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Matrix Isolation and Computer Simulation Spectra of $Cr(CO)_6$ and $Mo(CO)_6$

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The low-frequency infrared spectra of $Cr(CO)_6$ and $Mo(CO)_6$ have been obtained in argon, nitrogen, and oxygen matrices. The ν_7 bands of $Cr(CO)_6$ and $Mo(CO)_6$ at about 670 and 600 cm^{-1}, respectively, both show metal isotopic structure in nitrogen matrix experiments. This isotopic structure has been reproduced by a computer simulation. The new isotopic frequencies allow a more complete force field calculation for the F_{1u} symmetry species. This calculation has been performed for $Cr(CO)_6$ and is in good agreement with earlier results.

Introduction

Many papers have appeared in the last 20 years on the infrared spectra of $Cr(CO)_6$ and $Mo(CO)_6$. In one of the first, Hawkins et al.[1] observed metal carbonyl gas infrared bands using a hot cell to increase the vapor pressure of these compounds. Subsequently, Danti and Cotton[2] reported the Raman spectra of chromium, molybdenum, and tungsten carbonyls in $CHCl_3$ solution. Kawai and Murata[3] calculated a very simple Urey–Bradley force field for $Cr(CO)_6$ and $Mo(CO)_6$ which was in fair agreement with the observed spectra. Jones et al.[4-10] have carried out a rather complete survey of the $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ species. In their most recent paper, they prepared ^{13}C and ^{18}O derivatives of these carbonyls and calculated complete sets of symmetry and valence force constants. Turner et al.[11,12] have recently studied the matrix isolation infrared spectrum of $Cr(CO)_6$ in the CO stretching region and the ultraviolet photolysis behavior of this compound.

Experimental Section

$Cr(CO)_6$ and $Mo(CO)_6$ highly diluted in argon, nitrogen, or oxygen were slowly deposited for infrared spectral investigation onto a cesium iodide window held at 15 K. The respective gas samples were prepared by adding approximately 300 mm of the diluent gases to the room-temperature vapor pressure of the carbonyls in a glass bulb using standard vacuum-line techniques.

After 6 hr of sample deposition, spectra were recorded on a Beckman IR-12 infrared spectrophotometer using a 10 cm^{-1}/in. chart expansion and a 3.2 cm^{-1}/min scan speed. Spectra were calibrated using the vibration–rotation bands of standard molecules.

Results

Since the matrix isolation spectrum of the CO stretching region of $Cr(CO)_6$ has been previously reported,[11,12] no further discussion of this region is necessary except to mention that the present results are in complete agreement with the earlier results.

The room-temperature vapor pressure of solid $Cr(CO)_6$ is approximately 150 μ;[13] this produces a matrix to $Cr(CO)_6$ ratio of approximately 2000:1. The frequencies of the ν_7 bands of $Cr(CO)_6$ in the various matrices are listed in Table I along with the assignments and the percentage natural abundances of the chromium isotopes. The nitrogen matrix spectra of ν_7 and ν_8 are shown in Figure 1B. Four bands were observed in the 670-cm^{-1} (ν_7) region which closely correspond to the expected chromium isotopic pattern, and the isotopic shift was measured to be 2.5 cm^{-1}/amu. Using these data and a 1.2-cm^{-1} half-bandwidth, the computer-simulated spectrum shown in Figure 1B (bottom) was reproduced. The ν_8 band at about 450 cm^{-1} also appeared to have some structure; a shoulder band was observed at 451.6 cm^{-1} in addition to the main peak at 447.4 cm^{-1} (^{52}Cr). If we assume that the former is due to the ^{50}Cr species, the isotope separation of ν_8 is about 2.1 cm^{-1}/amu. An attempted computer simulation using this separation and 2.0-cm^{-1} half-bandwidth produces the spectrum shown in the bottom of Figure 1B; the computed spectrum for the ν_8 band does not match the observed spectrum. Therefore, the observed fine structure was not attributed to metal isotopes.

Table I. Observed Frequencies (cm^{-1}) and Assignments of the ν_7 Band of $Cr(CO)_6$ in Various Matrices

Freq			Isotope	% natural abundance
Ar matrix	O_2 matrix	N_2 matrix		
675.6	677.0	676.5	^{50}Cr	4.31
678.1			$^{50}Cr^a$	
670.5	672.0	671.4	^{52}Cr	83.76
672.5	673.9		$^{52}Cr^a$	
668.5	670.0	669.5	^{53}Cr	9.55
			$^{53}Cr^a$	
665.7	667.2	666.4	^{54}Cr	2.38
668.5			$^{54}Cr^a$	

[a] As discussed in the text, two matrix sites were detected in Ar and O_2 matrices.

Figure 1A shows the argon matrix spectrum of the ν_7 band of $Cr(CO)_6$ at about 670 cm^{-1}. As the spectrum shows, there are at least six bands clearly resolved in this spectral region, and it can most easily be understood as being due to the four isotopic chromium species in two slightly different matrix sites. Using the assumptions that (1) the chromium isotopic shift is 2.5 cm^{-1}/amu, (2) the matrix shift for the second site is +2 cm^{-1}, (3) the half-bandwidth of all the bands is 1.2 cm^{-1}, and (4) the relative population of the molecules in the two sites is 2:1, a computer-simulated spectrum shown in the bottom of Figure 1A was obtained. The agreement is excellent.

Two distinct sites were also observed in the oxygen matrix. In this case, only five bands were observed, and a ratio of about 5:1 could be inferred for the relative populations of molecules in these sites. Only the ^{52}Cr isotopic species in the less populated matrix site was intense enough to be observed in our experiment.

The isotope frequencies of the ν_7 bands of $Mo(CO)_6$ are listed in Table II along with the natural abundances of molybdenum isotopes. The two top traces of Figure 2 show

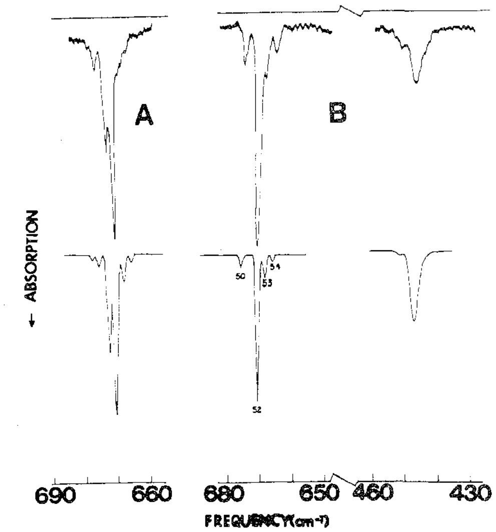

Figure 1. Infrared spectrum of $Cr(CO)_6$: (A) in an Ar matrix; (B) in an N_2 matrix. In each case, the bottom curve shows the computer-simulated spectrum.

Table II. Observed Frequencies and Assignments of the ν_7 Band of $Mo(CO)_6$ in an Ar Matrix

Freq, cm^{-1}	Isotope	% natural abundance	Freq, cm^{-1}	Isotope	% natural abundance
601.3	^{92}Mo	15.84		^{97}Mo	9.46
	^{94}Mo	9.04	597.9	^{98}Mo	23.78
599.0[a]	^{95}Mo	15.72		^{100}Mo	9.63
599.0[a]	^{96}Mo	16.53			

[a] These two peaks appear as an unresolved single band.

the ν_7 and ν_8 bands observed in a nitrogen matrix. The molybdenum isotopic pattern of the ν_7 band (near 600 cm^{-1}) is not immediately obvious. However, a computer simulation spectrum using a measured isotope shift of 0.6 cm^{-1}/amu (see Table II), 1.0-cm^{-1} half-bandwidth, and the natural abundance of the molybdenum isotopes nicely reproduces the observed nitrogen matrix spectrum and is shown in Figure 2 (middle). Decreasing the half-bandwidth further to 0.4 cm^{-1} enables the computer-simulated spectrum to resolve all seven molybdenum isotope peaks. This simulation is shown for the 600-cm^{-1} band, again using a 0.6-cm^{-1} isotopic shift/amu, at the bottom of Figure 2. The ν_8 band shown in Figure 2 is essentially structureless. A computer simulation using a 2.0-cm^{-1} half-bandwidth and 0.3-cm^{-1} isotopic shift reproduces fairly well the observed spectrum, but the significance of this simulation is doubtful since no individual isotope peaks were observed.

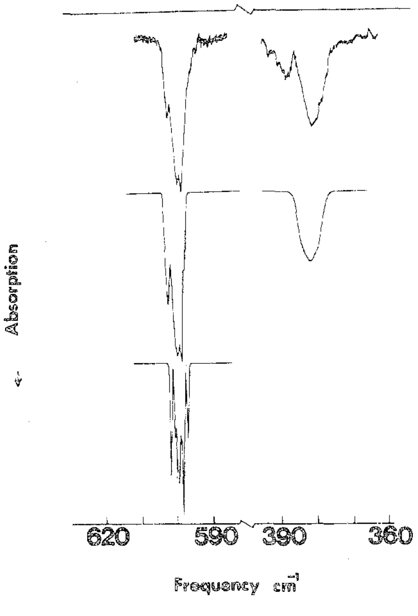

Figure 2. Infrared spectrum of $Mo(CO)_6$ in an Ar matrix (top curve). The middle and bottom curves show computer-simulated spectra as explained in the text.

Discussion

Resolution of the metal isotopic structure in the ν_7 infrared bands of $Cr(CO)_6$ and $Mo(CO)_6$ is only possible because of the extreme sharpness of the bands in a nitrogen matrix and the lack of rotational coupling; it is significant because it sheds new light upon the characteristics of these vibrations. The ν_7 mode has generally been considered as a bending mode with ν_8 being ascribed to the metal–carbon stretching mode.[3,8] Jones et al.,[10] following their calculations using fully substituted ^{13}C and ^{18}O isotopic molecules, concluded that ν_7 contains a significant amount of metal–carbon stretching motion. The present results confirm this conclusion since we have observed metal isotope structure of this band.

Normal-Coordinate Calculations. Normal-coordinate calculations have been performed for the F_{1u} symmetry block of $Cr(CO)_6$ using the new metal isotopic frequencies of the ν_7 mode along with the previously reported ^{13}C and ^{18}O isotopic data[10]. The new force field is similar to the one reported earlier for gaseous $Cr(CO)_6$.[10] Table III lists the eight symmetry force constants used in the present calculation and the calculated and observed frequencies for the ^{50}Cr, ^{52}Cr, ^{13}C, and ^{18}O isotopic species. The F_{68} and F_{69} symmetry force constants were set to zero because they are very nearly indeterminate. Our calculations show that the F_{68} constant has its largest influence on ν_8 which changes only 0.4 cm^{-1}/0.1

Table III. F_{1u} Symmetry Force Constants and Comparison of Observed and Calculated Frequencies (cm^{-1}) for Four Isotopic $Cr(CO)_6$ Molecules

Symmetry Force Constants[a,b]

$F_{66}(D) = 17.22, F_{77}(R) = 1.61, F_{88}(\beta) = 0.80, F_{99}(\alpha) = 0.538, F_{67}(D,R) = 0.78, F_{68}(D,\beta) = 0, F_{69}(D,\alpha) = 0, F_{78}(R,\beta) = -0.14, F_{79}(R,\alpha) = -0.35, F_{89}(\alpha,\beta) = -0.10$

Comparison of Observed and Calculated Frequencies

	$^{50}Cr(CO)_6$		$^{52}Cr(CO)_6$		$^{52}Cr(^{13}CO)$[c]		$^{52}Cr(C^{18}O)$[c]	
	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd
ν_6	2043.7[d]	2043.3	2043.7[d]	2043.3	1997.5[d]	1997.6	1994.7[d]	1994.5
ν_7	676.4	676.4	671.4	671.7	657.5	657.6	669.2[c]	667.7
ν_8		449.1	447.4	446.6	440.4[c]	439.5	436.8[c]	438.2
ν_9		97.5	97.2[d]	97.3		96.6	93.6[d]	93.2

[a] Precise definitions of these force constants are given in ref 10. Notations in the parentheses indicate the force constants involved: *D*, CO stretching; *R*, MC stretching; β, MCO bending; α, CMC bending; *D,R* etc., interaction terms. [b] These values are close to those given in ref 10 as the "best estimates" for gaseous $Cr(CO)_6$. Units are mdyn/Å for F_{66}, F_{77}, and F_{67}; mdyn/radian for F_{68}, F_{69}, F_{78}, and F_{89}; mdyn Å/radial^2 for F_{88}, F_{99}, and F_{89}. [c] These frequencies were obtained by assuming that $\Delta\nu = \nu(N_2 \text{ matrix}) - \nu(\text{gaseous phase})$ (ref 10) is the same for all isotopic molecules. [a] These frequencies were taken from ref 10 (gaseous phase).

Table IV. Potential Energy Distribution for the F_{1u} Vibrations of $Cr(CO)_6$[a,b]

Sym coord	ν_6	ν_7	ν_8	ν_9
$V_{66}(D)$	*1.02*	0.00	0.00	0.00
$V_{77}(R)$	0.03	*0.14*	*0.66*	*0.41*
$V_{88}(\beta)$	0.00	*0.57*	*0.22*	*0.27*
$V_{99}(\alpha)$	0.00	*0.15*	0.00	*1.07*
$V_{67}(D,R)$	−0.05	0.00	0.00	−0.01
$V_{68}(D,\beta)$	0.00	0.00	0.00	0.00
$V_{69}(D,\alpha)$	0.00	0.00	0.00	0.00
$V_{78}(R,\beta)$	0.00	−0.07	0.09	−0.08
$V_{79}(R,\alpha)$	0.00	*0.11*	0.01	*−0.50*
$V_{89}(\alpha,\beta)$	0.00	0.09	0.00	*−0.16*

[a] Precise definitions of symmetry coordinates are given in ref 10. Notations in parentheses indicate the nature of internal coordinates involved (D, R, β, and α are defined in Table III). [b] Only those which contribute more than 0.10 are italic.

mdyn per radian change. Similarly, 0.1 mdyn per radian change in F_{69} has its largest influence on ν_7 which changes only by 0.2 cm^{-1}. Obviously, even large changes in these two force constants will have little effect on the calculated frequencies. This result is expected because high-frequency CO stretching modes interact very little with low-frequency bending modes.

Previously, Jones et al.[10] constrained the value of F_{79} to −0.3 by taking the linear relationship between F_{79} and ζ_9 (Coriolis coupling constant) into consideration. In our calculations, we have used a value of −0.35 for F_{79}. As is shown in Table III, this set of force constants gives a ^{50}Cr to ^{52}Cr isotopic shift of 4.7 cm^{-1} for ν_7 as compared with the observed value of 5.1 cm^{-1}. Our calculations indicate that the Cr isotope shift increases as the value of F_{79} becomes more negative. In their preliminary calculations, Jones et al. obtained the F_{79} values of −0.67 and −0.88 for the solution and gaseous-phase spectra, respectively. If these values are used in the set of force constants given in Table III, the calculated Cr isotope shift becomes 6.0 and 6.7 cm^{-1}, respectively. These results demonstrate that the metal isotope shift data are useful in fixing the value of this particular force constant.

The new force field reproduces 13 frequencies with an average error of 0.5 cm^{-1} using eight force constants. It predicts a shift of 1.2 cm^{-1}/amu for ν_8. This result further confirms the previous conclusion that the observed fine structure of ν_8 in a nitrogen matrix is not due to chromium isotopes. The fact that the isotope shift per atomic mass unit is larger in ν_7 than in ν_8 suggests that the metal atom is moving more in ν_7 than in ν_8. This does not necessarily mean, however, that ν_7 has more metal–carbon stretching character than ν_8. According to the potential energy distribution shown in Table IV, the metal–carbon stretching, metal–carbon–oxygen bending, and carbon–metal–carbon bending modes are strongly coupled in ν_7, ν_8, and ν_9, and ν_8 has the largest contribution from the stretching coordinate among the three bands.

Computer-Simulated Spectra. The computer-simulated spectra shown in the lower traces of Figures 1 and 2 were drawn as the sum of gaussian-shaped bands vs. frequency. Input into this program was the position of each band, its relative intensity, and its half-bandwidth. With these very simple variables, it was possible to obtain excellent reproductions of the experimentally observed spectra as shown in the figures.

As shown previously, this program was particularly useful in assigning the spectrum of the modybdenum isotopes. To a good approximation, the observed ν_7 band of $Mo(CO)_6$ is a 1:2:2 triplet. The highest frequency band is due to the ^{92}Mo isotopic species. The middle band, which is broader, is essentially due to the overlap of ^{95}Mo and ^{96}Mo isotopic peaks. The ^{98}Mo species which is the most abundant gives the lowest frequency band. The other three isotopic species, ^{94}Mo, ^{97}Mo, and ^{100}Mo, are in less than 10% natural abundance and were not resolved.

The relative populations of $Cr(CO)_6$ in the two matrix sites can also be determined using this computer program. This ratio is about 2:1 in the argon matrix example shown in Figure 1 in favor of the lower frequency site. The nitrogen matrix reproduction of the chromium isotopic pattern for ν_7 is very simple since all the isotopic peaks were clearly resolved. An attempt to fit the ν_8 band shape by computer simulation is also shown in Figure 1. This fit is doubtful since a band with unexplained intensity appears on the high-frequency side of the main peak.

Previously, we have reported the metal isotope splitting pattern of the nickel–carbon stretching band of $Ni(CO)_4$ at ca. 430 cm^{-1} in an argon matrix.[14] This spectrum can also be reproduced by computer simulation.

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Registry No. $Cr(CO)_6$, 13007-92-6; $Mo(CO)_6$, 13939-06-5.

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