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Photochemistry of Matrix-Isolated $HMn(CO)_5$: Evidence for Two Isomers of $HMn(CO)_4$

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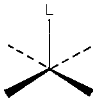
UV photolysis of $HMn(CO)_5$, isolated in Ar or CH_4 matrices at 20 K, produces $HMn(CO)_4$ and CO. A combination of ^{13}CO enrichment and IR spectroscopy is used to show that $HMn(CO)_4$ has a C_s structure (**3**). There is a substantial shift (2500 cm^{-1}) in the UV/visible absorption maximum between CH_4 and Ar matrices, probably due to a significant $HMn(CO)_4...CH_4$ interaction. Narrow-band photolysis (367 nm in CH_4 matrices, 403 nm in Ar) results in the formation of small amounts of a second isomer of $HMn(CO)_4$, most probably with C_{4v} structure (**2**). Prolonged irradiation of $HMn(CO)_5$ in an Ar matrix, with a pulsed ArF excimer laser (193 nm), yields a significant amount of $Mn(CO)_5$, but the quantum yield for H loss is much lower than that for CO loss from $HMn(CO)_5$.

Introduction

Matrix isolation has proved itself to be an extremely useful technique for determining the structures of coordinatively unsaturated transition-metal carbonyl species.[1] Studies on pentacoordinate d^6 systems have been particularly successful. For the group 6B metals, (Cr, Mo, and W) the pentacarbonyl fragment, $M(CO)_5$, has been shown[2] to have a C_{4v} square-pyramidal structure (**1**) and the substituted species, $M(CO)_4L$ (L = amine,[3] pyridine,[4] phosphine,[5] or CS[6]), adopt C_{4v} and C_s structures (**2** and **3**) based on the same square pyramid. The elucidation of these structures has had an important influence on the theoretical rationalization of molecular shapes[7] and has been crucial in the interpretation of flash photolysis experiments both in solution[8,9] and in the gas phase.[10]

1 C_{4v}

2 C_{4v}



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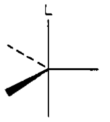
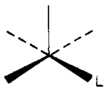
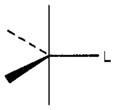


3 C_s



5 C_{2v}



Unexpectedly, the experiments revealed a significant interaction between $M(CO)_5$ and the matrix itself.[11] The principal evidence for the interaction is a substantial shift in the visible absorption band of $M(CO)_5$ from one matrix to another (e.g., $Ne\cdots Cr(CO)_5$ λ_{max} 624 nm, $Ar\cdots Cr(CO)_5$ λ_{max} 532 nm, and $CH_4\cdots Cr(CO)_5$ λ_{max} 494 nm). This shift arises from an interaction of a matrix atom or molecule with the vacant coordination site of the pseudooctahedral $M(CO)_5$ fragment, a shift toward shorter wavelength indicating a stronger interaction.[11,12] We will show in this paper that $HMn(CO)_4$, also a d^6 system, has a visible absorption, which displays even larger shifts between matrices, presumably because of similar interactions with a vacant coordination site.

Photolysis of $HMn(CO)_5$ is interesting for several reasons. First, there is the problem of whether H or CO is lost on photolysis. In the isoelectronic d^6 compound $H_2Fe(CO)_4$, loss of H_2 predominates in a matrix,[13] while in the d^9 monohydride, $HCo(CO)_4$, loss of CO is much faster[14] than loss of H. Second, what is the structure of $HMn(CO)_4$? Is it based on the C_{4v} pyramidal structure of the group 6B $M(CO)_4L$ species (**2** or **3**) or is it derived from a trigonal structure (**4** or **5**)? In other $HM(CO)_x$ species, the H atom seems to be almost inactive stereochemically. $HMn(CO)_5$ has bond angles[15] similar to those deduced[16] for matrix-isolated $Mn(CO)_5$ while the $Fe(CO)_4$ moiety in $H_2Fe(CO)_4$ has almost the same structure[15] as matrix-isolated[17] $Fe(CO)_4$.

$HMn(CO)_5$ was in fact one of the first transition-metal carbonyls to be studied in rare-gas matrices. Rest and Turner showed[18] that, in an Ar matrix, the primary photochemical step was loss of CO. The $HMn(CO)_4$ fragment had three C–O stretching bands in the IR spectrum and was presumed to have the C_{3v} structure **4**. Irradiation of $HMn(CO)_4$ with light, $\lambda > 285$ nm, regenerated $HMn(CO)_5$:

$$HMn(CO)_5 \underset{\lambda > 285\text{ nm}}{\overset{229\text{ nm}}{\rightleftarrows}} HMn(CO)_4 + CO$$

At that time, this type of photochemical addition reaction was unprecedented, but it now appears to occur in the matrix photochemistry of most metal carbonyls and has been explained in detail for the particular case of $M(CO)_6$ and $M(CO)_5CS$ species.[1,6,12] Rest and co-workers have since studied the matrix photochemistry of the related $XMn(CO)_5$ species (X = CH_3, Cl, Br, and I). Their early suggestion[19] that $CH_3Mn(CO)_4$ had a C_{3v} structure (**4**) was revised on the basis of ^{13}CO isotope enrichment to the C_{2v} trigonal structure[20] **5**.

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(1) Burdett, J. K. *Coord. Chem. Rev.* **1978**, *27*, 1–58. Turner, J. J. "Matrix Isolation Spectroscopy"; Barnes, A. J., Orville-Thomas, W. J., Müller, A., Gaufres, R., Eds.; Reidel: Boston, 1981; Chapter 21, p 495.

(2) Perutz, R. N.; Turner, J. J. *Inorg. Chem.* **1975**, *14*, 262.

(3) Boxhoorn, G.; Stufkens, D. J.; Oskam, A. *J. Chem. Soc., Dalton Trans.* **1980**, 1328.

(4) Boxhoorn, G.; Oskam, A.; McHugh, T. M.; Rest, A. J. *Inorg. Chim. Acta* **1980**, *44*, L1.

(5) Black, J. D.; Braterman, P. S. *J. Organomet. Chem.* **1973**, *63*, C19.

(6) Poliakoff, M. *Inorg. Chem.* **1976**, *15*, 2022, 2892.

(7) Burdett, J. K. "Molecular Shapes"; Wiley: New York, 1980. Elian, M.; Hoffman, R. *Inorg. Chem.* **1975**, *14*, 1058.

(8) Bonneau, R.; Kelly, J. M. *J. Am. Chem. Soc.* **1980**, *102*, 1220.

(9) Welch, J. A.; Peters, K. S.; Vaida, V. *J. Phys. Chem.* **1982**, *86*, 1941.

(10) Breckenridge, W. H.; Sinal, N. *J. Phys. Chem.* **1981**, *85*, 3557.

(11) Perutz, R. N.; Turner, J. J. *J. Am. Chem. Soc.* **1975**, *97*, 4791.

(12) Burdett, J. K.; Grzybowski, J. M.; Perutz, R. N.; Poliakoff, M.; Turner, J. J.; Turner, R. F. *Inorg. Chem.* **1978**, *17*, 147.

(13) Sweany, R. L. *J. Am. Chem. Soc.* **1981**, *103*, 2410.

(14) Sweany, R. L. *Inorg. Chem.* **1982**, *21*, 752.

(15) McNeill, E. A.; Scholer, F. R. *J. Am. Chem. Soc.* **1977**, *99*, 6243.

(16) Church, S. P.; Poliakoff, M.; Timney, J. A.; Turner, J. J. *J. Am. Chem. Soc.* **1981**, *103*, 7515.

(17) Poliakoff, M. *Chem. Soc. Rev.* **1978**, *7*, 527.

(18) Rest, A. J.; Turner, J. J. *J. Chem. Soc., Chem. Commun.* **1969**, 375.

(19) Rest, A. J. *J. Organomet. Chem.* **1970**, *25*, C30.

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Table I. Wavenumbers (cm^{-1}) of Bands Observed on UV Photolysis of Matrix-Isolated HMn(CO)$_5$

Ar matrix		CH$_4$ matrix	
ref 18[a]	this work[b]	this work[b,c]	assignt[d]
2094	2093.2	2089.9	ν_{C-O} a′
	2003.4	1998.8	ν_{C-O} a′ + a″
2001	2001.3	1997.6	
	2000.4	1995.1	
	1998.9	1993.0	
1970	1968.7	1964.9	ν_{C-O} a′
	1742[e]		ν_{Mn-H} a′

[a] Dilution HMn(CO)$_5$:Ar = 1:180; the bands were much broader and less resolved than in this work. [b] Dilution HMn(CO)$_5$:Ar = 1:4000. [c] See Figures 3b. [d] Based on C_s structure (3); see text. [e] See Figure 1b.

The same conclusion was reached[21] for ClMn(CO)$_4$. The IR spectra of CH$_3$Mn(CO)$_4$ and HMn(CO)$_4$ are similar, and it was suggested[20] that HMn(CO)$_4$ also has structure **5**.

We have already reported that UV photolysis of HMn(CO)$_5$ in pure CO matrices leads to square-pyramidal Mn(CO)$_5$ (**1**) and the HCO radical.[16] In this paper we show that, while the original IR observations[18] in Ar matrices were correct, the structures proposed[18,20] for HMn(CO)$_4$ were wrong. In both Ar and CH$_4$ matrices, the primary photolysis product of HMn(CO)$_5$ is HMn(CO)$_4$ with the C_s structure **3**, a conclusion supported by full ^{13}CO enrichment. In a CH$_4$ matrix, irradiation of this C_s isomer with light λ = 367 nm, leads to formation of a small amount of a second product, probably the C_{4v} isomer of HMn(CO)$_4$, **2**. Similar results are found for HRe(CO)$_4$. Finally we show that prolonged UV irradiation of HMn(CO)$_5$ in an Ar matrix using a pulsed ArF excimer laser eventually leads to the formation of Mn(CO)$_5$ and possibly Mn(CO)$_4$.

Experimental Section

The low-temperature apparatus, Air Products Displex CS-202A closed-cycle cooler, has been described elsewhere.[22] All matrices were prepared by pulsed deposition.[23] IR spectra were recorded on Perkin-Elmer Model 580A and 283B spectrophotometers or Nicolet 7199A or MX3600E Fourier transform interferometers. Interferometric spectra were recorded with 0.5-cm^{-1} (three degrees of zero filling) and 0.06-cm^{-1} resolution (one degree of zero-filling). UV/visible spectra were recorded with a Perkin-Elmer Model 356 spectrometer.

A Philips HPK125W medium-pressure Hg arc was used for photolysis, with Balzer's interference filters when appropriate. The ArF excimer laser photolysis was carried out with the Lambda Physik Model EMG 101 laser, in the laboratory of Dr. I. W. M. Smith (in the Department of Physical Chemistry, University of Cambridge) with our portable matrix isolation apparatus.[24] This portable apparatus was also used for preliminary FTIR experiments in Professor I. M. Mills' laboratory at the University of Reading.[24]

HMn(CO)$_5$ and HReCO)$_5$ were prepared by standard methods.[25] HRe(CO)$_5$ was enriched with ^{13}CO (BOC Prochem) by UV photolysis of HRe(CO)$_5$ in isopentane solution under 600 torr pressure gaseous ^{13}CO at room temperature. The method did not work reliably with HMn(CO)$_5$, which almost invariably photodecomposed to Mn$_2$(CO)$_{10}$. Finally, HMn(CO)$_5$ was enriched by a thermal reaction in the gas phase, with use of a CW CO$_2$ laser and SF$_6$ absorber for heating. This IR pyrolysis,[26] to be described more fully elsewhere,[27] allows the gas to be heated while the walls of the reactor remain essentially cold. The reaction conditions were HMn(CO)$_5$ (3 torr), ^{13}CO (130–150 torr), SF$_6$ (10 torr), CO$_2$ laser 10.6 μm (P22) line, power 1.0 W CW.

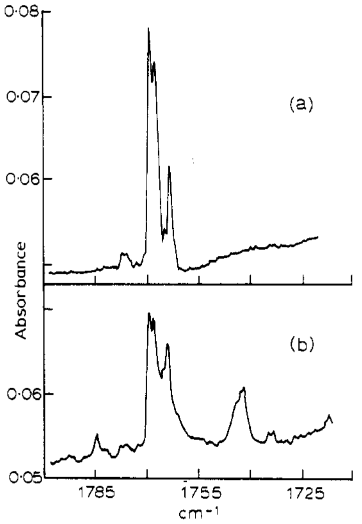

Figure 1. Mn–H stretching region of the IR spectrum of HMn(CO)$_5$ in an Ar matrix (dilution 1:2000) at 20 K: (a) after deposition; (b) after 5-min UV photolysis. Spectra were recorded on the MX3600E interferometer at 0.7-cm^{-1} resolution. Thorough purging of the interferometer with nitrogen was necessary to observe the weak absorptions.

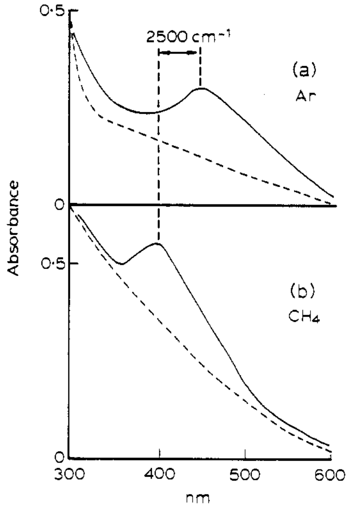

Figure 2. UV/visible absorption spectra of (a) Ar and (b) CH$_4$ matrices containing HMn(CO)$_5$ (dilution 1:2000): (---) spectrum after deposition; (—) spectrum after 2-min UV photolysis. Note the 2500-cm^{-1} (45-nm) shift between the absorption maxima of HMn(CO)$_4$ in the two matrices.

Matrix gases, Ar and CH$_4$, were BOC grade X or Messer Griesheim high-purity gases.

All force constant calculations were performed on an Apple II computer using simple iterative refinement programs.[2,28] IR spectra were simulated with the Nicolet 1280E computer and a program that constructed Lorentzian band shapes with use of intensity data derived from the Apple programs.

Results

UV Photolysis in Ar and CH$_4$ Matrices. In our experiments UV photolysis of HMn(CO)$_5$ in Ar matrices produced free CO and a carbonyl-containing product with three C–O stretching bands in the IR spectrum (see Table I), just as

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(20) McHugh, T. M.; Rest, A. J. *J. Chem. Soc., Dalton Trans.* **1980**, 2323.
(21) McHugh, T. M.; Rest, A. J.; Taylor, D. J. *J. Chem. Soc., Dalton Trans.* **1980**, 1803.
(22) Church, S. P. Ph.D. Thesis, University of Nottingham, 1982.
(23) Perutz, R. N.; Turner, J. J. *J. Chem. Soc., Faraday Trans. 2* **1973**, *69*, 452.
(24) Church, S. P.; Poliakoff, M.; Timney, J. A.; Turner, J. J. *J. Mol. Struct.* **1982**, *80*, 159.
(25) Eisch, J. J.; King, R. B. "Organometallic Syntheses"; Academic Press: New York, 1965; Vol. 1, p 158.
(26) Ryott, G. J. Ph.D. Thesis, University of Nottingham, 1982.
(27) Bristow, N. J.; Moore, B. D.; Poliakoff, M.; Ryott, G. J.; Turner, J. J., submitted for publication in *J. Organomet. Chem.*
(28) Perutz, R. N. Ph.D. Thesis, University of Cambridge, 1974.

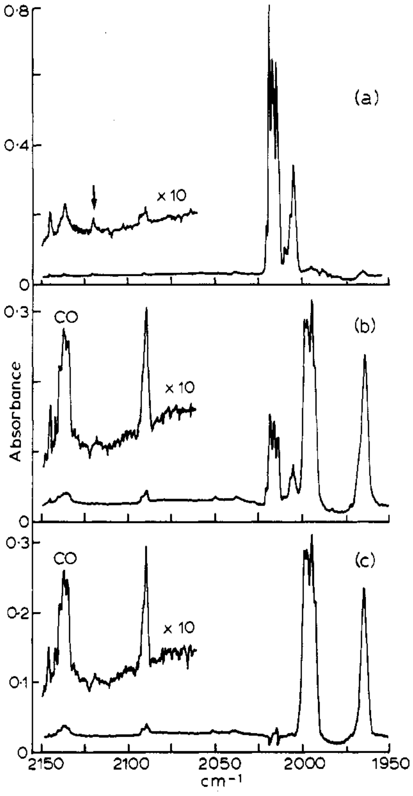


Figure 3. IR spectra illustrating UV photolysis of $HMn(CO)_5$ in a CH_4 matrix (dilution 1:4000) at 20 K: (a) spectrum of regenerated[35] $HMn(CO)_5$ (peak marked by an arrow is the very weak high-frequency a_1 mode of $HMn(CO)_5$); (b) spectrum after 2-min UV photolysis (note the expanded ordinate scale relative to spectrum a); (c) scaled computer subtraction—spectrum b *minus* 0.18 times spectrum a—to eliminate the residual absorptions of $HMn(CO)_5$ from spectrum b.

reported by Rest and Turner.[18] However, their evidence that the photolysis product contained hydrogen was circumstantial because of the extreme weakness of the ν_{Mn-H} absorptions. We have now succeeded in obtaining good IR spectra in the Mn–H stretching region (Figure 1), despite the weakness of the bands and the strong absorptions of atmospheric water vapor at these frequencies. It is clear that the photolysis product *does* have an ν_{Mn-H} absorption.

Rest and Turner's observation[18] of reversible photolysis of $HMn(CO)_5$ implies that $HMn(CO)_4$ has one or more UV/visible absorptions at $\lambda > 285$nm. This deduction can now be quantified by the UV/visible spectra (Figure 2a), where the product clearly has an absorption maximum at 445 nm. Irradiation with light $\lambda > 375$ nm, corresponding to this absorption, regenerates $HMn(CO)_5$. Thus, the photolysis of $HMn(CO)_5$ in Ar can be summarized

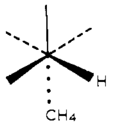
$$HMn(CO)_5 \underset{\lambda > 375\ \text{nm}}{\overset{\text{UV}}{\rightleftharpoons}} HMn(CO)_x + CO$$
$$(\lambda_{max} = 445\ \text{nm})$$

Photolysis of $HMn(CO)_5$ in a CH_4 matrix is similar to that in Ar but with an important difference. The visible absorption, λ_{max} 400 nm, of the product is substantially shifted to the blue (cf. Figure 2) while the IR spectra (Figure 3 and Table I) are almost the same. In both Ar and CH_4 matrices the three groups of ν_{C-O} bands and the visible absorption appear to belong to a single $HMn(CO)_x$ product although there is some change in the splittings of the ν_{C-O} bands as photolysis proceeds, particularly ~1995 cm^{-1} in a CH_4 matrix. These splittings are similar to those observed in other metal carbonyl fragments, e.g. $Fe(CO)_4$[17] or $Cr(CO)_5$.[2,28] Nevertheless, they caused considerable confusion in the early stages of our experiments but we are now confident that they arise at least in part from a weak interaction between the $HMn(CO)_x$ fragment and the photoejected CO group. Apart from these detailed splittings, the IR spectra are so similar that even at this stage the structure of the $HMn(CO)_x$ species appears to be the same in Ar and CH_4 matrices.

Since $HMn(CO)_x$ has three ν_{C-O} bands, it must be $HMn(CO)_4$ or $HMn(CO)_3$. For all of the metal carbonyls, $M(CO)_x$, that have so far been studied by matrix isolation, the primary photolysis product formed by CO loss has been an $M(CO)_{x-1}$ fragment.[1] Thus, the product in this case is almost certainly $HMn(CO)_4$, but what is the structure? The C_{4v} structure (**2**) (ν_{C-O} a_1 + e IR active) can clearly be eliminated. However, the IR spectrum (Figure 3c) is consistent not only with a C_{3v} structure (**4**) (ν_{C-O} $2a_1$ + e) but also with the C_s (**3**) (ν_{C-O} 3a′ + a″) or C_{2v} structure (**5**) (ν_{C-O} $2a_1 + b_1 + b_2$), because the absorption at ~1995 cm^{-1} is broader than the other two bands and could represent two overlapping fundamental bands (cf. matrix-isolated[29] $Mn(CO)_4NO$).

Braterman and co-workers have shown that there is a weak coupling between the ν_{Mn-H} (a_1) and ν_{C-O} (a_1) vibrations of $HMn(CO)_5$ with the result that there is a small, ~1 cm^{-1}, shift in the frequencies of the two a_1, ν_{C-O} absorptions when the hydrogen is substituted by deuterium.[30] The e symmetry ν_{C-O} absorption however is unshifted. When a mixture of $HMn(CO)_5$ and $DMn(CO)_5$ is photolyzed in an Ar matrix, both the lower frequency ν_{C-O} bands of the product are broadened. Thus, the ν_{C-O} vibrations giving rise to both of these absorptions must be coupled to the ν_{Mn-H} vibration of $HMn(CO)_4$. Such coupling is incompatible with a C_{3v} structure (**4**), which requires these bands to be assigned to ν_{C-O} a_1 and e. The ν_{Mn-H} vibration, necessarily a_1, could only couple with the a_1 ν_{C-O}. The C_{3v} structure would be expected anyway to have an E electronic ground state and to be Jahn–Teller unstable. We must therefore choose between C_s and C_{2v} structures, **3** and **5**.

Any proposed structure for $HMn(CO)_4$ not only has to be consistent with the IR spectra but also must explain the blue shift in the visible absorption between Ar and CH_4 matrices (Figure 2). This shift, 2500 cm^{-1}, is 50% larger than the corresponding shift, 1700 cm^{-1}, observed[11] for matrix-isolated $Cr(CO)_5$, where it was attributed to the interaction of CH_4 with the vacant coordination site of the square-pyramidal $M(CO)_5$ (**1**). The C_s structure of $HMn(CO)_4$ clearly has a vacant coordination site which could interact with CH_4 in a similar way (**6**) to produce the observed shift. On the other hand, there is no obvious site for such an interaction in the C_{2v} structure (**5**). The visible spectra, therefore, are more easily explained on the basis of the C_s structure. We now use ^{13}CO enrichment to confirm this structure.



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Photolysis of ^{13}CO-Enriched $HMn(CO)_5$. The use of ^{13}CO for determining the structures of matrix-isolated metal carbonyls has been extensively reviewed[1,33] but the photolysis of ^{13}CO-enriched $HMn(CO)_5$ reveals an interesting limitation to the method, which is discussed below. As explained in the Experimental Section, the ^{13}CO enrichment of $HMn(CO)_5$ is not easy, but once the IR spectrum of $HMn(^{12}CO)_{5-x}$-

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(29) Rest, A. J.; Taylor, D. J. *J. Chem. Soc., Chem. Commun.* **1977**, 717.
(30) Braterman, P. S.; Harril, R. W.; Kaesz, H. D. *J. Am. Chem. Soc.* **1967**, *89*, 2851.
(31) Ibers, J. A.; Hamilton, W. C.; La Placa, S. J.; Davison, A. *Inorg. Chem.* **1969**, *8*, 1928.
(32) Braterman, P. S.; Bau, R.; Kaesz, H. D. *Inorg. Chem.* **1967**, *6*, 2097.
(33) Burdett, J. K.; Dubost, H.; Poliakoff, M.; Turner, J. J. *Adv. Infrared Raman Spectrosc.* **1976**, *2*, 1–52.

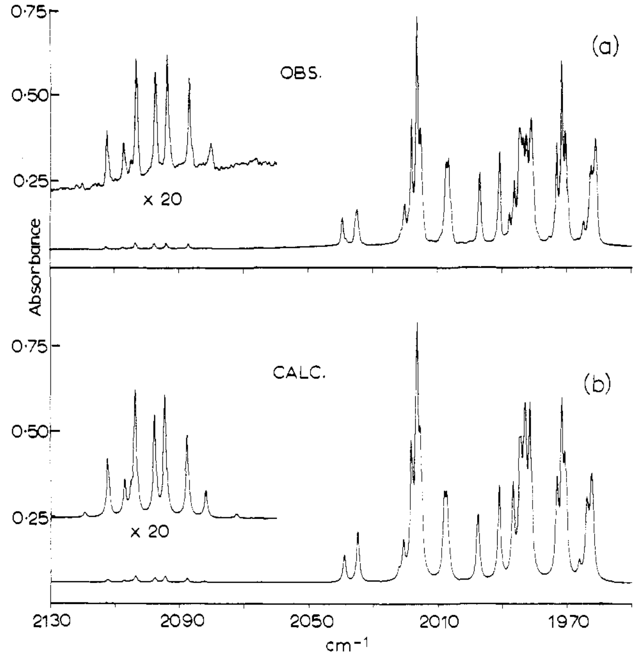

Figure 4. (a) Observed IR spectrum of $HMn(CO)_5$ with 49% ^{13}CO enrichment, isolated in a CH_4 matrix (1:4000) at 20 K. (b) Spectrum calculated[34] by using a bond angle of 97.4° and the force constants given in Table II and a Lorentzian band shape, 2-cm^{-1} fwhm. Note the excellent agreement between the observed and calculated spectra, without including coupling between Mn–H and C–O stretching vibrations.

$(^{13}CO)_x$ species has been obtained, it can be accurately fitted with a C–O factored force field, completely ignoring the coupling with the Mn–H vibration (Table II). The agreement between the observed and calculated spectra in Figure 4 is particularly striking,[34] and therefore it seems reasonable to ignore ν_{C-O}/ν_{Mn-H} coupling in our analysis of the spectrum of $HMn(^{12}CO)_{4-x}(^{13}CO)_x$. In order to calculate the relative intensities of the ν_{C-O} bands of $HMn(^{12}CO)_{5-x}(^{13}CO)_x$ species (Figure 4b), one needs to know the axial–equatorial bond angle of $HMn(CO)_5$ and the dipole derivative ratio, μ_{ax}/μ_{eq}. Fortunately, given accurate frequency-factored force constants, the relative intensities of the three IR-active modes of $HMn(^{12}CO)_5$ provide enough information to calculate both the angle and ratio. We observed relative integrated intensities (a_1(high):a_1(low): e = 1:60:225) which gave an angle of 97.4°, close to previous values (electron diffraction[15] 95°, X-ray diffraction[31] 97°, and solution IR spectra[32] 96°), and a dipole derivative ratio of 1.00 (solution IR[32] 1.04).

In Figure 3, we showed that, given the IR spectrum of a CH_4 matrix containing both $HMn(^{12}CO)_5$ and $HMn(^{12}CO)_4$, the bands due to $HMn(^{12}CO)_5$ could be removed completely by computer subtraction.[35] A similar computer subtraction

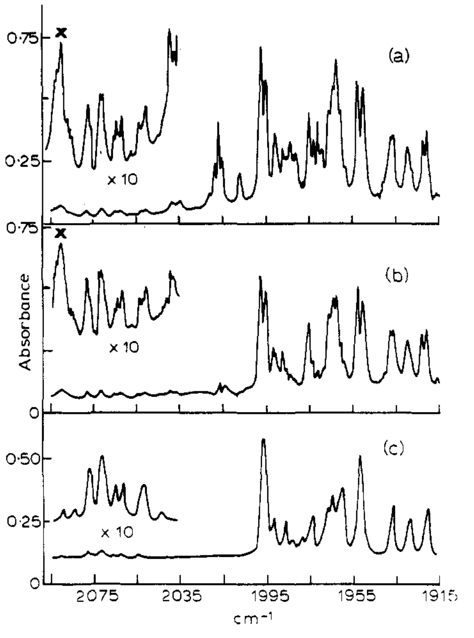

Figure 5. (a) IR spectrum obtained by UV photolysis of a CH_4 matrix containing ^{13}CO-enriched $HMn(CO)_5$ (see Figure 4a for the spectrum before photolysis). The band marked X is due to photoejected ^{13}CO. (b) Spectrum obtained after computer subtraction of peaks due to residual $HMn(CO)_5$ (cf. Figure 3b,c). (c) Spectrum calculated for C_s $HMn(CO)_4$ (3) by using the force field defined in Figure 6 and Lorentzian band shapes, 4-cm^{-1} fwhm. Again note the good agreement between observed and calculated spectra.

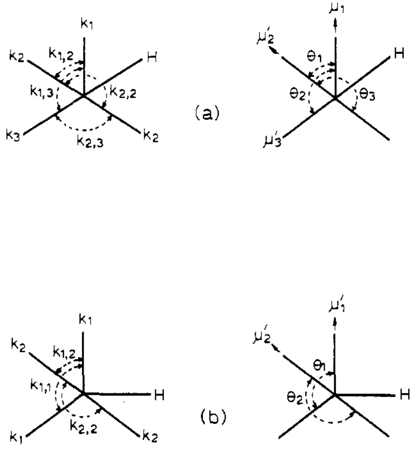

Figure 6. Force fields, bond angles, and dipole derivatives used for predicting the IR spectra of (a) C_s $HMn(CO)_4$ and (b) C_{2v} $HMn(CO)_4$.

can be used to obtain the spectrum of $HMn(^{12}CO)_{4-x}(^{13}CO)_x$ in the absence of $HMn(^{12}CO)_{5-x}(^{13}CO)_x$ (Figure 5b). This spectrum is consistent with a C_s structure (3), and using the force field defined in Figure 6a, we obtain good agreement between observed and calculated spectra (Figure 5c and Table III). The calculation of the band intensities requires three bond angles and two dipole derivative ratios (Figure 6a). Unfortunately, the spectrum of $HMn(^{12}CO)_4$ does not contain enough information to calculate all of these angles and ratios independently. We have arbitrarily set both dipole derivative ratios to unity and assumed that $\theta_1 = \theta_2$ to calculate the spectrum shown in Figure 5c, with the result that the bond angles used, $\theta_1 = \theta_2 = 98°$ and $\theta_3 = 167°$, do not represent a unique solution. The spectrum of $HMn(^{12}CO)_{4-x}(^{13}CO)_x$ in an Ar matrix could be fitted with a similar C_s force field (Table IV, available as supplementary material), supporting our contention that $HMn(CO)_4$ has the same structure in Ar and CH_4 matrices.

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(34) In the spectrum of $HMn(^{12}CO)_5$, the e mode is split into three well-defined components by site effects. These same three splittings appear in the observed spectrum of 49% ^{13}CO-enriched $HMn(CO)_5$. The e mode and related vibrations of $HMn(^{13}CO)_5$ is similarly split (see Figure 4). The origin of these splittings is uncertain, but since we are now aware of their presence, we can allow for them in the calculated spectrum by dividing the total intensity of the calculated e mode into three components of the appropriate relative intensities. As observed with other carbonyls,[33] the other bands of $HMn(^{12}CO)_{5-x}(^{13}CO)_x$ appear to be much less split.

(35) When a matrix-isolated metal carbonyl with splittings in its IR spectrum is photolyzed, one often finds that the relative intensities of these splittings change with progressive photolysis. Hence, the subtraction of parent carbonyl absorptions will not work very well. However, if the UV photolysis is reversed with visible light, it is often observed that the pattern of the matrix splittings of the parent carbonyl bands is unchanged by subsequent UV photolysis. Thus, it was necessary to photolyze and regenerate the $HMn(CO)_5$ before good quality subtraction spectra could be obtained.

Table II. Observed and Calculated Wavenumbers (cm^{-1}) of the IR Bands of Different $\mathrm{HMn(^{12}CO)_{5-x}(^{13}CO)_x}$ Species in a $\mathrm{CH_4}$ Matrix at 20 K (Figure 4)

molecule	mode	obsd	calcd^e
$\mathrm{HMn(^{12}CO)_5}$ (C_{4v})	a_1	2120.0	2119.5
	b_1	*b*	2045.2
	e	2016.6^d	2016.5
	a_1	2006.2	2006.7
$\mathrm{HMn(^{12}CO)_4(^{13}CO)_{ax}}$ (C_{4v})	a_1	*a*	2114.7
	b_1	*b*	2045.2
	e	2016.6^d	2016.5
	a_1	*c*	1966.4
$\mathrm{HMn(^{12}CO)_4(^{13}CO)}$ (C_s)	a'	2112.7	2112.3
	a'	2039.5	2039.2
	a''	2016.6^d	2016.5
	a'	2006.9	2007.5
	a'	1982.8^d	1983.2
$\mathrm{HMn(^{12}CO)_3(^{13}CO)_2}$ (C_s ax, eq)	a'	2107.5	2107.1
	a'	*c*	2039.0
	a''	2016.6^d	2016.5
	a'	1986.4	1986.9
	a'	1964.9	1964.2
$\mathrm{HMn(^{12}CO)_3(^{13}CO)_2}$ (C_s eq, eq (cis))	a'	2103.6	2103.7
	a''	2035.0	2034.9
	a'	2007.0	2008.3
	a'	*c*	1984.8
	a''	1981.2	1981.5
$\mathrm{HMn(^{12}CO)_3(^{13}CO)_2}$ (C_{2v} eq, eq (trans))	a_1	*a*	2105.1
	a_1	*c*	2022.2
	b_1	2016.6^d	2016.5
	a_1	*c*	1997.8
	b_1	1971.7^d	1971.6
$\mathrm{HMn(^{12}CO)_2(^{13}CO)_3}$ (C_s eq, eq, eq)	a'	2093.9	2094.5
a	a'	2020.3	2020.8
	a'	1997.2	1997.9
	a'	1983.7	1982.8
	a''	1971.7^d	1971.6
$\mathrm{HMn(^{12}CO)_2(^{13}CO)_3}$ (C_s ax, eq, eq (cis))	a'	2097.6	2097.7
	a''	2035.0	2034.9
	a'	1991.0	1991.2
	a''	1981.2	1981.5
	a'	1962.8	1962.8
$\mathrm{HMn(^{12}CO)_2(^{13}CO)_3}$ (C_{2v} ax, eq, eq (trans))	a_1	*a*	2099.4
	a_1	*c*	2016.9
	b_1	2016.6^d	2016.5
	b_1	1971.7^d	1971.6
	a_1	*c*	1963.7
$\mathrm{HMn(^{12}CO)(^{13}CO)_4}$ (C_{4v})	a_1	*a*	2081.9
	b_1	*b*	1999.6
	a_1	*c*	1997.4
	e	1971.7^d	1971.6
$\mathrm{HMn(^{12}CO)(^{13}CO)_4}$ (C_s)	a'	2087.1	2087.6
	a'	*c*	2016.9
	a'	1984.8	1984.2
	a''	1971.7^d	1971.6
	a'	*c*	1962.4
$\mathrm{HMn(^{13}CO)_5}$ (C_{4v})	a_1	*a*	2072.2
	b_1	*b*	1999.6
	e	1971.7^d	1971.6
	a_1	*c*	1962.0

[a] Not observed but predicted to be weak. [b] IR inactive. [c] Not observed, predicted to be overlapped or obscured by bands of other $\mathrm{HMn(^{12}CO)_{5-x}(^{13}CO)_x}$ species. [d] Mean value of matrix-split bands[35] used in refinement, e.g., e mode of $\mathrm{HMn(^{12}CO)_5}$ is split 2018.4, 2016.4, and 2014.9 cm^{-1}. [e] Each observed frequency was only entered once into the least-squares refinement: 24 frequencies, root-mean-square error 0.46 cm^{-1}. Force constants (N m^{-1}): $k_{\mathrm{ax}} = 1652.83$, $k_{\mathrm{eq}} = 1690.96$, $k_{\mathrm{ax,eq}} = 32.51$, $k_{\mathrm{eq,eq(cis)}} = 24.74$, $k_{\mathrm{eq,eq(trans)}} = 48.21$.

Table III. Observed and Calculated Wavenumbers (cm^{-1}) of the IR Bands of the C_s Isomer (**3**) of $\mathrm{HMn(CO)_4}$ in a $\mathrm{CH_4}$ Matrix at 20 K (Figure 5)

no.^{a}	molecule	mode	obsd	calcd^e
1	$\mathrm{HMn(^{12}CO)_4}$ (C_s)	a'	2089.9	2089.7
		a''	1996.6^b	1996.7
		a'	*c*	1995.5
		a'	1964.9	1964.6
2	$\mathrm{HMn(^{12}CO)_3(^{13}CO)_{ax}}$ (C_s)	a'	*d*	2084.2
		a''	1996.6^b	1996.7
		a'	*c*	1990.8
			1929.6^f	1930.3
3	$\mathrm{HMn(^{12}CO)_3(^{13}CO)_{eq}}$ (C_s)	a'	*d*	2085.3
		a''	1996.6^b	1996.7
		a'	*c*	1982.6
		a'	1937.7^f	1937.3
4	$\mathrm{HMn(^{12}CO)_3(^{13}CO)_{eq}}$ (C_1)		2077.7	2077.4
			c	1995.7
			c	1967.4
			c	1960.7
5	$\mathrm{HMn(^{12}CO)_2(^{13}CO)_2}$ (C_s ax, eq)	a'	*d*	2079.9
		a''	1996.6^b	1996.7
		a'	*c*	1959.8
		a'	*c*	1921.2
6	$\mathrm{HMn(^{12}CO)_2(^{13}CO)_2}$ (C_s eq, eq)	a'	*c*	1979.1
		a'	1962.8	1962.9
		a''	1951.9^b	1952.2
7	$\mathrm{HMn(^{12}CO)_2(^{13}CO)_2}$ (C_1 ax, eq)		2070.5	2070.8
			c	1991.9
			c	1965.2
			c	1929.0
8	$\mathrm{HMn(^{12}CO)_2(^{13}CO)_2}$ (C_1 eq, eq)		2071.7	2071.9
			c	1986.3
			c	1961.5
			1936.2	1937.0
9	$\mathrm{HMn(^{12}CO)_3(^{13}CO)}$ (C_s eq, eq, eq)	a'	2053.7	2053.5
		a'	*c*	1968.8
		a''	1951.9^b	1952.2
		a'	*c*	1936.9
10	$\mathrm{HMn(^{12}CO)_3(^{13}CO)}$ (C_s ax, eq, eq)	a'	*d*	2052.4
		a'	*c*	1978.7
		a''	1951.9^b	1952.2
		a'	1928.2	1928.2
11	$\mathrm{HMn(^{12}CO)_3(^{13}CO)}$ (C_1)		2065.0	2065.3
			1975.4	1974.9
			c	1951.2
			1921.6^b	1920.9
12	$\mathrm{HMn(^{13}CO)_4}$ (C_s)	a'	*d*	2043.1
		a''	1951.9^b	1952.2
		a'	*c*	1951.0
		a'	*c*	1920.8

[a] Molecules numbered as in ref 6. [b] Mean value of matrix splitting entered. [c] Not observed, predicted to be overlapped or obscured by bands of $\mathrm{HMn(^{12}CO)_{5-x}(^{13}CO)_x}$ or $\mathrm{HMn(^{12}CO)_{4-x}(^{13}CO)_x}$ species. [d] Not observed, predicted to be weak. [e] Each frequency was only entered once into the least-squares refinement: 17 frequencies, root-mean-square error 0.40 cm^{-1}, maximum error 0.82 cm^{-1}. Force constants (see Figure 6, N m^{-1}): $k_1 = 1601.56$, $k_2 = 1664.62$, $k_3 = 1611.62$, $k_{1,2} = 40.04$, $k_{1,3} = 45.59$, $k_{2,2} = 53.98$, $k_{2,3} = 31.13$. [f] Band position determined from an experiment with 5% ^{13}CO-enriched $\mathrm{HMn(CO)_4}$.

Our analysis of the spectra favors a C_s structure for $\mathrm{HMn(CO)_4}$, but it is clear from Figure 6 that the force fields for C_s and C_{2v} structures are not very different. In fact the spectrum of any C_{2v} molecule could be reproduced with use

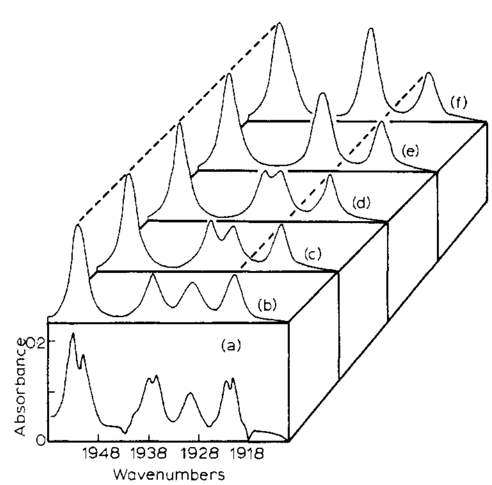


Figure 7. Illustration of the differences between the spectra predicted for C_s (3) and C_{2v} (5) structures of $HMn(CO)_4$: (a) observed spectrum of ^{13}CO-enriched $HMn(CO)_4$ (cf. Figure 5b); (b) predicted spectrum for C_s $HMn(CO)_4$ with optimized force constants (see Table III); (c–e) predicted spectra as the values of k_1 and k_3, and k_{12} and k_{23}, become more nearly equal; (f) predicted spectrum for a C_{2v} structure (5), where $k_1 = k_3$ and $k_{12} = k_{23}$. The values of force constants (N m^{-1}) used are as follows (k_1, k_3, k_{12}, k_{23}, respectively): (f) 1606.6, 1606.6, 35.58, 35.58; (e) 1605.0, 1607.4, 36.04, 34.5; (d) 1604.6, 1608.6, 37.04, 33.5; (c) 1603.6, 1609.6, 38.04, 32.5; (b) 1601.56, 1611.62, 40.04, 31.13.

of the C_s force field in which $k_1 = k_3$ and $k_{12} = k_{23}$. For our simulated spectrum of $HMn(CO)_4$ in CH_4 (Figure 5c) k_1 (1601.6 N m^{-1}) is quite close to k_3 (1611.6 N m^{-1}) and it is reasonable to wonder whether $HMn(CO)_4$ is not C_{2v} after all. Fortunately, there is a significant difference between the spectra predicted for C_s and C_{2v} structures, as shown in Figure 7. The four lowest frequency bands in the observed spectrum of $HMn(^{12}CO)_{4-x}(^{13}CO)_x$ (Figure 7a) closely resemble the spectrum predicted by our optimized C_s force constants (Figure 7b). However, as k_1 becomes more nearly equal to k_3, and k_{12} to k_{23}, the two central bands in the simulated spectra coalesce, until for a C_{2v} structure (5) only three bands are predicted in this region (Figure 7f). Our observation of four bands, therefore, means that a C_{2v} structure (5) is improbable and that $HMn(CO)_4$ almost certainly has the C_s structure (3).

Unfortunately, the converse of this argument is not true. Namely, three bands in this region of the spectrum (e.g. Figure 7f) do not automatically imply a C_{2v} structure for an $XMn(CO)_4$ molecule since such a spectrum can also be fitted with a C_s force field where $k_1 \neq k_3$ and $k_{12} \neq k_{23}$. In such a case,[20,21] analysis of the IR spectrum of the ^{13}CO-enriched $XMn(CO)_4$ species would not by itself be able to distinguish between the two structures and additional experiments would be required (e.g. shifts in UV/visible spectra etc.). Thus, we are particularly fortunate that, in the case of $HMn(CO)_4$, ^{13}CO enrichment experiments provide conclusive evidence for the C_s structure.

The Second Isomer of $HMn(CO)_4$. Some d^6 $M(CO)_4L$ species have previously been shown to have two isomers,[5,6] C_{4v} (2) and C_s (3), which can be interconverted by UV/visible irradiation. Although the C_s isomer of $HMn(CO)_4$ (3) is the primary photolysis product of $HMn(CO)_5$, a second isomer can be generated in small amounts by subsequent selective-wavelength irradiation. In CH_4 matrices, $HMn(CO)_4$ has a broad visible absorption band, λ_{max} 400 nm (q.v.), and irradiation at 367 nm, corresponding to the short-wavelength edge of this absorption, causes a broadening and red shift of the band (see Figure 8). At the same time, in the IR spectrum there is an increase in the intensity of the absorptions of $HMn(CO)_5$ and a decrease in those of $HMn(CO)_4$ (Figure 9b) but interestingly there is also a small but reproducible change in the relative intensities of these $HMn(CO)_4$ bands. The original relative intensities can be restored by irradiation with light, λ = 544 nm, corresponding to the tail of the "new" visible absorption. Computer subtraction of the appropriate IR spectra show that these intensity changes are due to the growth and decay of a single ν_{C-O} band at a frequency, 1966 cm^{-1}, very close to the lowest frequency band of C_s $HMn(CO)_4$ (Figure 9c). This band cannot be due to a "matrix splitting" of the C_s $HMn(CO)_4$ absorptions because in that case no change would be expected in the relative integrated intensities of the IR bands or the position of the UV/visible absorption. It must, therefore, be assigned to a new species.

Unfortunately, the yield of this new species is low in CH_4 matrices and even lower in Ar, and no convincing spectra could

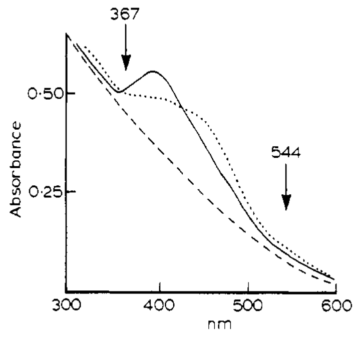


Figure 8. UV/visible absorption spectra showing changes occurring when the second isomer of $HMn(CO)_4$ is formed: (- - -) spectrum after deposition of a CH_4 matrix containing $HMn(CO)_5$ (dilution 1:2000); (—) spectrum after 2-min UV photolysis; (···) spectrum after 90-min irradiation at 367 nm. The arrow on the right indicates the wavelength (544 nm) of light that destroys the second isomer of $HMn(CO)_4$.

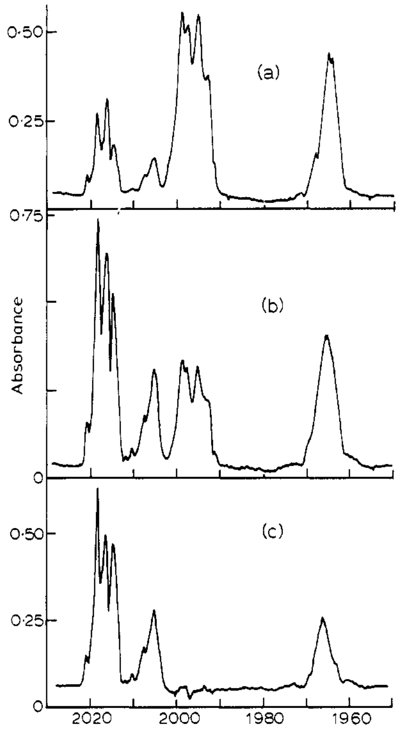


Figure 9. IR spectra illustrating the formation of the second isomer of $HMn(CO)_4$ in a CH_4 matrix (1:4000) at 20 K: (a) spectrum after 2-min UV photolysis of $HMn(CO)_5$ (cf. Figure 3b; the strongest bands are due to the C_s isomer of $HMn(CO)_4$); (b) spectrum after 90-min irradiation with λ = 367 nm; (c) scaled computer subtraction (spectrum b *minus* 0.57 times spectrum a) to remove absorption due to the C_s isomer of $HMn(CO)_4$. The band near 1960 cm^{-1} is due to a second, C_{4v}(?), isomer of $HMn(CO)_4$.

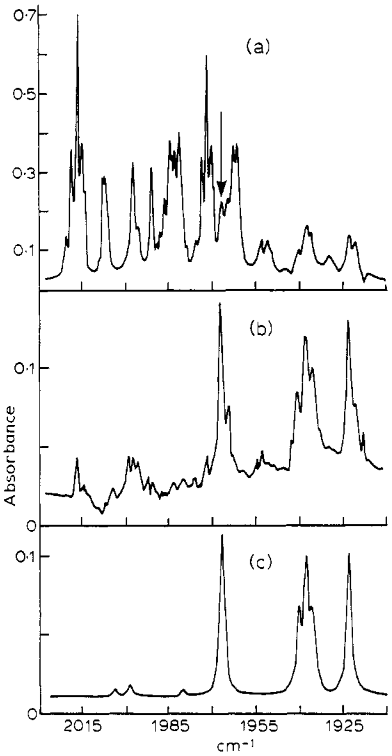


Figure 10. (a) IR spectrum of a CH_4 matrix containing ^{13}CO-enriched $HMn(CO)_5$ and photolysis products. (b) Spectrum of the second isomer of $HMn(CO)_4$ obtained by computer subtraction of absorptions due to isotopomers of $HMn(CO)_5$ and the C_s isomer of $HMn(CO)_4$ from spectrum a. Note that there is a ×4 expansion in the ordinate scale relative to spectrum a. The band marked with an arrow in spectrum a becomes the most intense band in spectrum b, after computer subtraction. (c) Spectrum predicted, with Lorentzian bands (4-cm^{-1} fwhm), for a C_{4v} isomer (**2**) of $HMn(CO)_4$ (see Table V).

Table V. Observed and Calculated Wavenumbers (cm^{-1}) of the IR Bands of the Second Isomer of $HMn(CO)_4$ with ^{13}CO Enrichment in a CH_4 Matrix at 20 K (Figure 10)

obsd	calcd[b]	assignt
1966.3[a]	1966.5	e, $HMn(^{12}CO)_4$
1940.6	1940.1	a″, $HMn(^{12}CO)_2(^{13}CO)_2$ C_s
1937.7	1937.9	a′, $HMn(^{12}CO)_3(^{13}CO)$
	1937.3	a′, $HMn(^{12}CO)(^{13}CO)_3$
1935.3	1935.5	a″, $HMn(^{12}CO)_2(^{13}CO)_2$ C_s
1922.3[a]	1922.7	e, $HMn(^{13}CO)_4$

[a] This band is matrix split. [b] Calculated for C_{4v} $HMn(CO)_4$ (**2**): root-mean-square error 0.33 cm^{-1}, maximum error 0.5 cm^{-1}. Force constants (N m^{-1}): $k = 1625.0$, $k_{\text{cis}} = 26.53$, $k_{\text{trans}} = 62.73$.

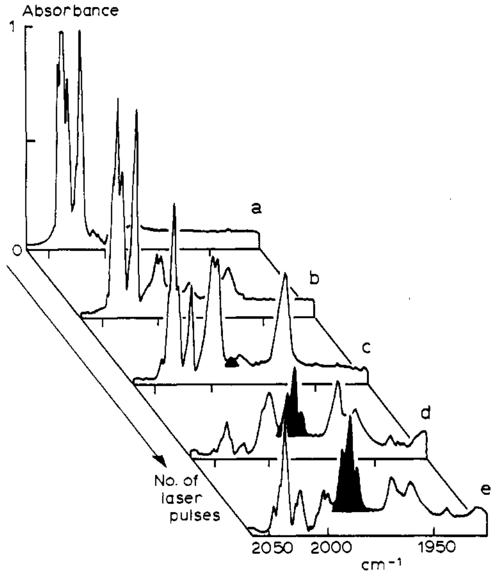


Figure 11. IR spectra illustrating the effects of ArF laser irradiation, 193 nm, on $HMn(CO)_5$ in an Ar matrix (1:4000) at 20 K: (a) after deposition; (b) after 10 laser pulses; (c) after 260 laser pulses; (d) after 4 × 10^5 laser pulses at 30 Hz (bands colored black are due to $Mn(CO)_5$); (e) after a further 1 h photolysis with light λ > 375 nm. Note that these spectra are recorded with a change in wavenumber scale at 2000 cm^{-1} and with a spectrometer of lower resolution than that used for the spectra shown in the other figures in this paper.

be obtained in the $\nu_{\text{Mn-H}}$ region. However, the UV/visible absorption band of the product appeared to shift to longer wavelength in Ar:

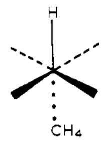
CH_4 matrix

$$HMn(CO)_4\ (C_s,\ \lambda_{\max}\ 400\ \text{nm}) \underset{544\ \text{nm}}{\overset{367\ \text{nm}}{\rightleftarrows}} X$$

Ar matrix

$$HMn(CO)_4\ (C_s,\ \lambda_{\max}\ 445\ \text{nm}) \underset{589\ \text{nm}}{\overset{403\ \text{nm}}{\rightleftarrows}} X$$

The presence of only one $\nu_{\text{C-O}}$ band in this region limits the possible structures for X (i.e. $HMn(CO)_4$ C_{4v} (**2**) $HMn(CO)_3$ C_{3v}, and $Mn(CO)_4$ D_{4h} or T_d, etc.), although some of these assignments presume a weak unobserved high-frequency band. However, X is unlikely to be $HMn(CO)_3$, as it is not formed by prolonged UV photolysis of $HMn(CO)_4$, which should promote formation of $HMn(CO)_{4-x}$ species. $Mn(CO)_4$ has been predicted to have a C_{2v} structure[7] ($\nu_{\text{C-O}}$ $2a_1 + b_1 + b_2$), incompatible with the single IR band of X, and also $HMn(CO)_4$ would not be expected to lose H under such mild photochemical conditions (see below). Thus the C_{4v} isomer of $HMn(CO)_4$ is the most probable assignment for X. The spectrum obtained for ^{13}CO-enriched X (Figure 10b) is strikingly similar to the spectrum calculated for a C_{4v} $HMn(CO)_4$ fragment (Figure 10c and Table V). The shift in UV/visible absorption of X between CH_4 and Ar matrices is similar to that of the C_s isomer of $HMn(CO)_4$ and could be best explained by an interaction between the matrix material and the vacant coordination site of C_{4v} $HMn(CO)_4$ (**7**). Thus, the evidence suggests that X is a C_{4v} isomer of $HMn(CO)_4$ but that, unlike $Cr(CO)_4CS$, the C_s isomer of $HMn(CO)_4$ is significantly more stable in the matrix than the C_{4v}. This difference between $Cr(CO)_4CS$ and $HMn(CO)_4$ is what might have been expected on simple π-bonding grounds, if CS were a better acceptor than CO.



7

Photochemical Cleavage of the Mn-H Bond—ArF Laser Photolysis. UV photolysis of $HMn(CO)_5$ in solution rapidly leads to the formation of $Mn_2(CO)_{10}$, the source of the problem in synthesizing $HMn(^{12}CO)_{5-x}(^{13}CO)_x$ (q.v.). This reaction may well be a radical chain reaction,[36] but nevertheless it is surprising that our IR spectra show little evidence for loss of H during UV photolysis of $HMn(CO)_5$ in Ar matrices, particularly since $Mn(CO)_5$ can be detected by ESR spectroscopy after such an irradiation.[37] We have previously shown that the quantum yield for CO loss in matrices is much higher than for H loss but that $Mn(CO)_5$ can be produced in pure CO matrices, where CO loss is effectively surpressed.[16]

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(36) Timney, J. A. Ph.D. Thesis, University of Newcastle-upon-Tyne, 1979.
(37) Sweany, R. L.; Symons, M. C. R. *Organometallics* **1982**, *1*, 834.

Table VI. Wavenumbers (cm^{-1}) of IR Bands Observed[a] on ARF Laser (193 nm) Photolysis of $HMn(CO)_5$ in Ar Matrices at 20 K (Figure 11)

band	assignt	band	assignt
1992.5	$Mn(CO)_5$	1961	$HMn(CO)_x$ ($x < 4$)
1990		1944	
1986		1929	

[a] Excluding bands due to $HMn(CO)_4$ (see Table I).

After prolonged (e.g. hours) UV photolysis of $HMn(CO)_5$ in Ar matrices with an unfiltered Hg arc, one can observe weak IR bands, possibly due to $Mn(CO)_5$. More convincing evidence for formation of $Mn(CO)_5$ in an Ar matrix comes from photolysis with an ArF excimer laser (193 nm, 30 mJ/pulse at matrix, 30-Hz repetition rate), a single pulse of which produces an effect similar to 1-s irradiation with an unfiltered Hg arc. The results are shown in Figure 11. ArF laser photolysis initially generates $HMn(CO)_4$, the IR bands of which rapidly reach a steady-state intensity. As the photolysis proceeds, other bands gradually grow in until after 4×10^5 pulses, the bands colored black are the strongest in the spectrum (see Table VI). Although the frequencies of these bands are slightly different from those of $Mn(CO)_5$ in a pure CO matrix,[16] they can be shown to be due to $Mn(CO)_5$ by doping the matrix with CO. This reduces the yield $HMn(CO)_4$ and increases the production of $Mn(CO)_5$. The final yield of $Mn(CO)_5$ can be increased in a pure Ar matrix by irradiation with light, $\lambda > 375$ nm, after the ArF laser photolysis (Figure 11). This observation implies that $Mn(CO)_5$ is itself photolyzed by the laser to some lower carbonyl, perhaps $Mn(CO)_4$, which can recombine with CO to regenerate $Mn(CO)_5$, when irradiated with $\lambda > 375$ nm light. Excimer laser excitation of metal carbonyl compounds in the gas phase has been shown to lead to the simultaneous loss of two or more CO groups,[38] e.g.

$$M(CO)_x \xrightarrow{h\nu} M(CO)_{x-2} + 2CO$$

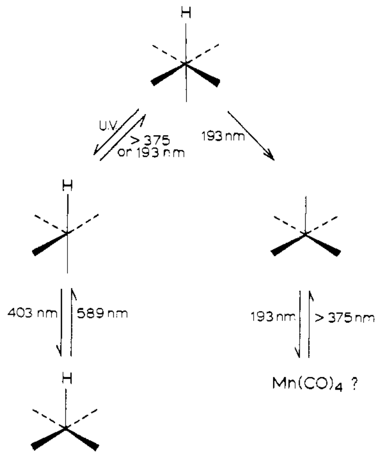
There is no evidence from our experiments that such a process is occurring with matrix-isolated $HMn(CO)_5$, presumably because the matrix deactivates the excited carbonyl fragments before a second CO group can be expelled. Similar results have been found for laser photolysis of other metal carbonyls in condensed media.[9] Thus, the formation of $Mn(CO)_5$ in Ar matrices does not apparently involve exotic laser-induced effects. The absence of $Mn(CO)_5$ from our conventional UV photolysis experiments is merely a reflection of low quantum yields and the relative insensitivity of IR as a means of detecting reaction products. Both these problems have been overcome by the use of the excimer laser, which produces a UV light intensity on the matrix so much higher than with arc lamps that a high conversion to $Mn(CO)_5$ can be achieved without excessively long photolysis times.

Photolysis of $HRe(CO)_5$. The photochemistry of $HRe(CO)_5$ in Ar and CH_4 matrices appears to be broadly similar to that of $HMn(CO)_5$. The primary photolysis product has IR spectra consistent with a C_s isomer of $HRe(CO)_4$, and this can be converted photochemically into a second species, probably the C_{4v} isomer. In general, the matrix splittings of the IR bands are greater than those of the corresponding $HMn(CO)_x$ species with the result that quantitative interpretation is more difficult. (See Figure 12, available as supplementary material.)

Conclusion

The photochemistry of matrix-isolated $HMn(CO)_5$ is summarized in Scheme I. It has been surprisingly difficult to unravel, but we believe that the principal features are now established. We have shown that the structure of $HMn(CO)_4$ is based on the same square-based pyramid as other d^6 five-coordinate species.[1] Furthermore, the photochemical mechanism,[12] proposed for $Cr(CO)_5$, would also explain the observed behavior of $HMn(CO)_4$.

Scheme I. Photochemistry of $HMn(CO)_5$/Ar



The C_s structure of $HMn(CO)_4$ (**3**) was determined by ^{13}CO enrichment. However, it has become clear that this technique cannot always distinguish between C_s and C_{2v} structures (**3** and **5**), but fortunately in this case the results were unambiguous. Whether the H ligand is stereochemically active is perhaps more open to dispute. On one hand it can be argued that $HMn(CO)_4$ is a typical five-coordinate square pyramid, but on the other hand it could be suggested that the carbonyl moiety has the same geometry[39] as $Cr(CO)_4$. The C_s structure of $HMn(CO)_4$ is consistent with molecular orbital predictions,[40,41] one of which[41] predicts little energy difference between the C_{4v} (**2**) and C_s (**3**) structures of $HMn(CO)_4$. However, our experiments provide strong evidence that the $HMn(CO)_4$ fragment interacts with CH_4 matrices, so a more realistic comparison might be with calculations for $Mn(CO)_4L_2$ species,[40] which predict that the cis-substituted compound (**6**) is more stable for weak σ-donor ligands. Our results suggest that $HMn(CO)_4$ may well interact with hydrocarbon solvents in room-temperature reactions, and such interactions should clearly be considered when the mechanisms of these solution reactions are interpreted.

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Registry No. 2 (L = H), 87069-55-4; 3 (L = H), 87069-54-3; $HMn(CO)_5$, 16972-33-1; Ar, 7440-37-1; CH_4, 74-82-8; CO, 630-08-0.

Supplementary Material Available: Observed and calculated frequencies of C_s $HMn(^{12}CO)_{4-x}(^{13}CO)_x$ species in an Ar matrix (Table IV) and IR spectra of $HRe(CO)_5$ and $HRe(CO)_4$ in CH_4 matrices (Figure 12) (5 pages). Ordering information is given on any current masthead page.

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(38) Tumes, W.; Gitlin, B.; Rosan, A. M.; Yardley, J. T. *J. Am. Chem. Soc.* **1982**, *104*, 55.

(39) Perutz, R. N.; Turner, J. J. *J. Am. Chem. Soc.* **1975**, *97*, 4800.

(40) Burdett, J. K. *Inorg. Chem.* **1976**, *15*, 212.

(41) Lichtenberger, D. L.; Brown, T. L. *J. Am. Chem. Soc.* **1978**, *100*, 366.