

Gold carbonyl challenge problem

In a paper published in 1990 in the journal *Inorganic Chemistry*, Willner and Aubke prepared several Gold(I) carbonyl complexes in superacidic conditions. Gold powder is treated with a mixture of HSO_3F (13 equiv.) and $\text{S}_2\text{O}_6\text{F}_2$ (3.3 equiv) until all the gold oxidizes and dissolves, forming an orange solution. The excess $\text{S}_2\text{O}_6\text{F}_2$ is removed and gaseous CO (3.3 equiv). is added. The CO reacts rapidly, causing the solution to turn yellow and then colorless. All volatile compounds (CO , CO_2 , $\text{S}_2\text{O}_5\text{F}_2$ and HSO_3F) are removed under vacuum and the product is sublimed to give a white solid identified as gold carbonyl fluorosulfate, $\text{Au}(\text{CO})(\text{SO}_3\text{F})$. The reaction is complicated, but the peroxydisulfuryl difluoride in superacid oxidizes the gold to Au(III), and the gold is reduced to Au(I) with excess CO (forming CO_2 and $\text{S}_2\text{O}_5\text{F}_2$). The authors repeated the experiment with ^{13}CO as well to verify their assignment of the CO stretching frequencies in the IR.

The reported ^{12}CO stretching frequencies for $\text{Au}(\text{CO})(\text{SO}_3\text{F})$ and the related $\text{Au}(\text{CO})\text{Cl}$ are 2195 and 2163 cm^{-1} respectively. The IR stretching frequency for free CO is 2143 cm^{-1} . The metal complex CO stretching frequencies are *higher* than that of free CO. The Dewar-Chatt-Duncanson model of bonding predicts a high degree of π -backbonding from the metal to the CO ligand, resulting in a *decrease* in CO stretching frequency. Because of this strange result, the authors took care to also prepare and analyze the ^{13}C labeled complex.

Isotopic labeling is used in IR spectroscopy regularly to help identify bands, especially when they are weak or in the fingerprint region. CO stretches are isolated and strong so this substitution really wasn't necessary in the 1990 paper, however, since they are proposing a strange result, the CO stretch in the gold complex is *higher* than that of free CO, the labeling was used to confirm the assignments.

If we assume that the force constants are the same for ^{12}CO and ^{13}CO stretches (a reasonable assumption), it is relatively straightforward to calculate the expected stretch for the labeled complex using the following formula, where ν is the stretching frequency, k is the force constant, and μ is the reduced mass for two masses (m_1 and m_2) on a spring.

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \qquad \mu = \frac{m_1 m_2}{m_1 + m_2}$$

- 1) Calculate the reduced mass for ^{12}CO and ^{13}CO
- 2) Using the ^{12}CO stretching frequency, predict the ^{13}CO stretching frequency.
- 3) The reported value is 2145 cm^{-1} . Does your prediction match experiment?
- 4) Challenge problem: why is the gold complex ν_{CO} greater than that of the free CO ν_{CO} ? This answer will require (at least) a carefully constructed MO diagram for CO.