5-10 GHz range were made using a Flygare-Balle-type pulsed-beam Fourier transform microwave spectrometer.<sup>6</sup> The sample of  $\text{CpRe}(\text{CO})_3$  was purchased from Strem Chemicals (CAS# [12079-73-1]) and was used without further purification. A neon carrier gas was used to transfer the volatile compound into the vacuum

chamber. It was necessary to heat the valve and sample cell to 40°C in order to produce sufficient vapor pressure for reasonable signal detection. Three sets of  $R$ -branches transitions,  $J=4\leftarrow 3, 5\leftarrow 4$  and  $6\leftarrow 5$  were measured in absorption. Over two hundred lines were measured of which 165 were definitely assigned. These transitions are listed with their assignments and calculated frequencies in Tables I and II. The measurements were made relative to a local frequency standard which is periodically calibrated to WWVH (Boulder, CO), and the relative accuracy is  $1 \times 10^{-9}$ , or better. The typical uncertainties in the measured line positions are in the range of 1–10 kHz, depending on the available signal to noise ratio, and possible splitting of the lines. The frequency uncertainties due to the reference or calibration errors are at least an order of magnitude less than this range. A few cases of what we believe are “instrumental” splittings of 10–20 kHz, due to combinations of high stimulating power, residual Doppler effects, and complex cavity modes were observed, and are indicated in Tables I and II.

The rhenium atom is very close to the center of mass in this compound, and thus isotopic substitution of this atom does not cause very large shifts in the frequencies of the microwave transitions with the same quantum numbers. Furthermore, the electric field gradient at the rhenium nucleus is not expected to change upon isotopic substitution of the rhenium atom. The result is that the spectra for the two rhenium isotopomers overlapped considerably, and splitting of corresponding transitions was primarily due to the small difference in the nuclear quadrupole moments [ $Q(^{185}\text{Re})/Q(^{187}\text{Re}) = 1.05668(3)$ ] of the rhenium isotopes.

## III. DATA ANALYSIS AND RESULTS

The high density of transitions in narrow frequency regions allowed the measurement of multiple line frequencies

TABLE I. Measured and calculated transition frequencies (MHz) for  $\text{Cp}^{187}\text{Re}(\text{CO})_3$ . The uncertainty indicated on the measured frequency is the standard deviation for four measurements of that transition, and we believe this is a good indication of the precision ( $1\sigma$ ) and accuracy of the measurements (1 to 10 kHz).

Measured	Calculated	Difference	<i>J</i>	<i>K</i>	<i>F</i>	<i>J</i>	<i>K</i>	<i>F</i>
5773.6393 (13)	5773.6410	-0.0017	4	1	4	3	1	4
5778.0460 (14)	5778.0529	-0.0069	4	2	7	3	2	6
5781.6026 (26)	5781.6057	-0.0031	4	2	3	3	2	2
5782.8185 (39)	5782.8309	-0.0124	4	2	3	3	2	3
5791.0387 (28)	5791.0577	-0.0190	4	1	7	3	1	6
5791.6142 (09)	5791.5821	0.0321	4	0	6	3	0	5
5795.3689 (09)	5795.3305	0.0384	4	0	7	3	0	6
5798.2155 (31)	5798.2009	0.0146	4	3	4	3	3	3
5798.5232 (30)	5798.4956	0.0276	4	1	6	3	1	5
5804.1209 (12)	5804.0952	0.0257	4	0	5	3	0	4
5805.8890 (06)	5805.8853	0.0037	4	0	5	3	0	5
5808.8962 (21)	5808.8957	0.0005	4	2	4	3	2	3
5810.0984 (38)	5810.1120	-0.0136	4	2	4	3	2	4
5810.2187 (39)	5810.2193	-0.0006	4	1	5	3	1	5
5812.913 (30) <sup>a</sup>	5812.9234	-0.0104	4	1	3	3	1	2
5813.0409 (75)	5813.1010	-0.0601	4	0	2	3	0	1
5816.1338 (16)	5816.1449	-0.0111	4	1	4	3	1	3
5818.7336 (04)	5818.7112	0.0224	4	0	4	3	0	3
5820.1470 (06)	5820.1554	-0.0084	4	2	6	3	2	5
5823.4795 (23)	5823.4867	-0.0072	4	2	6	3	2	6
5823.7355 (10)	5823.7162	0.0193	4	0	3	3	0	2
5824.5274 (05)	5824.5355	-0.0081	4	2	5	3	2	5
5827.0626 (03)	5827.0522	0.0104	4	2	5	3	2	4
7200.9794 (18)	7200.9858	-0.0064	5	3	3	4	3	2
7207.1482 (11)	7207.1291	0.0191	5	4	8	4	4	7
7224.7430 (09)	7224.7318	0.0112	5	3	8	4	3	7
7231.2305 (43)	7231.2370	-0.0065	5	3	4	4	3	3
7231.8994 (15)	7231.9131	-0.0137	5	2	3	4	2	2
7244.1100 (42)	7244.0810	0.0290	5	0	7	4	0	6
7246.7019 (51)	7246.6615	0.0404	5	0	8	4	0	7
7247.096 (50) <sup>a</sup>	7247.1174	-0.0214	5	1	7	4	1	6
7248.5627 (44)	7248.5761	-0.0134	5	2	4	4	2	3
7250.7360 (27)	7250.7936	-0.0576	5	1	3	4	1	2
7251.0039 (27)	7251.0685	-0.0646	5	0	6	4	0	5
7254.3716 (12)	7254.3507	0.0209	5	1	6	4	1	5
7255.8317 (37)	7255.8524	-0.0207	5	3	4	4	3	4
7256.4121 (07)	7256.4287	-0.0166	5	2	7	4	2	6
7257.1561 (12)	7257.1421	0.0140	5	0	3	4	0	2
7259.3292 (31)	7259.3166	0.0126	5	1	4	4	1	3
7259.5837 (64)	7259.5581	0.0256	5	0	5	4	0	4
7259.7901 (23)	7259.7706	0.0195	5	1	5	4	1	4
7260.4076 (31)	7260.4064	0.0012	5	2	5	4	2	4
7261.4613 (35)	7261.4585	0.0028	5	3	5	4	3	4
7262.9310 (15)	7262.9234	0.0076	5	4	5	4	4	4
7264.1298 (21)	7264.1239	0.0059	5	2	6	4	2	5
7265.3725 (32)	7265.3716	0.0009	5	0	6	4	0	6
7266.0694 (14)	7266.0744	-0.0050	5	1	6	4	1	6
7268.4873 (16)	7268.5040	-0.0167	5	2	6	4	2	6
7272.6568 (09)	7272.6437	0.0131	5	3	7	4	3	6
7273.6268 (42)	7273.6541	-0.0273	5	3	6	4	3	6
7276.5731 (06)	7276.5980	-0.0249	5	3	5	4	3	5
7280.1641 (16)	7280.1536	0.0105	5	3	6	4	3	5
7283.2975 (17)	7283.3102	-0.0127	5	4	6	4	4	6
7296.9381 (15)	7296.9134	0.0247	5	4	7	4	4	6
7301.8531 (69)	7301.8626	-0.0095	5	2	7	4	2	7
7302.0438 (07)	7302.0231	0.0207	5	4	6	4	4	5
7322.4588 (18)	7322.4692	-0.0104	5	4	5	4	4	5
7340.1668 (17)	7340.1682	-0.0014	5	1	7	4	1	7
7352.8748 (14)	7352.8722	0.0026	5	0	7	4	0	7
8691.1284 (56)	8691.1436	-0.0152	6	2	4	5	2	3
8691.4718 (37)	8691.5003	-0.0285	6	2	9	5	2	8
8694.6895 (17)	8694.6985	-0.0090	6	3	5	5	3	4
8695.5869 (44)	8695.5571	0.0298	6	0	8	5	0	7
8695.9925 (82)	8695.9628	0.0297	6	1	9	5	1	8
8697.083 (60) <sup>a</sup>	8697.1205	-0.0375	6	1	8	5	1	7
8697.4810 (23)	8697.4428	0.0382	6	0	9	5	0	8

TABLE I. (Continued.)

Measured	Calculated	Difference	$J'$	$K'$	$F'$	$J$	$K$	$F$
8701.8678 (76)	8701.8686	-0.0008	6	2	8	5	2	7
8704.4171 (18)	8704.4039	0.0132	6	0	4	5	0	3
8705.6498 (30)	8705.6296	0.0202	6	0	6	5	0	5
8706.1985 (30)	8706.1874	0.0111	6	1	6	5	1	5
8707.7716 (37)	8707.7989	-0.0273	6	2	7	5	2	6
8707.8472 (39)	8707.8452	0.0020	6	2	6	5	2	5
8708.0951 (28)	8708.0829	0.0122	6	0	5	5	0	4
8709.9887 (47)	8709.9867	0.0020	6	3	8	5	3	7
8714.2868 (15)	8714.2796	0.0072	6	4	6	5	4	5
8717.0840 (55)	8717.1154	-0.0314	6	5	7	5	5	7
8717.4606 (37)	8717.4644	-0.0038	6	3	7	5	3	6
8718.9115 (09)	8718.9077	0.0038	6	5	6	5	5	5
8719.8402 (56)	8719.8742	-0.0340	6	2	7	5	2	7
8720.9076 (20)	8720.9265	-0.0189	6	1	7	5	1	7
8721.8128 (39)	8721.7963	0.0165	6	4	8	5	4	7
8730.8974 (26)	8730.8841	0.0133	6	4	7	5	4	6
8737.7985 (32)	8737.7831	0.0154	6	5	8	5	5	7
8747.9438 (37)	8747.9342	0.0096	6	5	7	5	5	6

<sup>a</sup>These transitions were split by instrumental effects(see text), the frequency used in the fit is the average and the uncertainty represents the splitting in kHz.

at each microwave stimulating frequency. This reduced the amount of time necessary for measurement of the lines but also made it more difficult to determine the relative line strengths. Generally, components closer to the stimulating frequency show stronger intensity in the Fourier transform spectra. The presence of many lines in each transform sometimes made intensity assignments ambiguous. The intensities followed the pattern predicted for quadrupole splitting within  $J$  rotational levels. The  $J=5 \leftarrow 4$  transitions had the best signal to noise ratio and hence many of the lines measured were in this region of the spectrum. The relative intensities in the power spectrum fell in the range from 5-165 (arbitrary units) (1-30 S/N), 1-3 orders of magnitude smaller than measured lines<sup>7</sup> for another rhenium compound,  $\text{CH}_3\text{ReO}_3$ , which had intensities near 2000 (arbitrary units) (400 S/N). This was not unexpected since  $\text{CpRe}(\text{CO})_3$  has smaller rotational constants, requiring the measurement of higher  $J$  transitions in the 4-16 GHz range of the spectrometer. The pulsed beam system tends to populate the lowermost rotational levels and transitions for these levels were not measured. Quadrupole hyperfine structure becomes more complex and compressed in microwave spectra as the  $J$  values increase and more  $K$  states are available. Furthermore, the dipole moment of  $\text{CpRe}(\text{CO})_3$  is expected to be smaller than that of  $\text{CH}_3\text{ReO}_3$  because the charge is more effectively balanced by the CO and Cp groups as opposed to electron withdrawing oxo groups and an electron donating methyl group.

The measured transitions conform well to a prolate symmetric top rigid rotor model with quadrupole coupling parameters and centrifugal distortion constants. The data were fit with a nonlinear least squares fitting routine, using the programs written by Pickett.<sup>8</sup> The values obtained from this fit are listed in Table III. The standard deviations for the fits were 22 and 23 kHz. Since there were problems with overlapping lines, rather conservative,  $4\sigma$  error limits are given for the molecular constants. The deviation of the two  $D_{JK}$

values is larger than indicated errors, and this could be due to correlation with the much larger quadrupole coupling constants. The quadrupole moment ratio (Table IV) for the two rhenium isotopes are in agreement out to 5 significant figures with the other values and we believe the rotational constants and quadrupole constants (Table III) are accurate and precise to seven and five significant figures, respectively.

It is very likely that the  $\text{CpRe}(\text{CO})_3$  molecule undergoes hindered internal rotation. The results of low frequency IR and Raman studies<sup>3</sup> have indicated the presence of a torsional frequency and the calculated barrier height to internal rotation was  $10 \text{ kJ mol}^{-1}$ . However, the effects of this internal motion would not be generally observable in the microwave spectrum of a symmetric top molecule. Isotopic substitution of any atom other than the Re atom would render the molecule an asymmetric top and thus allow determination of whether or not the internal rotation is seen on the microwave time scale. Spectra for the  $^{13}\text{C}$  isotopomers were searched for in natural abundance [2.2 and 3.6% for  $\text{Cp}^{187}\text{Re}^{13}\text{CO}(\text{CO})_2$  and  $^{13}\text{CC}_4\text{H}_5^{187}\text{Re}(\text{CO})_3$ , respectively] but were not observed. The low observed S/N ratio of the parent compounds indicates that signals associated with the  $^{13}\text{C}$  substituted species are most likely below the detection limits of the instrument. Further structural analysis and treatment of internal rotation of this compound will have to be done with an isotopically enriched sample.

#### IV. CONCLUSIONS

The rotational constant measured for the main isotopomer,  $B(^{187}\text{Re}) = 724.9794(2)$ , agrees well with the value calculated from the crystal structure data<sup>1</sup>  $(B+C)/2(^{187}\text{Re}) = 741.153$ . However, the solid state structure was found to deviate from symmetric top symmetry ( $\kappa = -0.97$ ) through distortion of the Cp ring. IR and Raman spectroscopic analyses of the solid phase also indicate reduction of the local  $C_{5v}$

TABLE II. Measured and calculated transition frequencies (MHz) for  $\text{Cp}^{185}\text{Re}(\text{CO})_3$ .

Measured	Calculated	Difference	<i>J</i>	<i>K</i>	<i>F</i>	<i>J</i>	<i>K</i>	<i>F</i>
5772.1620 (12)	5772.1701	-0.0081	4	1	4	3	1	4
5776.854 (15) <sup>a</sup>	5776.8511	0.0031	4	2	7	3	2	6
5780.5221 (34)	5780.5312	-0.0091	4	2	3	3	2	2
5781.8838 (31)	5781.9022	-0.0184	4	2	3	3	2	3
5790.579 (25) <sup>a</sup>	5790.5775	0.0015	4	1	7	3	1	6
5791.1408 (28)	5791.1222	0.0186	4	0	6	3	0	5
5795.1164 (33)	5795.0843	0.0321	4	0	7	3	0	6
5798.1856 (37)	5798.1836	0.0020	4	3	4	3	3	3
5798.4194 (15)	5798.3980	0.0214	4	1	6	3	1	5
5804.3272 (27)	5804.3055	0.0217	4	0	5	3	0	4
5809.3950 (33)	5809.3977	-0.0027	4	2	4	3	2	3
5810.5434 (14)	5810.5277	0.0157	4	1	5	3	1	4
5813.6521 (26)	5813.6457	0.0064	4	1	3	3	1	2
5817.050 (16) <sup>a</sup>	5817.0510	-0.0010	4	1	4	3	1	3
5819.7875 (14)	5819.7698	0.0177	4	0	4	3	0	3
5821.2371 (06)	5821.2491	-0.0120	4	2	6	3	2	5
5824.9553 (21)	5824.9690	-0.0137	4	2	6	3	2	6
5825.0966 (41)	5825.0802	0.0164	4	0	3	3	0	2
5825.8144 (06)	5825.8253	-0.0109	4	2	5	3	2	5
5828.6427 (06)	5828.6359	0.0068	4	2	5	3	2	4
7198.1964 (31)	7198.2063	-0.0099	5	3	3	4	3	2
7204.7263 (10)	7204.7104	0.0159	5	4	8	4	4	7
7223.3388 (28)	7223.3314	0.0074	5	3	8	4	3	7
7230.1674 (25)	7230.1745	-0.0071	5	3	4	4	3	3
7230.8568 (43)	7230.8780	-0.0212	5	2	3	4	2	2
7236.3196 (09)	7236.3021	0.0175	5	2	8	4	2	7
7243.6853 (39)	7243.7621	-0.0768	5	0	7	4	0	6
7243.946 (40) <sup>a</sup>	7243.9576	-0.0116	5	1	8	4	1	7
7246.5182 (66)	7246.4888	0.0294	5	0	8	4	0	7
7246.9767 (77)	7246.9589	0.0178	5	1	7	4	1	6
7248.4769 (63)	7248.4843	-0.0074	5	2	4	4	2	3
7250.8037 (30)	7250.8435	-0.0398	5	1	3	4	1	2
7251.0950 (18)	7251.1260	-0.0310	5	0	6	4	0	5
7254.6167 (06)	7254.6012	0.0155	5	1	6	4	1	5
7256.7810 (36)	7256.7724	0.0086	5	2	7	4	2	6
7257.5697 (22)	7257.5598	0.0099	5	0	3	4	0	2
7259.7901 (23)	7259.8472	-0.0571	5	1	4	4	1	3
7260.1180 (76)	7260.0997	0.0183	5	0	5	4	0	4
7260.4076 (31)	7260.3273	0.0803	5	1	5	4	1	4
7261.0050 (38)	7261.0067	-0.0017	5	2	5	4	2	4
7262.1314 (07)	7262.1303	0.0011	5	3	5	4	3	4
7263.7083 (25)	7263.7003	0.0080	5	0	4	4	0	3
7264.9460 (12)	7264.9435	0.0025	5	2	6	4	2	5
7267.0095 (08)	7267.0210	-0.0115	5	1	6	4	1	6
7269.4980 (28)	7269.5197	-0.0217	5	2	6	4	2	6
7273.9158 (17)	7273.9051	0.0107	5	3	7	4	3	6
7274.8784 (25)	7274.9112	-0.0328	5	3	6	4	3	6
7278.1059 (04)	7278.1293	-0.0234	5	3	5	4	3	5
7281.9006 (05)	7281.8928	0.0078	5	3	6	4	3	5
7285.1853 (08)	7285.1934	-0.0081	5	4	6	4	4	6
7299.6721 (10)	7299.6465	0.0256	5	4	7	4	4	6
7304.8740 (33)	7304.8903	-0.0163	5	2	7	4	2	7
7305.0082 (34)	7305.0240	-0.0158	5	4	4	4	4	4
7326.5581 (30)	7326.5654	-0.0073	5	4	5	4	4	5
7345.3042 (13)	7345.3076	-0.0034	5	1	7	4	1	7
8690.6212 (18)	8690.6381	-0.0169	6	2	4	5	2	3
8691.0072 (34)	8691.0402	-0.0330	6	2	9	5	2	8
8694.3839 (35)	8694.3971	-0.0132	6	3	5	5	3	4
8695.3387 (99)	8695.3213	0.0174	6	0	8	5	0	7
8695.7763 (50)	8695.7509	0.0254	6	1	9	5	1	8
8696.165 (49) <sup>a</sup>	8696.1734	-0.0084	6	4	4	5	4	4
8696.9741 (36)	8696.9669	0.0072	6	1	8	5	1	7
8697.3571 (65)	8697.3135	0.0436	6	0	9	5	0	8
8700.0441 (08)	8700.0266	0.0175	6	0	7	5	0	6
8701.0834 (47)	8701.1430	-0.0596	6	1	4	5	1	3
8701.9810 (82)	8701.9700	0.0110	6	2	8	5	2	7
8704.6749 (57)	8704.6656	0.0093	6	0	4	5	0	3

TABLE II. (Continued.)

Measured	Calculated	Difference	<i>J</i>	<i>K</i>	<i>F</i>	<i>J</i>	<i>K</i>	<i>F</i>
8705.9698 (72)	8705.9525	0.0173	6	0	6	5	0	5
8706.9641 (40)	8706.9506	0.0135	6	1	5	5	1	4
8708.2233 (88)	8708.2517	-0.0284	6	2	7	5	2	6
8708.2989 (38)	8708.3009	-0.0020	6	2	6	5	2	5
8708.5574 (59)	8708.5502	0.0072	6	0	5	5	0	4
8710.5511 (56)	8710.5356	0.0155	6	3	8	5	3	7
8711.1687 (07)	8711.1795	-0.0108	6	3	6	5	3	5
8715.1135 (33)	8715.1076	0.0059	6	4	6	5	4	5
8718.4629 (55)	8718.4698	-0.0069	6	3	7	5	3	6
8722.1343 (30)	8722.1491	-0.0148	6	1	7	5	1	7
8722.5727 (23)	8722.5712	0.0015	6	0	7	5	0	7
8723.0404 (15)	8723.0234	0.0170	6	4	8	5	4	7
8732.6649 (36)	8732.6503	0.0146	6	4	7	5	4	6
8739.9957 (31)	8739.9781	0.0176	6	5	8	5	5	7

<sup>a</sup>These transitions were split by instrumental effects (see text), the frequency used in the fit is the average and the uncertainty represents the splitting in kHz.

symmetry of the Cp group. Furthermore, a photoelectron study in the gas phase indicated splitting of the “ $e_1$ ” orbital by 0.43 eV, which may result from reduction of cylindrical symmetry on the rhenium atom. This data suggest a possible, slightly asymmetric conformation for the CpRe(CO)<sub>3</sub> molecule. The ability to assign and fit 165 microwave transitions to a symmetric top, rigid rotor with quadrupole coupling indicates this molecule is quite symmetric in the gas phase. The high barrier height from the IR experiments (10 kJ mol<sup>-1</sup>) would produce splittings too small to observe for the ground torsional states, but if the Cp group were distorted, we would have expected to see an asymmetric top microwave spectrum. Hindered rotor effects might still be observable in the PES experiments since higher energy states would also be observed.

Rhenium quadrupole coupling in gas phase molecules has been studied for only a few molecules. These molecules are HRe(CO)<sub>5</sub>,<sup>9</sup> CH<sub>3</sub>ReO<sub>3</sub>,<sup>7</sup> and CpRe(CO)<sub>3</sub>. Each of these molecules has an axially symmetric electric field gradient tensor, and each presents a different ligand environment surrounding the Re atom. The molecules are listed in decreasing order of anisotropy in the electric field gradient. The values of this electric field gradient ( $eq$ ) coupled with the nuclear quadrupole moments  $Q(^{187}\text{Re})$  and  $Q(^{185}\text{Re})$  are useful for comparisons with similar structures, since the electric field gradients arise from electronic distributions about the quadrupolar nucleus. The present  $eQq$  values for CpRe(CO)<sub>3</sub> are about 5% larger than corresponding solid-state values ob-

tained using nuclear quadrupole resonance<sup>10</sup> (nqr) spectroscopy. A detailed study of the electric field gradient tensors in Mn and Re compounds was performed using nqr spectroscopy<sup>10</sup> and a large number of nqr results have been reviewed recently by Brill.<sup>11</sup> The values determined in microwave studies are consistently larger (in magnitude) than those reported in the solid state nqr studies, but are in reasonable qualitative agreement for both magnitude and sign of the quadrupole coupling constants. A summary of the  $eQq$  values measured using microwave spectroscopy in the gas phase are given in Table IV. The  $eQq$  values for CH<sub>3</sub>ReO<sub>3</sub> and CpRe(CO)<sub>3</sub> only differ by 15%, but there is a change in sign for HRe(CO)<sub>5</sub>. This large and dramatic difference in the electric field gradient for the hydride can be related to the electron withdrawing (or donating) properties of the ligands and to the relative occupation of the rhenium atom  $d$ -orbitals. For direct comparison of electronic donation between compounds it will be useful to study isostructural molecules such as Re(CO)<sub>5</sub>X, X=H, F, Cl, Br, I or CpReL<sub>3</sub>, L=O, CO. Quadrupole coupling parameters are also very sensitive to local structural changes and therefore may be very helpful for study of complexes in which the Re center has coordinated another molecule such as CH<sub>3</sub>ReO<sub>3</sub>M, M=NH<sub>3</sub>, H<sub>2</sub>O or N(CH<sub>3</sub>)<sub>3</sub>.

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TABLE III. Calculated spectral parameters for CpRe(CO)<sub>3</sub> obtained by fitting the measured transitions listed in Tables I and II. Listed uncertainties are  $4\sigma$  based on 1 kHz uncertainties in each line position,  $\sigma_{\text{fit}}$  is the overall standard deviation of the least squares fit.

Parameter	Cp <sup>187</sup> Re(CO) <sub>3</sub>	Cp <sup>185</sup> Re(CO) <sub>3</sub>
<i>B</i> (MHz)	724.9794(2)	724.9795(2)
<i>D<sub>J</sub></i> (kHz)	0.016(4)	0.021(4)
<i>D<sub>JK</sub></i> (kHz)	-0.096(6)	-0.060(8)
<i>eQq</i> (MHz)	614.464(12)	649.273(14)
$\sigma_{\text{fit}}$ (kHz)	22	23

TABLE IV. Quadrupole coupling parameters for several gas phase rhenium compounds measured using microwave spectroscopy. Quadrupole coupling parameters are listed in MHz. The average value of the nuclear quadrupole moment ratio is 1.05668(3).

Compound	$eQq(^{187}\text{Re})$	$eQq(^{185}\text{Re})$	$Q(^{185}\text{Re})/Q(^{187}\text{Re})$
HRe(CO) <sub>5</sub>	900.13(3)	951.15(2)	1.05668(5)
CH <sub>3</sub> ReO <sub>3</sub>	716.546(17)	757.187(25)	1.05672(6)
CpRe(CO) <sub>3</sub>	614.464(12)	649.273(14)	1.05665(4)

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