

at  $1430\text{ cm}^{-1}$ ). RR bands between  $700$  and  $800\text{ cm}^{-1}$  and some weaker bands near  $500\text{ cm}^{-1}$  in "blue" copper proteins could originate from carbonyl bending modes,  $\delta(\text{C}=\text{O})$ , and the shoulder at  $\sim 260\text{ cm}^{-1}$ , from a Cu-N (imidazole) vibration (by comparison with A and B, Figure 2) or a Cu-S(cys) vibration.<sup>17</sup> Other weak bands near  $450$  and  $330\text{ cm}^{-1}$ , yet to be assigned, may arise from bending modes,  $\delta(\text{CNC})$  or  $\delta(\text{CCN})$ .

The number of coordinating ligands in "blue" copper is unknown; however, the presence of low energy electronic absorption ( $800\text{--}900\text{ nm}$ ) suggests a five-coordinate<sup>18</sup> or flattened tetrahedral<sup>19</sup> geometry. Core structures of the type  $\text{CuN}_3\text{S}$ ,  $\text{CuN}_4\text{S}$  or  $\text{CuN}_2\text{OS}$ , and  $\text{CuN}_3\text{OS}$  where N (amide), S (cysteine), and O (carbonyl) are ligands appear to be the most favored. The presence of a sulfur atom provides a logical mechanism for the intensification (analogous to the intensity enhancement of the spin-forbidden  ${}^6\text{A}_1 \rightarrow {}^4\text{T}_1$ , band<sup>20</sup> of  $\text{Fe}^{\text{III}}\text{S}_4$  in rubredoxin and spinach ferredoxin) of the "blue" copper ligand field bands.

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(21) Issued as N.R.C.C. Publication No. 14187.

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Received April 4, 1974

## Synthesis and Infrared Spectroscopic Detection of Rhenium Pentacarbonyl

Sir:

The  $\text{Re}(\text{CO})_5$  radical was first detected by Junk and Svec<sup>1</sup> in a mass spectroscopic study of  $\text{Re}_2(\text{CO})_{10}$  vapor. These data yielded useful information concerning the Re-Re and Re-C bond dissociation energies. More recently, Wrighton and Bredesen<sup>2</sup> have investigated the photoreaction of  $\text{Re}_2(\text{CO})_{10}$  with  $\text{CCl}_4$  and have provided evidence for an efficient homolytic fission mechanism and a  $\text{Re}(\text{CO})_5$  radical intermediate. In this context it is noteworthy that a variety of stable, paramagnetic phosphine substituted carbonyls<sup>3-6</sup> have been prepared from photochemical and thermal reactions of  $\text{Re}_2(\text{CO})_{10}$  with substituted phosphines, examples being *trans*- $\text{Re}(\text{CO})_3(\text{P}(\text{C}_6\text{H}_5)_3)_2$  and *cis*- $\text{Re}(\text{CO})_3(\text{MeP}(\text{C}_6\text{H}_5)_2)_2$ . However, vibrational, uv-visible and ESR spectroscopic data have not previously been reported

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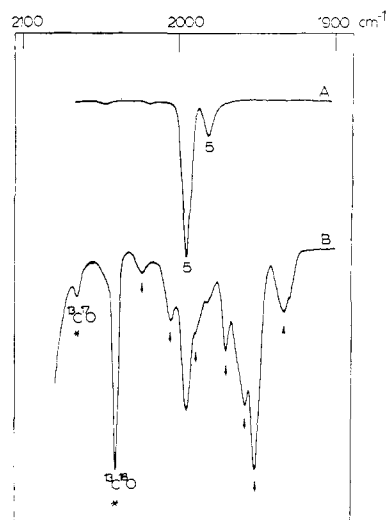


Figure 1. Matrix infrared spectrum of the products of the cocondensation reaction of Re atoms with (A)  ${}^{12}\text{C}^{16}\text{O}/\text{Ar} \cong 1/10$  and (B)  ${}^{12}\text{C}^{16}\text{O}/{}^{13}\text{C}^{16}\text{O}/\text{Ar} \cong 1/1/20$  at  $10^\circ\text{K}$ .

for  $\text{Re}(\text{CO})_5$ , all of which are capable of yielding pertinent information concerning the nature of the bonding and the molecular and electronic structure of the radical.

Our previous experiences with metal atom synthetic techniques<sup>7</sup> have led us to believe that cocondensation reactions in reactive matrices favor the product with highest stoichiometry, examples being  $\text{Pt}(\text{CO})_4$ ,<sup>8</sup>  $\text{Ni}(\text{N}_2)_4$ ,<sup>9</sup> and  $\text{Pd}(\text{O}_2)_2$ ,<sup>10</sup> suggesting that a direct preparative route to  $\text{Re}(\text{CO})_5$  could be through the Re atom CO matrix reaction. In this communication we report preliminary matrix infrared spectroscopic data which show that this is indeed the case. Using the matrix infrared set-up and furnace arrangement described previously,<sup>11</sup> Re atoms were cocondensed with pure  ${}^{12}\text{C}^{16}\text{O}$  at  $15^\circ\text{K}$ . With a  $\text{CO}:\text{Ar} \cong 1:10$  matrix and a  $20^\circ\text{K}$  deposition, it was found that sufficient matrix diffusion of CO occurred to yield a spectrum essentially the same as that observed in pure CO. The infrared spectra of the product (Figure 1A) shows two major lines at  $1995$  (s) and  $1977$  (w)  $\text{cm}^{-1}$  with absorption intensities approximately 4:1, respectively. These lines retained the same relative intensities during matrix depositions and warm-up experiments indicating that they belong to a single species. The spectrum obtained is quite distinct from that of matrix isolated  $\text{Re}_2(\text{CO})_{10}$  in Ar which is shown in Table I for the purposes of comparison.

The general pattern of CO stretching modes compared to  $\text{Mn}(\text{CO})_5$ <sup>12</sup> and  $\text{Cr}(\text{CO})_5$ <sup>13</sup> and the general shift to lower frequencies compared to  $\text{Re}_2(\text{CO})_{10}$  strongly suggest that the product of the Re-CO reaction is  $\text{Re}(\text{CO})_5$  with a square pyramidal molecular struc-

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**Table I.** Matrix Infrared Spectra of  $\text{Re}_2(\text{CO})_{10}$  and  $\text{Re}(\text{CO})_5$  in Solid Argon

Re/CO/Ar reaction (10°K)	Matrix isolated $\text{Re}_2(\text{CO})_{10}$ in Ar (10°K)
1995 s	2070 w
1977 w	2018 vs 1976 mw

ture. The observed 4:1 relative intensity pattern is consistent with a square pyramidal pentacarbonyl, rather than a trigonal bipyramidal pentacarbonyl, as the latter would be expected to display a 2:3 intensity pattern.<sup>14</sup> The  $A_1$  equatorial CO stretching mode was too weak to observe, which is to be expected for a square pyramidal pentacarbonyl with a  $C_{\text{ap}}\text{-Re-C}_{\text{equ}}$  angle close to  $90^\circ$ .<sup>13,14</sup>

The experiments were repeated using  $^{12}\text{C}^{16}\text{O}/^{13}\text{C}^{16}\text{O} \approx 1/1$  and  $^{12}\text{C}^{16}\text{O}/^{13}\text{C}^{16}\text{O}/\text{Ar} \approx 1/1/20$  isotopic mixtures, a typical infrared spectrum being shown in Figure 1B.

The pattern of observed isotope lines is characteristic of a pentacarbonyl containing a unique CO ligand (apical) and a group of four equivalent (equatorial) CO ligands coordinated to a rhenium atom. The apical ( $A_1$ )  $^{12}\text{C}^{16}\text{O}$  absorption originally at  $1977\text{ cm}^{-1}$  produces a *single*  $^{13}\text{C}^{16}\text{O}$  counterpart line at  $1933\text{ cm}^{-1}$  while the equatorial (E)  $^{12}\text{C}^{16}\text{O}$  absorption originally at  $1995.5\text{ cm}^{-1}$  produces *six* new isotope lines, *four* in the  $^{13}\text{C}^{16}\text{O}$  stretching region  $1951.0$ ,  $1957.5$ ,  $1969.5$ , and  $1988.0\text{ cm}^{-1}$  and *two* observable lines in the  $^{12}\text{C}^{16}\text{O}$  stretching region at  $2005.0$  and  $2024.0\text{ cm}^{-1}$  (the commercially available  $^{12}\text{C}^{16}\text{O}/^{13}\text{C}^{16}\text{O}$  mixtures contain some  $^{13}\text{C}^{17}\text{O}$  ( $2064.8\text{ cm}^{-1}$ ) and  $^{13}\text{C}^{18}\text{O}$  ( $2040.2\text{ cm}^{-1}$ ), marked with an asterisk in Figure 1B, which could obscure one of the isotope lines in the  $^{12}\text{C}^{16}\text{O}$  stretching region). This is the pattern of lines qualitatively predicted for square pyramidal  $\text{Re}(^{12}\text{C}^{16}\text{O})_n(^{13}\text{C}^{16}\text{O})_{5-n}$  (where  $n = 0-5$ ).

**Acknowledgments.** We wish to thank the Research Corporation and the National Research Council of Canada for financial support.

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### Circularly Polarized Raman Scattering. A Direct Approach to the Determination of Vibrational Symmetries

Sir:

The Raman scattering of circularly polarized laser radiation has been the subject of a number of recent reports.<sup>1</sup> These studies have concentrated on optically active molecules in order to obtain information on mo-

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lecular dissymmetry from differential scattering of left and right circularly polarized radiation. In this communication we demonstrate that Raman vibrations stimulated by circularly polarized laser radiation radiate circularly polarized light. This phenomenon is general and not restricted to optically active molecules. The sign and magnitude of circular polarization may be used in assigning the symmetries of Raman-active vibrations.

This study continues a current program to investigate the interaction of polarized radiation with molecular systems which has emphasized the importance of circularly polarized light in studies of resonant and non-resonant emission processes.<sup>2-4</sup> This is particularly the case for molecules under the influence of an external magnetic field. However, the unique selection rules of circularly polarized radiation also lead to new information in zero-field experiments.<sup>2</sup>

The results presented here were obtained using apparatus similar to that described recently.<sup>5</sup> Argon laser radiation is circularly polarized by a quarter wave plate and the stimulated radiation analyzed by means of a photoelastic modulator.<sup>6</sup> The circular intensity difference ( $I_+ - I_-$ ) is displayed as a function of frequency and we define a circular polarization ratio as  $(I_+ - I_-)/(I_+ + I_-)$ . This definition differs from the reversal coefficients given by Chiu for example<sup>7</sup> but is consistent with polarization ratios defined in related experiments.<sup>2</sup> Raman active vibrations are termed polarized or depolarized according to the ratio of linear polarization of the scattered radiation in directions perpendicular to the propagation vector. The measurement of depolarization ratios consists of rotating a polarizer placed before the monochromator and recording the light level for two mutually perpendicular orientations. Unless precautions are taken to depolarize the light before it enters the monochromator, spurious effects may dominate. This problem is avoided in the experiments described herein since the orientation of the final polarizer is fixed. The main advantage of our method, however, is that modulation techniques increase the sensitivity of polarization measurements by at least two orders of magnitude, and thus our polarization ratios are high in sensitivity and precision.

The spectra shown in Figures 1-4 are of a number of simple molecules in the liquid state and they illustrate clearly the power of the technique. The upper trace shows the Raman spectrum excited by circularly polarized light recorded with no polarization analysis of the scattered radiation; *i.e.*, it records  $(I_+ + I_-)$ . The lower curve is the circular polarization, and the polarization of the input radiation is shown on each figure. The most striking feature of the spectrum is that the circular polarization curves have *sign* as well as magnitude. In  $\text{CCl}_4$  for example one band has the same sign polarization as the incident laser radiation while the others have opposite sign. This phenomenon involves the electric dipole-electric dipole or even parity Raman

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