(43) L. Meites, "Polarographic Techniques", 2nd ed, Interscience, New York, N.Y., 1965, p 86.
(44) J. Heyrovsky and J. Kuta, "Principles of Polarography", Academic Press, New York, N.Y., 1966, p 148.
(45) I. M. Kolthoff and J. J. Lingane, "Polarography", Vol. I, 2nd ed, Interscience, New York, N.Y., 1952, Chapter XII.
(46) Manganese salicylate complexes require higher ligand concentrations for stability than do the other aromatic polyhydroxy ligands.
(47) Increasing the hydroxide concentration in glycerate solutions also favors the formation of the $Mn(III_B)$ complex. This may be explained by the fact that glycerate anions are better stabilized by increasing basicity.
(48) C. G. Smith and D. T. Sawyer, to be submitted for publication in *Inorg. Chem.*
(49) M. M. Morrison and D. T. Sawyer, *J. Am. Chem. Soc.*, **99**, 257 (1977).
(50) Y. Toshino, I. Taminaga, M. Kokiso, and T. Vehiro, *Bull. Chem. Soc. Jpn.*, **47**, 2787 (1974).

Contribution from the Departments of Inorganic Chemistry, University of Newcastle upon Tyne,
Newcastle upon Tyne, NE1 7RU, Great Britain, and University of Oxford, Oxford, OX1 3QR, Great Britain

Characterization by Infrared and Raman Spectroscopy of Matrix-Isolated $M(CO)_5N_2$ (M = Cr, Mo, or W) Produced by Photolysis of $M(CO)_6$[1a]

JEREMY K. BURDETT,*[1b] ANTHONY J. DOWNS,*[1c] GEOFFREY P. GASKILL,[1c] MICHAEL A. GRAHAM,[1b]
JAMES J. TURNER,*[1b] and ROBERT F. TURNER[1b]

Received June 16, 1977

Photolysis of matrix-isolated molybdenum hexacarbonyl in the presence of dinitrogen leads to the formation of the hitherto unknown molybdenum pentacarbonyl dinitrogen $Mo(CO)_5N_2$; the product has been detected by its infrared and Raman spectra which, with the aid of polarization measurements and isotopic variations involving ^{15}N and ^{13}CO enrichment, serve to characterize its stoichiometry and geometry. The formation under similar conditions of the analogous species chromium and tungsten pentacarbonyl dinitrogen has been demonstrated unequivocally by monitoring the Raman spectra of matrices containing the corresponding hexacarbonyls in the presence of dinitrogen. Confirmation of the C_{4v} symmetry of the molybdenum pentacarbonyl dinitrogen molecule, with the linear $Mo—N{\equiv}N$ unit thus implied, is provided by an analysis using a frequency-factored force field of the infrared-active C—O stretching modes of the isotopic variants $Mo(^{12}CO)_x(^{13}CO)_{5-x}N_2$ (x = 0–5), and an estimate of 90 ± 4° for the OC_{ax}–Mo–CO_{eq} bond angle has been derived from the relative intensities of the bands due to $Mo(^{12}CO)_5N_2$. Consideration is given, insofar as the results allow, to the likely contribution made by the N_2 oscillator to the force field of $Mo(CO)_5N_2$; hence it is evident that some provision must be made for CO,N_2 coupling if the finer details of the vibrational properties are to be interpreted. The species $M(CO)_5N_2$ (M = Cr, Mo, or W), unlike $X\cdots M(CO)_5$ (X = Ar or CH_4), is stable with respect to irradiation in the green region of the visible spectrum, and a scheme has been devised for the photochemical interconversion of the three species $Mo(CO)_6$, $Mo(CO)_5N_2$, and $X\cdots M(CO)_5$ in a mixed matrix composed of N_2 and X molecules.

1. Introduction

To the familiar binary carbonyls and the more recently described binary dinitrogen derivatives of transition metals, synthesized in low-temperature matrices,[2-7] have been added mixed carbonyl dinitrogen species. For example, $Ni(CO)_3N_2$ has been made[8] by photolysis of nickel tetracarbonyl in a solid nitrogen matrix, and the complete series of molecules $Ni(CO)_x(N_2)_{4-x}$ (x = 1–3) later identified[9] in the products formed by cocondensing nickel atoms with nitrogen/carbon monoxide mixtures at 10 K. Such molecules are of interest not merely because of their novelty but also because of the light shed by their structures, vibrational properties, and photochemistry on the bonding and reactions of the moieties M–CO and M–N_2 formed by a metal M. In this paper we describe the characterization in terms of its infrared and Raman spectra of the molecule $Mo(CO)_5N_2$ prepared by photolysis of molybdenum hexacarbonyl in matrices composed of pure nitrogen or mixtures of nitrogen with either methane or argon. The use of ^{15}N-enriched N_2 or ^{13}CO-enriched $Mo(CO)_6$ leaves no doubt about the stoichiometry of the product; less certain is the mode of coordination of the N_2 molecule although all the spectroscopic information available is compatible with a molecular model with C_{4v} symmetry and with a linear $Mo—N{\equiv}N$ moiety. We consider here the vibrational force field, structure, ultraviolet/visible spectrum, and photochemistry of the new species.

Similar both in mode of formation and in structure, it appears, are the molecules $Cr(CO)_5N_2$ and $W(CO)_5N_2$ identified by their Raman spectra following the photolysis of either a nitrogen matrix or a methane matrix doped with nitrogen incorporating the corresponding hexacarbonyl. Although the carbonyl dinitrogen systems of chromium, molybdenum, and tungsten are evidently closely related in the spectral patterns and photochemistry which they exhibit, the present account is concerned preeminently with the molybdenum system for which there is maximum common ground between the infrared and Raman measurements carried out for the most part independently in our two laboratories.[10] The formation and trapping in matrices of other mixed carbonyl dinitrogen derivatives of molybdenum, which have been characterized only by their infrared spectra, will be treated separately in a future paper;[11] elsewhere too will be found a more detailed account of the experiments exploring the suitability of the Raman effect for monitoring photochemical changes of matrix-isolated metal carbonyls.[12]

To the best of our knowledge, the only allusion hitherto made to a mixed carbonyl dinitrogen derivative of the group 6 elements concerns the chromium compound $Cr(CO)_5N_2$ predicted to be thermodynamically stable on the grounds of a theoretical study.[13] This compound has also been postulated by Nasielski and Wyart[14] as an intermediate in the photochemical reactions of chromium hexacarbonyl contained in cyclohexane solution and with an overpressure of gaseous nitrogen. The results of flash photolysis experiments have shown an absorption at 370 nm which has been attributed to the transient $Cr(CO)_5N_2$; the half-life of this species varies with the nitrogen pressure but is in the order of seconds at room temperature. A new band has also been observed to develop at ca. 1970 cm^{-1} in the infrared spectrum of a cyclohexane solution of the hexacarbonyl held at room temperature under an atmosphere of nitrogen, but only for as long as the solution is irradiated.

2. Raman Spectra of the Matrix-Isolated Molecules $M(CO)_6$ and $M(CO)_5$ (M = Cr, Mo, or W)

It has now been established beyond doubt that the photolysis of the hexacarbonyl $M(CO)_6$ (M = Cr, Mo, or W) in an argon or methane matrix generates the corresponding pentacarbonyl

0020-1669/78/1317-0523$01.00/0 © 1978 American Chemical Society

$M(CO)_5$.[15] This product interacts weakly with the molecules comprising the matrix cage via the vacant sixth coordination position and is therefore more realistically described as $X\cdots M(CO)_5$ (X = Ar or CH_4).[16] The square-pyramidal geometry of the $M(CO)_5$ framework has been substantiated by a detailed analysis[15] of the C–O stretching region of the infrared spectra due to the isotopic variants $M(^{12}CO)_x(^{13}CO)_{5-x}$. The pentacarbonyl is susceptible to photolysis in the visible region as a result of which the hexacarbonyl is regenerated.[17]

$$M(CO)_6 + X \underset{\text{visible}}{\overset{\text{UV}}{\rightleftharpoons}} X\cdots M(CO)_5 + CO \qquad (1)$$

$$(X = \text{e.g., Ar or } CH_4)$$

The mechanism of this intriguing process we discuss elsewhere.[18]

Raman spectra of a quality comparable with those of the corresponding infrared spectra have been measured for $M(CO)_6$ molecules (M = Cr, Mo, or W) suspended in solid methane at 20 K. Formed by pulsed deposition, the matrices were characterized by ratios $CH_4{:}M(CO)_6$ of ca. 2000:1; under these conditions all the Raman-active fundamentals of the $M(CO)_6$ molecules could be discerned, some of the line widths (at half-height) being no more than 1 cm^{-1}. The most intense features of the spectra are due to the a_{1g} and e_g fundamentals originating predominantly in C–O stretching and M–C stretching motions of the $M(CO)_6$ molecule.[12]

Ultraviolet photolysis of the matrix for ca. 2 min, followed by examination of the Raman scattering excited by laser radiation at 514.5 nm, revealed only one new feature in the region of the spectrum associated with C–O stretching modes; invariably of low intensity, this appeared at 2002.7 ± 0.5 cm^{-1} for M = Mo. The frequency is to be compared with the value of 2001.5 cm^{-1} calculated[15] on the basis of a Cotton–Kraihanzel force field for the b_1 C–O stretching fundamental of $Mo(CO)_5$ (isolated in methane), a mode which is inactive in infrared absorption but likely to give rise to more intense Raman scattering than any other mode involving C–O stretching.[19] The agreement between calculated and observed frequencies, though close, is noticeably worse than that achieved with the infrared-active C–O stretching fundamentals of the molecules $Mo(^{12}CO)_x(^{13}CO)_{5-x}$ (x = 0–5).[15] Evidently Raman-active fundamentals of species like $Mo(CO)_5$ and $Mo(CO)_6$ are accommodated less precisely than the infrared-active fundamentals by the approximations of the frequency-factored force field; the reasons for this fall outside the scope of the present paper.[20] We find evidence in our Raman experiments, then, for the production of $Mo(CO)_5$, but only in poor yield. By contrast, the experience of infrared measurements[15,17] testifies to the formation in relatively high yield of the pentacarbonyl following only brief exposure to ultraviolet radiation of the matrix-isolated hexacarbonyl. To explain the outcome of the Raman experiments we are bound to conclude that the laser radiation used to excite light scattering from the matrix induces the reversal of reaction 1, with the regeneration of the hexacarbonyl. That, despite this, some residual pentacarbonyl persists in the matrix is then consistent with the assumption that, for a proportion of the $M(CO)_5$ fragments, the photoejected CO molecule has become so remote as to prevent recombination.[21]

Support for the proposed sequence of events derives (i) from visual examination of the matrix following photolysis with ultraviolet radiation and (ii) from a closer scrutiny of the way in which the Raman scattering due to the matrix-isolated hexacarbonyl molecule changes with photolysis. First, after irradiation with unfiltered ultraviolet light, the matrix is seen to assume a uniform yellow coloration characteristic of the species $CH_4\cdots M(CO)_5$,[16] whereas exposure to the laser beam (with λ 514.5 nm) used to excite the Raman scattering brings about localized bleaching of the matrix. Second, we remark that the Raman spectrum of the matrix-isolated hexacarbonyl exhibits, prior to ultraviolet photolysis, a band corresponding to the e_g C–O stretching fundamental which is clearly split into two components separated by ca. 3 cm^{-1} (see Figure 1). A similar effect has been noted previously for the infrared-active t_{1u} C–O stretching mode,[17] and studies of alternate ultraviolet and visible photolysis steps have shown that, whereas ultraviolet radiation tends to destroy both components of the doublet, the lower frequency component (more intense of the two following deposition) is preferentially regenerated by visible photolysis. With due allowance for the reversal of eq 1 by the radiation used to excite the Raman spectra, we encounter analogous behavior in the Raman experiment; as Figure 1 depicts, the scattering due to the e_g mode excited by laser radiation at 514.5 nm witnesses with progressive ultraviolet photolysis an enhancement in the intensity of the component at 2018 cm^{-1} relative to that at 2021 cm^{-1}. That a very similar splitting is exhibited by an infrared band due to an a_1 mode of the species $Mo(^{12}CO)_5(^{13}CO)$ argues against a distortion of the hexacarbonyl molecule impressed by the matrix cage or a reduction in its site symmetry.[22,23] By elimination we are left to conclude that, on deposition, the hexacarbonyl molecules find themselves in two different trapping sites.

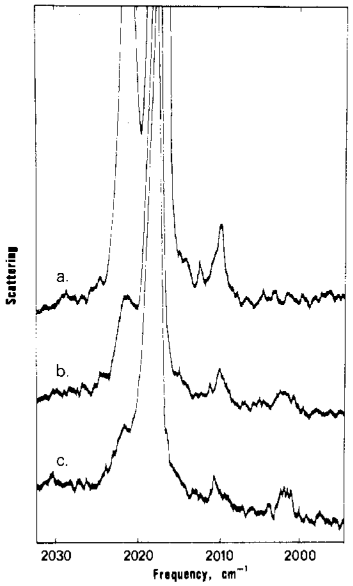


Figure 1. Raman spectrum of $Mo(CO)_6$ isolated in a CH_4 matrix at 20 K, showing the effects of UV photolysis in the vicinity of the e_g C–O stretching fundamental. The traces refer to the following conditions: (a) prior to photolysis; (b) after UV photolysis for 1.5 min; (c) after UV photolysis for a further 1.5 min.

The possibility of photochemical reactions induced within a matrix by the exciting radiation is one factor tending to restrict the usefulness of the Raman effect for monitoring the progress of photolysis reactions and for characterizing potentially photosensitive species. Other factors include absorption of the exciting radiation to induce local annealing of the matrix and the vulnerability of the Raman effect to the optical quality of the matrix which is apt to deteriorate with photolysis. Despite the success initially claimed for the exploitation of the Raman effect to characterize a number of matrix-isolated metal carbonyls,[9,24] the photosensitivity to visible light characteristic of binary carbonyls—and particularly of unsaturated carbonyl fragments like $Fe(CO)_4$[25]—is likely to handicap attempts to measure their Raman scattering. Evidence has been found, nevertheless, for a product which is photolytically stable to green light when a hexacarbonyl $M(CO)_6$ (M = Cr, Mo, or W) is subjected to ultraviolet

Table I. New Spectral Features in the Region 1900–2300 cm^{-1} Arising after UV Photolysis of $Mo(CO)_6$ Trapped in a Nitrogen Matrix at 20 K

Property	Frequencies,[d] cm^{-1}				
Ir absorption	2253.3[a] w	2092.8[a] w		1978.2[a] vs	1964.4[a] m
Raman scattering	2253.4[a] m	2092.3 m	2012.2 s		1962.9 m
State of polarization of Raman lines	p	p	*b*		p
Assignment:[c] mode	ν(N-N)	ν(C–O)	ν(C–O)	ν(C–O)	ν(C–O)
Symmetry class	a_1	a_1	b_1	e	a_1

[a] Average frequency for a band split into two or more components. [b] Overlap with the e_g C–O stretching fundamental of $Mo(CO)_6$ precludes any proper assessment of the state of polarization of this feature. [c] Based on an $Mo(CO)_5N_2$ molecule having C_{4v} symmetry. [d] Key: s, strong; m, medium; w, weak; v, very; p, polarized.

irradiation in the presence of a potential ligand capable of reestablishing kinetic and/or thermodynamic saturation of the central atom.[12] Such a ligand is dinitrogen, and the findings of our experiments in which a matrix-isolated hexacarbonyl is photolyzed in the presence of dinitrogen are described in the next section. It is noteworthy, however, that the Raman experiment gives particularly clear-cut information about the carbonyl dinitrogen product which survives the action of laser irradiation at 514.5 nm, whereas lower carbonyls like $M(CO)_5$, also formed by ultraviolet photolysis, are selectively destroyed. By contrast, the infrared experiment reveals the presence of both lower carbonyls and saturated carbonyl dinitrogen derivatives unless production of the former is suppressed by the use of a nitrogen-rich matrix.

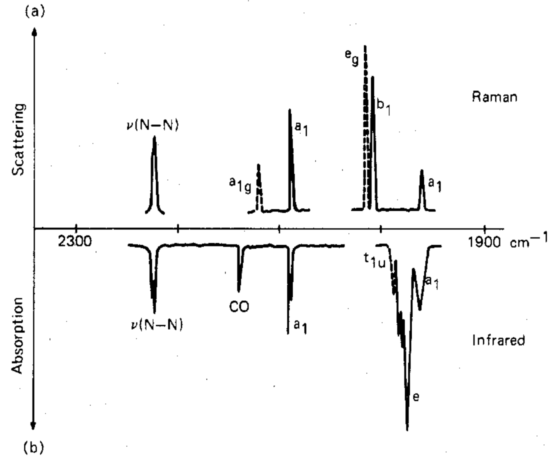


Figure 2. Effects of UV photolysis on $Mo(CO)_6$ isolated in solid N_2, as witnessed in the spectral region 1900–2300 cm^{-1} (a) by the Raman spectrum and (b) by the infrared spectrum of the matrix: (---) features due to $Mo(CO)_6$; (—) features which develop on photolysis and which are attributed to $Mo(CO)_5N_2$.

3. Photoproduction of the Species $M(CO)_5N_2$ (M = Cr, Mo, or W) in Pure N_2 Matrices and in Mixed N_2/Ar and N_2/CH_4 Matrices

When molybdenum hexacarbonyl isolated in a solid nitrogen matrix at 20 K is photolyzed with ultraviolet radiation (λ ~314 nm), the infrared and Raman bands due to the parent molecule decrease in intensity with the simultaneous appearance and growth of new spectral features (see Figure 2). Investigation of the growth and decay of band intensities leaves no doubt that all the prominent bands which develop with photolysis in the infrared and Raman spectra of the matrices are associated with a single molecular product. Some very much weaker bands which also appear in infrared absorption on photolysis of the sample can be eliminated by using very dilute matrices, e.g., with N_2:$Mo(CO)_6$ ≈ 10 000:1, and are therefore assigned to polymeric species. The frequencies, intensities, and polarization properties of the new features observed in the region 1900–2300 cm^{-1} are summarized in Table I.

Similar results were found when the hexacarbonyl is photolyzed in mixed nitrogen/argon or nitrogen/methane matrices, with matrix gas:$Mo(CO)_6$ ratios of 2000–3000:1. For example, the Raman spectra displayed after photolysis by a nitrogen/methane matrix (N_2:CH_4 = 1:10–200) resembled closely that of a solid nitrogen matrix. That, in a given photolysis time, the product was typically formed in higher yield in solid methane thus doped with nitrogen than in pure nitrogen matrices is possibly a function of the superior optical quality which characterized methane matrices; certain it is that the optimum spectroscopic results were secured with *methane-rich* rather than with solid nitrogen matrices. The Raman scattering of nitrogen/methane matrices has also been turned to advantage to monitor the photolysis of chromium and tungsten hexacarbonyls. The frequencies, intensities, and polarization properties of the Raman lines attributed in each case to the photolysis product are listed, together with their likely assignments, in Table II. Whereas the Raman spectra of nitrogen-containing matrices gave no hint of the pentacarbonyl $M(CO)_5$, infrared absorptions due to $Mo(CO)_5$ were clearly in evidence when $Mo(CO)_6$ suspended in a nitrogen/argon or nitrogen/methane mixture was submitted to ultraviolet irradiation. Indeed it was necessary to use *nitrogen-rich* matrices for the infrared experiments in order to bring about adequate buildup of the absorptions due to the new photolysis product. Accordingly the photosensitivity of the species X···$Mo(CO)_5$ (X = matrix molecule) discussed in the preceding section has a profound effect on the efficiency of photoproduction of the new species and on the conduct of the infrared and Raman experiments.

In previous investigations of matrix-isolated dinitrogen and carbonyl complexes, vibrational fundamentals with frequencies less than 1000 cm^{-1} have eluded detection more often than not. Such transitions tend to be intrinsically less intense, notably in infrared absorption, than the transitions largely internal to the CO and N_2 ligands, a condition difficult to reconcile with the low concentrations of matrix-isolated species demanded by efficient isolation. Doubtless, too, some of the transitions are located at frequencies inaccessible to the particular spectrometer used. The paucity of data makes it all the more remarkable that the Raman spectrum we have measured for each of the products formed by photolysis of the hexacarbonyls $M(CO)_6$ (M = Cr, Mo, or W) in the presence of dinitrogen contains, at frequencies below 500 cm^{-1}, no less than three weak but quite well-defined lines (see Table II).

The feature at highest frequency exhibited by each of the photoproducts formed from the hexacarbonyls $M(CO)_6$ (M = Cr, Mo, or W) occurs in the region associated with the stretching of coordinated dinitrogen.[26] When $^{15}N_2$ is used in place of $^{14}N_2$, the band is reduced in frequency by 73 cm^{-1} for the molybdenum compound and by 67 cm^{-1} for the tungsten compound (compared with a shift of ca. 76 cm^{-1} to be expected for an isolated N_2 unit), confirming that it arises from what is substantially an N–N stretching mode. The origin in C–O stretching modes of the other bands at fre-

Table II. Frequencies (in cm^{-1}) and Assignments of Raman Lines due to $M(CO)_5N_2$ Molecules (M = Cr, Mo, or W) Isolated in CH_4 Matrices Doped with N_2

Assignment		$Cr(CO)_5N_2$				$Mo(CO)_5N_2$				$W(CO)_5N_2$			
Approx description of fundamental	Symmetry class	$^{14}N^{14}N$	$^{14}N^{15}N$	$^{15}N^{15}N$	Intensity,[e] state of polarization	$^{14}N^{14}N$	$^{14}N^{15}N$	$^{15}N^{15}N$	Intensity,[e] state of polarization	$^{14}N^{14}N$	$^{14}N^{15}N$	$^{15}N^{15}N$	Intensity,[e] state of polarization
ν(N-N)[a]	a_1	2240.6	2205.8	2170.2	m, p	2247.5	2212.6	2176.2	m, p	2226.9	2193.0	2160.4	m, p
ν(C-O)[b]	a_1	2086.8		2084.1	m, p	2091.3		2089.2	m, p	2089.2		2083.1	m, p
ν(C-O)[b]	b_1	2009.5		2009.8	s[c]	2009.8		2010.1	s[c]	2003.9		2003.8	s[c]
ν(C-O)[d]	e					(1976.1)							
ν(C-O)[a]	a_1	1959.5		1960.1	m, p	1958.5		1957.6	m, p	1961.1		1960.5	m, p
ν(M-C)[a]	a_1	456.0		456.5	w, p	436.0		436.4	w, p	451.5		451.8	w, p
ν(M-C)[a]	a_1	393.6		393.6	w, p	397.2		397.8	w, p	426.5		426.4	w, p
ν(M-N)[a]	a_1	307.7		300.6	vw, p	279.3		272.7	vw	294.0		285.6	vw

[a] Frequency error limits ±1.0 cm^{-1}. [b] Frequency error limits ±0.4 cm^{-1}. [c] Probably depolarized but overlap with the e_g C-O stretching fundamental of unchanged $M(CO)_6$ molecules precludes any proper assessment of the state of polarization of this feature. [d] Observed only in infrared absorption; frequency error limits ±0.2 cm^{-1}. [e] Key: s, strong; m, medium; w, weak; v, very; p, polarized.

quencies exceeding 1900 cm^{-1} is suggested by their frequencies and confirmed by the effects of ^{13}CO enrichment. Of the three lines located in the region 250–500 cm^{-1} in the Raman spectrum of each photoproduct, the two highest in frequency are strongly polarized (with depolarization ratios <0.1) and insensitive (within experimental error) to the substitution of $^{15}N_2$ for $^{14}N_2$. In keeping with the behavior of related molecules,[19] these findings imply that the lines in question originate in totally symmetric M–C stretching modes of the metal carbonyl fragment. It proved difficult to assess the state of polarization of the line lowest in frequency, which is also the weakest of the three, although under optimum conditions (realized with the chromium derivative) it appeared to be strongly polarized. There could be no doubt, however, that the line is reduced in frequency by 6–9 cm^{-1} when $^{15}N_2$ replaces $^{14}N_2$ in the matrix. Either the M—N stretching or the M—N≡N bending mode of a metal–dinitrogen moiety would show this sort of response to $^{15}N_2$ substitution,[27] but, unless the axial symmetry of the M—N≡N unit is not maintained, only the M–N stretching mode is capable of generating a polarized Raman line.

Two other aspects presented by the new bands merit attention. First, the intense Raman line due to the new molybdenum compound near 2010 cm^{-1} appears to be without a counterpart in the infrared spectrum, whereas the reverse applies to the feature near 1980 cm^{-1}, which is intense in infrared absorption but goes undetected in Raman scattering. Second, according to the measured depolarization ratios of the Raman lines due to this compound isolated in solid methane doped with nitrogen, the features in the region 1900–2300 cm^{-1} differ from those at lower frequencies in that none of them is strongly polarized, although the lines near 2250, 2090, and 1960 cm^{-1} exhibit ratios of 0.26, 0.56, and 0.71, respectively, consistent with their origin in totally symmetric fundamentals. We have been able to measure these ratios with some confidence, with error limits ±0.05, since the scattering arising from the unchanged hexacarbonyl provided an internal reference, affording a means of assessing, and correcting for, the extraneous effects of matrix birefringence and internal reflection. With methane matrices, these effects caused the Raman lines due to the hexacarbonyl remaining in the matrix to exhibit depolarization ratios apparently exceeding the values appropriate to an ideal fluid by no more than 0.02–0.09. Since we have checked, moreover, that the measured depolarization ratios are not significantly affected by variations in the angle of incidence of the exciting radiation falling on the matrix, it seems reasonable to suppose that the polarization properties relate to molecules randomly and not specifically oriented within the matrix.

The C–O stretching region of the infrared spectrum presents for the molybdenum photoproduct an overall spectral pattern strongly reminiscent of that characterizing the species X···$Mo(CO)_5$ in a matrix of X molecules (where X is methane or a noble gas),[15] although no bands attributable to X···$Mo(CO)_5$ were observed in these experiments in the absence of appreciable concentrations of X. Taken with the other spectroscopic evidence and with the circumstances of the photolysis experiment, this analogy leads us to identify the photoproduct as the molecule $Mo(CO)_5N_2$ which we tentatively assign to the C_{4v} point group. Assignments consistent with such a molecule, set out in Tables I and II, account for all the new infrared and Raman bands observed to develop with photolysis. Of the C–O stretching fundamentals we note that, as in the structurally related molecules $Mo(CO)_5PX_3$ (X = H, Cl, Et, Ph, OMe, or OPh),[19] and presumably X···$Mo(CO)_5$, the b_1 mode is the most intense in Raman scattering, while being inactive in infrared absorption; on the other hand, the corresponding e mode gives rise to strong

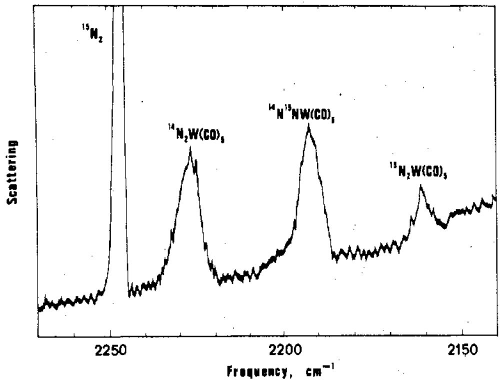


Figure 3. N–N stretching region of the Raman spectrum exhibited after UV photolysis of $W(CO)_6$ in a CH_4 matrix doped with N_2 having the approximate isotopic composition $^{14}N_2$:$^{14}N^{15}N$:$^{15}N_2$ = 4:4:1.

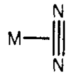
infrared absorption but is too weak to be detected (although formally allowed) in the Raman spectrum.

Proof of the stoichiometry and symmetry of the new species relies (i) on a demonstration that it contains but a single M—N≡N moiety presumed to be linear and (ii) on the infrared absorptions due to all possible combinations of ^{12}CO- and ^{13}CO-substituted products derived from $Mo(CO)_6$, analysis of which establishes the C_{4v} geometry of the $Mo(CO)_5$ part of the molecule.

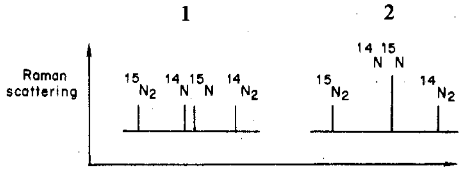
(i) That the new species contains only one molecule of coordinated dinitrogen is shown by the use of a methane matrix containing ^{15}N-enriched dinitrogen. Thus Figure 3 shows the Raman spectrum after photolysis of $W(CO)_6$ trapped in a methane matrix doped with dinitrogen ($W(CO)_6$:N_2:CH_4 = 1:100:2000), the isotopic composition of the dinitrogen $^{14}N_2$:$^{14}N^{15}N$:$^{15}N_2$ being approximately 4:4:1. The 4:4:1 pattern arising from the Raman line of the photoproduct highest in frequency is palpable proof, not only of the origin of the line in the N–N stretching mode but also of the presence of a single coordinated N_2 molecule. Photolysis of $Mo(CO)_6$ in the presence of ^{15}N-enriched dinitrogen affords in both the infrared and Raman spectra of the product results similar to those found for the tungsten analogue, although the Raman scattering due to isolated $^{15}N_2$ molecules obscures the N–N stretching mode of the species $Mo(CO)_5{}^{14}N_2$. Concerning the mode of coordination of the N_2 ligand, however, these findings are inconclusive. "End-on" coordination of the N_2 with a linear M—N≡N unit (**1**) implies a difference in energy for the N—N stretching vibrations of M—^{14}N≡^{15}N and M—^{15}N≡^{14}N, as elegantly demonstrated[28] in the infrared spectrum of RhN_2; with "side-on" coordination of N_2 and a triangular skeleton (**2**), this distinction disappears to give only one N–N stretching vibration for the species M($^{14}N^{15}N$). The Raman scattering associated with this mode of the photoproducts derived from $Mo(CO)_6$ and $W(CO)_6$ in the presence of $^{14}N^{15}N$ is in each case no more than a single line not perceptibly broader than the components due to the products containing $^{14}N_2$ or $^{15}N_2$. Accordingly we are not in a position at this stage to decide whether the M—N≡N unit is linear and the energy difference between the two ^{14}N—^{15}N stretching vibrations too small to be detected or whether the MN_2 unit assumes a triangular structure.

M—N≡N

1



2



Of the Raman scattering exhibited at low frequencies, the weak line near 300 cm^{-1} is judged by its response to $^{15}N_2/^{14}N_2$ interchange and by its depolarization ratio (at least, in the case of the chromium compound) to approximate to the M–N stretching fundamental of the new species. Here too there is, in principle, the possibility of distinguishing the mode of coordination of the N_2 molecule, depending on whether the unsymmetrically labeled ligand $^{14}N^{15}N$ gives rise to one or two M–N stretching modes; a highly plausible demonstration of this strategy is afforded, for example, by the Fe–O stretching region in the resonance Raman spectrum of oxyhemerythrin.[29] Although the scattering near 300 cm^{-1} exhibits a $^{14}N_2/^{15}N_2$ isotopic shift of 6.6–8.4 cm^{-1}, its width at half-height was typically at least 7 cm^{-1}, and with the chromium compound there were also signs of a doublet structure even with isotopically pure components. In these circumstances it was scarcely feasible to evaluate properly the effect of using dinitrogen mixtures relatively rich in $^{14}N^{15}N$. On the other hand, we remark that the a_{1g} M–C stretching mode of an $M(CO)_6$ molecule (M = Cr, Mo, or W) appears to vary in frequency in direct proportion to $1/m_{CO}{}^{1/2}$, where m_{CO} is the *total* mass of the CO ligand.[30] With its implication that the CO group functions as an essentially rigid unit, at least with respect to M–C stretching, this observation tends seriously to weaken the practical impact of measurements involving isotopically unsymmetrical ligands like $^{14}N^{15}N$, making it all the more striking that the frequency of the feature associated with Fe–O stretching in the resonance Raman spectrum of oxyhemerythrin[29] should appear on ^{18}O substitution to be sensitive primarily to the mass of the substituent directly linked to the metal atom.

(ii) To prove that the carbonyl part of the molecule contains five carbonyl groups and conforms to C_{4v} symmetry we have recourse to an analysis of the infrared-active C–O stretching modes of all the species $Mo(^{12}CO)_x(^{13}CO)_{y-x}N_2$ (x = 0–y); the details of this analysis are treated in the next section. It may be noted, however, that establishment of C_{4v} symmetry for the $M(CO)_5$ part of the molecule implies, even if it does not strictly require, a linear rather than a triangular MN_2 unit. Indeed, no compelling evidence has been presented to date to suggest that any of the mononuclear metal complexes of dinitrogen characterized by matrix isolation possess triangular MN_2 units; even the claim that such a unit exists in the species alleged to be CoN_2 has been informed by second thoughts.[31]

4. Analysis of Infrared-Active C–O Stretching Modes of the Photoproduct Formed by $Mo(CO)_6$

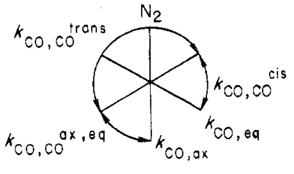
There is now a well-established procedure[32] for the analysis of the vibrational frequencies and relative intensities of the infrared absorptions due to the C–O stretching modes of a set of isotopic molecules $M(^{12}CO)_x(^{13}CO)_{y-x}$ to elucidate the value of y and the symmetry of the binary carbonyl $M(CO)_y$, as well as to give quantitative estimates of bond angles not constrained by the molecular point group. To extend these studies, and in particular related analyses of the pentacarbonyls $M(CO)_5$ (M = Cr, Mo, or W),[15] to the case of $Mo(CO)_5N_2$ requires an understanding of the likely influence of the N_2 unit on both the force field analysis and the relative band intensities calculated for the C–O stretching modes of the molecule. Since the free ligand has a reduced mass, force constant, and electronic structure comparable to those of CO, we may expect N_2 to behave in many ways like a carbonyl ligand, albeit with distinctive properties.

Photolysis of ^{13}CO-enriched $Mo(CO)_6$ trapped in solid nitrogen produces a very complex set of bands in the region 1900–2300 cm^{-1} associated with the products $Mo(^{12}CO)_x$-$(^{13}CO)_{y-x}N_2$, the details being summarized in Table III. If

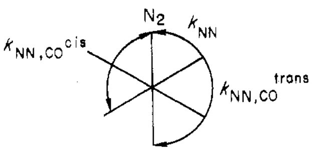
Table III. Observed and Calculated C–O Stretching Frequencies (in cm^{-1}) for $Mo(CO)_5N_2$ Isolated in an N_2 Matrix at 20 K

Frequency		Sym-		Point
Obsd[c]	Calcd	metry	Isotopic molecule	group
2092.8[a]	2092.6	a_1	$Mo(^{12}CO)_5(N_2)$	C_{4v}
2012.2[b]	2011.1	b_1		
1978.2[a]	1978.2	e		
1964.4[a]	1965.0	a_1		
n	2089.2	a_1	$Mo(^{12}CO)_4(^{13}CO)(N_2)$	C_{4v}
i	2011.1	b_1		
1978.2[a]	1978.2	e		
n	1924.3	a_1		
2085.0	2084.9	a′	$Mo(^{12}CO)_4(^{13}CO)(N_2)$	C_s
n	2004.7	a′		
1978.2[a]	1978.2	a″		
1965.7	1966.0	a′		
n	1946.6	a′		
2081.7	2081.2	a′	$Mo(^{12}CO)_3(^{13}CO)_2(N_2)$	C_s
n	2004.6	a′		
1978.2[a]	1978.2	a″		
1949.4	1949.3	a′		
1922.2	1922.9	a′		
2076.5	2077.0	a_1	$Mo(^{12}CO)_3(^{13}CO)_2(N_2)$	C_{2v}
n	1986.2	a_1		
1978.2[a]	1978.2	b_1		
1959.8	1959.9	a_1		
1933.8	1934.1	b_2		
2075.4	2075.6	a′	$Mo(^{12}CO)_3(^{13}CO)_2(N_2)$	C_s
2000.0	1999.9	a″		
1966.7	1966.9	a′		
1948.1	1948.1	a′		
1944.8	1944.9	a″		
2072.6	2073.1	a_1	$Mo(^{12}CO)_2(^{13}CO)_3(N_2)$	C_{2v}
n	1983.5	a_1		
1978.2[a]	1978.2	b_2		
1933.8	1934.1	b_1		
n	1922.5	a_1		
2070.6	2071.5	a′	$Mo(^{12}CO)_2(^{13}CO)_3(N_2)$	C_s
2000.0	1999.9	a″		
1953.5	1953.1	a′		
1944.8	1944.9	a″		
1921.5	1921.9	a′		
2065.4	2065.7	a′	$Mo(^{12}CO)_2(^{13}CO)_3(N_2)$	C_s
n	1984.5	a′		
1959.8	1960.1	a′		
1947.0	1946.3	a′		
1933.8	1934.1	a″		
2060.4	2061.0	a′	$Mo(^{12}CO)(^{13}CO)_4(N_2)$	C_s
n	1982.5	a′		
n	1947.4	a′		
1933.8	1934.1	a″		
1921.5	1921.6	a′		
2052.5	2052.3	a_1	$Mo(^{12}CO)(^{13}CO)_4(N_2)$	C_{4v}
i	1966.3	b_1		
1959.3	1959.0	a_1		
1933.8	1934.1	e		
2045.5	2045.9	a_1	$Mo(^{13}CO)_5(N_2)$	C_{4v}
i	1966.3	b_1		
1933.8	1934.1	e		
1920.6	1921.2	a_1		

[a] Averaged frequency for band exhibiting multiplet structure. Attempts to eliminate this splitting by annealing the matrix were found to be counterproductive. [b] Infrared inactive; observed only in Raman scattering. [c] Key: i, infrared inactive; n, not observed.



3



4

the presence of the N_2 unit is simply ignored and the frequencies in the C–O stretching region are treated as arising purely via vibrations of the $M(CO)_y$ fragment, these isotopic results are readily accommodated[33] assuming that $y = 5$ and using the frequency-factored force field of **3** with the methods developed previously.[15] The standard deviation between observed and calculated frequencies is 0.33 cm^{-1} for the force constants given in Table IV. Such excellent agreement is typical of the results obtained using this approach. An important check on the method is also provided by comparing the frequency of 2012.2 ± 0.4 cm^{-1} observed for the Raman-active (infrared-inactive) b_1 vibration of $Mo(^{12}CO)_5N_2$ with the value of 2011.1 cm^{-1} predicted using the force field defined by the infrared-active modes. Again the agreement is highly satisfactory. In addition, the isotopic intensity pattern is well matched by the C_{4v} model and is very different from that expected for a trigonal-bipyramidal geometry.

As we show elsewhere,[34] leaving the N_2 ligand out of the vibrational problem in this way is expected to accommodate well the observed frequencies but in terms of force constants and eigenvectors which do not accurately represent the coupling between the various internal coordinates. This is important when we consider infrared intensities, the interpretation of which is complicated by the inclusion of the N_2 oscillator in the frequency-factored force field. **4** shows that there are, in addition to a diagonal NN stretching force constant, two interaction force constants linking the NN unit to axial and equatorial CO groups. Experimentally, however, the facts are as follows.

(i) Only the high-frequency a_1 vibration of the $Mo(CO)_5$ unit shows a (small) shift in frequency—being reduced by 2.6 cm^{-1}—when $^{15}N_2$ is substituted for $^{14}N_2$, thereby vouching for vibrational mixing between the CO and N_2 groups.

(ii) The N–N stretching mode suffers no change of frequency when the carbonyl part of the molecule undergoes isotopic change, although a small shift would be difficult to detect in view of the weakness and multiplet character of this absorption for nitrogen matrices and its diffuseness for mixed matrices.

These findings, combined with the measurements of the $^{14}N_2/^{15}N_2$ frequency shift, provide us with enough information to determine only two of the vibrational parameters involving the N_2 group, namely, the diagonal stretching force constant and one interaction force constant. In an earlier determination[9] of the force field of $Ni(CO)_3N_2$ by Kündig, Moskovits, and Ozin, $^{12}C^{16}O/^{12}C^{18}O$ isotopic shifts arising from the carbonyl part of the molecule were observed together with the $^{14}N_2/^{15}N_2$ isotopic shift exhibited by the band associated predominantly with the N–N stretching mode. However, since *no* nitrogen isotopic effects were observed in the C–O stretching region and likewise *no* oxygen isotopic effects in the N–N stretching region, the coupling between the two sorts of ligand was necessarily undetermined. By way of contrast, Rest[8] had previously observed a decrease of 2 cm^{-1} in the frequency of the a_1 C–O stretching fundamental of the same molecule when $^{15}N_2$ replaces $^{14}N_2$. Perhaps the relatively broad bands associated with the product formed by cocondensation of metal atoms with the potential reagents—the method favored by Kündig, Moskovits, and Ozin—had the effect of obscuring a frequency shift of this magnitude.

As an approximation (and we emphasize that in our case it can be only an approximation), we draw on the vibrational solution for the carbonyl part of the molecule, noting that the high-frequency a_1 vibration is located predominantly in the equatorial plane of the molecule, whereas the low-frequency a_1 mode is located mainly in the axial CO ligand. Thus the NN,CO cis interaction force constant may well be susceptible to estimation by reference to the shift induced in the high-frequency a_1 vibration of the $M(CO)_5$ moiety by the isotopic switch of $^{15}N_2$ for $^{14}N_2$, thereby giving some idea of the coupling between the N_2 and CO oscillators. The results of

Table IV. A Summary of the CO and NN Frequency-Factored Force Constants (N m^{-1}) of $Mo(CO)_5N_2$

Model[a]	Rms error/cm^{-1}	$k_{CO,ax}$	$k_{CO,eq}$	$k_{CO,CO}^{ax,eq}$	$k_{CO,CO}^{cis}$	$k_{CO,CO}^{trans}$	k_{NN}	$k_{NN,CO}^{cis}$	$k_{NN,CO}^{trans}$
1	0.40	1519.92	1621.66	38.12	31.63	59.1			
2	0.33	1578	1636	30.28	28.60	55.72			
3	0.36	1597.06	1633.67	41.18	26.04	53.51_5	2076.84	23.89	0.0
4	0.38	1591.04	1634.92	38.34	27.14	54.40	2078.39	16.08	29.78
5	0.37	1590.96	1635.62	36.35	27.76	55.00	2074.85	11.30	53.65

[a] 1, $Mo(CO)_5$ (from ref 15). 2, $Mo(CO)_5N_2$, ignoring N_2 oscillator. 3, $Mo(CO)_5N_2$, $k_{NN,CO}^{trans} = 0$. 4,5, $Mo(CO)_5N_2$, $k_{NN,CO}^{trans}$ allowed to vary.

such a calculation where we have refined the frequencies of $Mo(^{12}CO)_5{}^{14}N_2$, $Mo(^{12}CO)_5{}^{15}N_2$, and one of the ^{13}CO-substituted molecules[35] are shown in Table IV. The root mean square deviations between the observed and calculated frequencies are again small with the assumption of a cis CO,NN interaction force constant comparable in magnitude with, if a little smaller than, the CO,CO interaction force constants. Allowing the trans CO,NN interaction force constant to vary leads, on the other hand, to very different results (sets 4 and 5 of Table IV) depending upon the initial parameters of the refinement process. Hence a clear demonstration is provided that this force constant is just not well defined by the spectroscopic data.

The interaction constant $k_{NN,CO}$ linking the N_2 and CO parts of the molecule contains contributions from two different effects. Firstly, the CO and N_2 internal modes may be vibrationally coupled, leading to a "dilution" of N–N stretching character in the vibration associated predominantly with that motion. On substitution of $^{15}N_2$ for $^{14}N_2$, the isotopic shift then falls short of what it would have been had the mode originated exclusively in N–N stretching. Secondly, even in the absence of such coupling, the ratio $\nu^2(^{14}N_2)/\nu^2(^{15}N_2)$ may not be exactly reproduced by the inverse ratio of the masses of the N_2 groups; for this particular substitution, we have shown elsewhere[20] that anharmonicity is the only factor contributing to the breakdown of the frequency-factored force field, and the interaction constant is then a suitable means of absorbing some of this error. The first effect is probably the more important here, and, according to the spectroscopic data available, the interaction force constant can be estimated on the basis of either (i) the defect in the $^{14}N_2/^{15}N_2$ isotopic shift alone (as in the analysis of $Ni(CO)_3N_2$ by Kündig, Moskovits, and Ozin[9]) or (ii) this defect *plus* the observed shifts in the high-frequency C–O stretching region (as in this work).

Additional information about the force field appropriate to the high-frequency fundamentals of the molecule $Mo(CO)_5N_2$ is to be gained from the polarization properties of the Raman scattering in the region 1900–2300 cm^{-1}. Calculations along the lines described by Bigorgne[36] lead us to expect, in the event of minimal coupling between the N_2 and CO oscillators, that the two a_1 modes corresponding to ν(N–N) and the higher in frequency of the ν(C–O) vibrations should give rise to strongly polarized Raman lines (i.e., each with a depolarization ratio, $\rho < 0.1$), whereas the lower in frequency of the two a_1 ν(C–O) modes should give rise to a Raman line that is virtually depolarized ($\rho = 3/4$). Such a pattern complies, for example, with the Raman spectrum measured for $Mn(CO)_5Br$.[37] On the other hand, the depolarization ratios measured for the three a_1 modes of $Mo(CO)_5N_2$ [ν(N–N), $\rho = 0.26$; ν(C–O), $\rho = 0.56$ and 0.71, in order of decreasing frequency] are manifestly at odds with these expectations, and so it would appear that the premise of minimal interaction between the CO and N_2 oscillators cannot be sustained. With allowance for NN,CO interaction, employing for example model 3 of the approximate analysis we have described (see Table IV), it is possible to use Bigorgne's approach[36] to calculate any one of the depolarization ratios of the three Raman lines due to the high-frequency a_1 fundamentals given the depolarization ratios of the other two lines. Hence we calculate a value of $\rho = 0.60 \pm 0.07$ for the lower in frequency of the two a_1 C–O stretching modes assuming $\rho = 0.26$ and 0.56 for the two lines at higher frequency. In view of the experimental errors and approximations involved, this compares satisfactorily with the measured value of 0.71 ± 0.05, thereby providing further vindication of the self-consistency of the approximate frequency-factored force field.

In summary, we draw the following conclusions. (i) An excellent fit is obtained for the frequencies of ^{13}CO-substituted versions of the photoproduct derived from molybdenum hexacarbonyl on the basis of a square-pyramidal $Mo(CO)_5$ unit, consistent with our assignment of the new species to a pseudooctahedral molecule $Mo(CO)_5N_2$ belonging to the C_{4v} point group. (ii) The part of the force field containing NN,CO interactions is underdetermined but an approximation is possible. The significance of this becomes clearer in the next section where we discuss the use of these results, in conjunction with the relative intensities measured for the infrared absorptions, to determine the angle subtended by the axial and equatorial carbonyl groups in the new molecule.

5. Determination of the Bond Angle OC_{ax}–Mo–CO_{eq} in the Molecule $Mo(CO)_5N_2$

The intensity of an infrared absorption band is proportional to the following sum over the vectorial contributions in the molecule-fixed directions x, y, and z:

$$I \propto \left[\sum_{g=x,y,z} \sum_i \sum_j L_{ik} U_{ij} \left(\frac{\partial \mu_g}{\partial R_j} \right) \right]^2 \qquad (2)$$

Here $\partial\mu_g/\partial R_j$ is the dipole moment derivative at equilibrium in the gth direction with respect to the jth internal coordinate R_j. The internal coordinates (R) are related to symmetry coordinates (S) by $\mathbf{R} = \mathbf{U}^{-1}\mathbf{S}$ and the symmetry coordinates (S) are related in turn to the normal coordinates (Q) by the eigenvectors $\mathbf{S} = \mathbf{L} \cdot \mathbf{Q}$. When considering the relative intensities of the infrared bands in the carbonyl stretching region of metal carbonyls, it is frequently a good approximation to ignore coupling between the CO internal coordinates and other internal coordinates, though strictly the analysis refers to the M—C≡O unit as a whole.[32] We employ then the approximation of a localized dipole moment derivative, assuming that the derivative ($\mu'_{CO,ax}$, $\mu'_{CO,eq}$, and μ'_{NN}) lies parallel to the M—C≡O or M—N≡N vector and that the force field is well represented by the frequency-factored model. The errors and approximations of this strategy are discussed elsewhere;[32,34] suffice it to say that for metal carbonyl fragments such methods appear to give realistic structural parameters. In the present context, however, we wish to investigate the influence of the N_2 group on the calculation.

For this system we use the model **5** and define the symmetry and internal coordinates as in Chart I. Because S_4 corresponds to a unique mode, L_{44} is equal to $\mu_{CO}^{1/2}$ (since $\mathbf{L} \cdot \tilde{\mathbf{L}} = \mathbf{G}$, the Wilson G matrix), and it follows that the intensity of the associated infrared absorption is given by

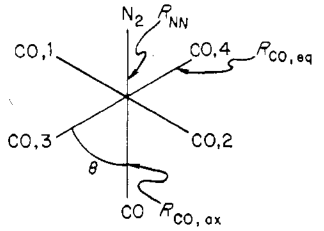
$$I(e) \propto 4\mu_{CO}\mu'_{CO,eq} \sin^2 \theta \qquad (3)$$

Table V. Geometry of $Mo(CO)_5N_2$ as Deduced from the Intensities of the High-Frequency Infrared Absorptions

System	Solution[a]	$\mu'_{NN}/\mu'_{CO,eq}$	$\mu'_{CO,ax}/\mu'_{CO,eq}$	OC_{ax}-Mo-Co_{eq} bond angle, θ°	Comments
$Mo(CO)_5$	1		1.163	90.94	CO oscillators in phase
			0.935	107.42	CO oscillators out of phase
$Mo(CO)_5N_2$, carbonyl part of molecule only	2		1.118	85.65	CO oscillators in phase
			0.763	111.69	CO oscillators out of phase
$Mo(CO)_5N_2$, with inclusion of the N_2 oscillator	3	0.355	1.092	88.05	CO oscillators in phase; CO/NN in phase
		0.421	1.069	91.68	CO oscillators in phase; CO/NN out of phase
	4	0.244	0.939	87.32	CO oscillators in phase; CO/NN in phase
		0.415	0.883	90.27	CO oscillators in phase; CO/NN out of phase

[a] See text in conjunction with the appropriate force field as defined in Table IV.

Chart I



5

Symmetry class	
a_1	$\begin{cases} S_1 = R_{NN} \\ S_2 = {}^1/_2(\Sigma R_{CO,eq}) \\ S_3 = R_{CO,ax} \end{cases}$
e	$S_4 = 2^{-1/2}(R_{CO,1} - R_{CO,2})$
b_1	$S_5 = {}^1/_2(R_{CO,1} + R_{CO,2} - R_{CO,3} - R_{CO,4})$

where μ_{CO} is the reciprocal of the reduced mass of the CO group, not to be confused with $\mu'_{CO,eq}$, the dipole moment derivative appropriate to the equatorial CO bonds. We have assumed, it should be emphasized, that the dipole moment derivative of an equatorial CO bond is located along the MCO vector. Because of the molecular symmetry the dipole moment derivatives for the NN and axial CO groups are parallel to the figure axis. The three a_1 modes mix together, and the general expression for the intensity of one of the infrared bands to which they give rise is

$$I(i) \propto (L_{i1}\mu'_{NN} + L_{i2}\mu'_{CO,ax} + 2L_{i3}\mu'_{CO,eq}\cos\theta)^2 \qquad (i = 1, 2, \text{or } 3) \tag{4}$$

where we expect that the "N–N stretching" mode will be dominated by L_{11} and that the two a_1 "C–O stretching" modes will likewise be dominated by the elements L_{22} and L_{33}. Measurement of the relative intensities of the four infrared-active bands provides us with three observable quantities, and a knowledge of the L_{ij} elements given by the solution of the force field allows us, in principle, to determine the values of the three parameters $\mu'_{NN}/\mu'_{CO,eq}$, $\mu'_{CO,ax}/\mu'_{CO,eq}$, and θ. In practice, we need to decide the relative phases of the three intensities since square roots of the intensity ratios are used, and herein lies an ambiguity in sign.

If we ignore coupling between the NN and CO coordinates, then this is tantamount to putting $f_{CO,NN}^{cis} = f_{CO,NN}^{trans} = 0$ implying that $L_{32} = L_{23}$ and $L_{33} = L_{22}$. The bond angle is simply obtained as

$$\theta = \tan^{-1} [R_2^{1/2}/(L_{22}R_1^{1/2} - L_{23})] \tag{5}$$

where $R_1 = I(2)/I(e)$ and $R_2 = I(3)/I(e)$. Using observed values of $R_1 = 0.231$ and $R_2 = 3.846$ (relative to $I(3) = 1$) and the refined force field specified in Table IV (set 2), we calculate the values of θ and $\mu'_{CO,ax}/\mu'_{CO,eq}$ given in Table V. The in-phase solution represents the situation where the roots of R_1 and R_2 have the same parity and the out-of-phase solution represents the case where they are of opposite parity. The experience of the previous analysis[15] of $Mo(CO)_5$ suggests that the only way to differentiate between the two solutions is to calculate the intensities of all the infrared-active C–O stretching bands for the isotopic species $Mo(^{12}CO)_x(^{13}CO)_{5-x}N_2$ and to compare the results with the experimental intensity patterns. As with $Mo(CO)_5$ itself, so also with $Mo(CO)_5N_2$ does the in-phase solution give a much better account of the observed intensities than does the out-of-phase solution. We have established[34] that the in-phase solution is appropriate to these circumstances, whereas for C_{2v} molecules like $Fe(CO)_4$[38] and *cis*-$Mo(CO)_4(N_2)_2$,[11,39] the out-of-phase solution is predicted[34] and observed[38,39] to be the correct one. The bond angle of 85.65° implied by the in-phase solution is similar to those calculated for the molecules $Mo(^{12}CO)_5{}^{13}CO$[40] and $Cr(CO)_5CS$[41] by ignoring the vibrational contributions of the ^{13}CO and CS groups, respectively. In the hexacarbonyl of course the true bond angle is 90°; to determine whether $Mo(CO)_5N_2$ and $Mo(CO)_6$ are vibrationally and structurally akin or whether the true bond angle in $Mo(CO)_5N_2$ departs significantly from 90°, we need to accommodate the NN oscillator, if only by an approximate force field. Table IV presents three choices. The force constants of sets 4 and 5 may not accurately represent the real state of affairs in view of the ill-defined nature of the trans NN,CO interaction constant; the sets do serve, however, as a useful test of the effect of including force constants of this magnitude, and some selected results of such calculations are featured in Table V. There are now six possible phase combinations when the N_2 oscillator is included. For the reasons already alluded to, we may exclude combinations which do not maintain the in-phase solution of the carbonyl part of the molecule, but we are unable to distinguish between the carbonyl dinitrogen in-phase and out-of-phase solutions. Both give bond angles close to 90°. If we allow a 50% error in the measurement of $I(1)/I(e)$, then

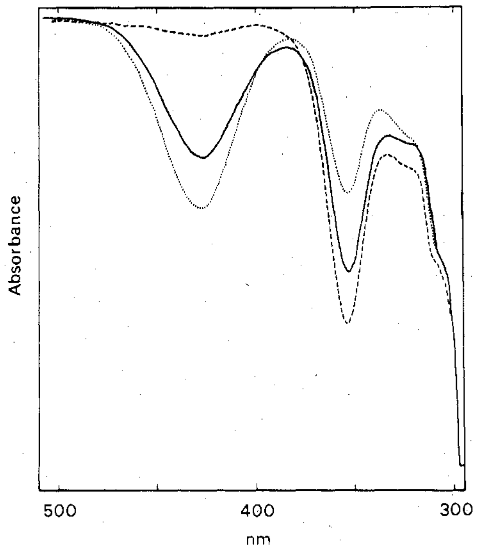


Figure 4. Illustration of the interconversion of $Mo(CO)_6$, $N_2Mo(CO)_5$ (λ_{max} in UV, 352 nm), and Ar···$Mo(CO)_5$ (λ_{max} 429 nm). Photolysis of $Mo(CO)_6$ in an Ar/N_2 (1:1) matrix with (i) λ 314 nm (—, 30 min), followed by (ii) λ 367 nm (···, 45 min), followed by (iii) λ 432 nm (---, 30 min).

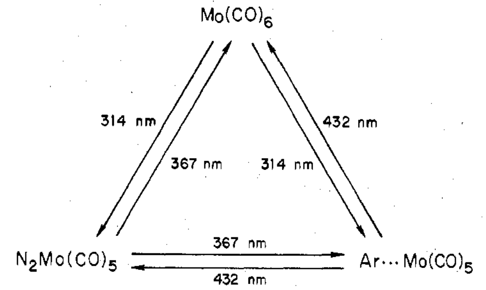
the resultant error in θ is negligibly small, but $\mu'_{NN}/\mu'_{CO,eq}$ changes by 0.11. Allowing a similarly pessimistic error in the measurement of $I(2)/I(e)$ or $I(3)/I(e)$ leads to errors of 2.5° in the estimate of θ and changes of ca. 0.03 in the values of $\mu'_{NN}/\mu'_{CO,eq}$ and $\mu'_{CO,ax}/\mu'_{CO,eq}$. Thus, incorporation in the force field of the coordinated dinitrogen ligand gives an OC_{ax}–Mo–CO_{eq} bond angle closer to 90°. Including both in-phase and out-of-phase carbonyl dinitrogen solutions produces an estimate of 90 ± 4°, even with a pessimistic view of the likely error limits. The comparatively large magnitude of the ratio $\mu'_{NN}/\mu'_{CO,eq}$ implied by the calculations reflects the appreciable intensity in infrared absorption of the mode principally involving N–N stretching; it is also a sign that the N_2 functions as a η^1 rather than a η^2 ligand.

6. Electronic Spectrum and Photochemistry of $Mo(CO)_5N_2$

On the evidence of our experiments, ultraviolet photolysis of a hexacarbonyl $M(CO)_6$ (M = Cr, Mo, or W) suspended in solid nitrogen or in nitrogen/argon or nitrogen/methane mixtures generates the molecule $M(CO)_5N_2$. The ultraviolet/visible spectra of these species have been found to consist of two intense bands in the ultraviolet and a weaker band in the near-ultraviolet region at 352 nm for M = Mo or 364 nm for M = Cr (see Figure 4). Nasielski and Wyart[14] observed that photolysis of a cyclohexane solution of $Cr(CO)_6$ at room temperature under a nitrogen atmosphere gives a transient species characterized by absorptions in the infrared (weakly) at ca. 1970 cm^{-1} and in the near-ultraviolet at 370 nm. Since we also find that the strongest infrared band of $Cr(CO)_5N_2$ isolated in solid nitrogen occurs at 1977 cm^{-1}, there are good reasons for identifying this transient species as $Cr(CO)_5N_2$.

We have already commented on the photochemical reversal of the reaction leading from the hexacarbonyl to the species $M(CO)_5$ and CO (eq 1). A similar reversal occurs with irradiation at wavelengths corresponding to the absorption band near 360 nm of $M(CO)_5N_2$. The photochemical interrelationship between the various species can be summarized in Scheme I which relates to $Mo(CO)_5N_2$ in a matrix comprising an N_2/Ar mixture. Detailed investigations of the photochemistry using polarized light[42] for both photolysis and spectroscopic measurements suggest that the intermediate $[M(CO)_5{}^*]$ (M = Cr or Mo) is generated from all three

Scheme I



species in the primary photochemical step. This excited molecule relaxes via a D_{3h} configuration to the C_{4v} ground state with an orientation which may be the same as, or different from, that of the parent molecule. The "rotation" of the $M(CO)_5$ group thus envisaged allows the sixth coordination site to scan the matrix environment and to "collect" CO, Ar, or N_2.[18,23,42] The apparent direction of the photochemical change is simply a consequence of the match or mismatch of the photolyzing radiation to the absorption properties of the species being considered.

Irradiation at wavelengths corresponding to the more intense ultraviolet bands of $M(CO)_5N_2$ produces further photochemical changes with the creation of molecules such as $M(CO)_4(N_2)_2$ and the coordinatively unsaturated $M(CO)_4N_2$. These products and also the species generated in experiments involving the cocondensation of metal atoms with CO/N_2 mixtures will be discussed in another paper.[11]

Experimental Section

Infrared experiments were carried out in Newcastle upon Tyne and Raman experiments more-or-less independently in Oxford. The principal features of the experiments corresponded to what has now become a relatively familiar pattern.[43] In outline, however, deposition of the samples from the vapor phase took place on a surface cooled to 8–30 K by means of a Displex refrigerator (Air Products, Model CS 202) incorporated in a conventional high-vacuum system operating at a pressure less than 10^{-7} Torr. For Raman studies a polished high-purity copper block provided a satisfactory deposition surface, whereas infrared measurements utilized a CsI window. Temperatures were measured with a chromel vs. iron-doped gold thermocouple or with a hydrogen vapor bulb; the assembly was equipped with an automatic temperature controller for the infrared measurements.

Metal hexacarbonyls (B.D.H. or Alfa), matrix gases (British Oxygen, grade "X"), and ^{15}N-enriched nitrogen (Onia, 31.3 atom % ^{15}N and Prochem, 95 atom % ^{15}N) were used without further purification. Samples of ^{13}CO-enriched hexacarbonyls were synthesized by gas-phase photolysis, the vapor of the hexacarbonyl, ^{12}CO and ^{13}CO (Prochem, 90% ^{13}CO), being photolyzed for 15 h using a high-pressure mercury arc, and the product being separated by passing the mixture slowly through a spiral trap held at 77 K. Matrices were formed by pulsed deposition[44] with matrix gas:hexacarbonyl ratios of 2000–3000:1, although some experiments designed to eliminate infrared absorptions due to polymer species entailed matrix ratios of 10 000:1.

The photolysis source was either a Philips HPK 125-W medium-pressure mercury arc (for the infrared experiments) or a Hanovia "Uvitron" 125-W high-pressure mercury arc (for the Raman experiments), in each case used in conjunction with a 4-cm quartz cell containing water to act as a heat filter. No other filter was used for the Raman experiments, but the wavelength of the radiation used in experiments involving measurements of the infrared or ultraviolet–visible spectra was selected using either Balzers interference filters or an Applied Photophysics M300 High Radiance monochromator (access to which was gained via f/4 quartz optics).

Infrared spectra were recorded using a Grubb Parsons "Spectromajor" or a Perkin-Elmer 521 or 125 spectrophotometer and were calibrated with cells containing DBr and DCl which were inserted in the beam before and after sample absorptions in each spectrum. The frequencies of bands were measured by interpolation between bands due to the calibrant using a Ferranti Freescan Digitizer. Such measurements were reproducible within 0.2 cm^{-1} for strong bands and within 0.4 cm^{-1} for weak ones; the resolution was invariably better than 0.5 cm^{-1}. Relative intensities of infrared absorptions were measured in terms of peak heights (if the half-widths were the same) or by tracing the peaks, cutting out, and weighing. The two methods were consistent with each other. Where bands exhibited splitting, all the components were added together to evaluate the intensity. No corrections were made for the finite slit width but the errors quoted are rather larger than is strictly necessary.

The Raman spectra were excited by the output from a Spectra Physics Model 165 Ar^+ laser and measured with a Spex Ramalog 5 spectrophotometer equipped with a third monochromator, an additional facility which provided for a marked enhancement in spectral quality. The wavelength of the exciting radiation was 514.5 nm, and the power levels at the sample were in the order of 200 mW. The atomic emission lines of a He–Ne lamp were superimposed on the spectra, and hence the frequencies of the bands due to the sample were calibrated by interpolation. Using this method, the measured frequencies were reproducible within 0.4 cm^{-1} for sharp lines and within 1 cm^{-1} for more diffuse features. Spectral slit widths of 1–2 cm^{-1} were usually employed.

All calculations were performed on a Hewlett-Packard 2000E computer.

Acknowledgment. We thank the Science Research Council both for grants for the purchase of equipment and for the award of studentships (to G.P.G., M.A.G., and R.F.T.). G.P.G. also acknowledges with gratitude the award of a Research Studentship by Linacre College, Oxford.

Registry No. $Cr(CO)_5N_2$, 34416-63-2; $Mo(CO)_5N_2$, 64364-80-3; $W(CO)_5N_2$, 65045-49-0; $Cr(CO)_6$, 13007-92-6; $Mo(CO)_6$, 13939-06-5; $W(CO)_6$, 14040-11-0; $Mo(^{12}CO)_4(^{13}CO)(N_2)$-$C_{4v}$, 65045-50-3; $Mo(^{12}CO)_4(^{13}CO)(N_2)$-$C_s$, 65084-91-5; $Mo(^{12}CO)_3(^{13}CO)_2(N_2)$-$C_s$ *(fac)*, 65084-92-6; $Mo(^{12}CO)_3(^{13}CO)_2(N_2)$-$C_{2v}$, 65084-93-7; $Mo(^{12}CO)_3(^{13}CO)_2(N_2)$-$C_s$ *(mer)*, 65045-45-6; $Mo(^{12}CO)_2(^{13}CO)_3(N_2)$-$C_{2v}$, 65045-46-7; $Mo(^{12}CO)_2(^{13}CO)_3(N_2)$-$C_s$ *(fac)*, 65084-88-0; $Mo(^{12}CO)_2(^{13}CO)_3(N_2)$-$C_s$ *(mer)*, 65084-89-1; $Mo(^{12}CO)(^{13}CO)_4(N_2)$-$C_s$, 65045-47-8; $Mo(^{12}CO)(^{13}CO)_4(N_2)$-$C_{4v}$, 65084-90-4; $Mo(^{13}CO)_5(N_2)$, 65045-48-9.

References and Notes

(1) (a) A preliminary account of the Raman experiments was presented at the 5th International Conference on Raman Spectroscopy, Freiburg, West Germany, Sept 1976. (b) University of Newcastle upon Tyne. (c) University of Oxford.

(2) J. K. Burdett and J. J. Turner, *Chem. Commun.*, 885 (1971).

(3) J. K. Burdett, M. A. Graham, and J. J. Turner, *J. Chem. Soc., Dalton Trans.*, 1620 (1972).

(4) H. Hüber, E. P. Kündig, M. Moskovits, and G. A. Ozin, *J. Am. Chem. Soc.*, **95**, 332 (1973).

(5) E. P. Kündig, M. Moskovits, and G. A. Ozin, *Can. J. Chem.*, **51**, 2710 (1973).

(6) The actual number of coordinated N_2 molecules reported in ref 2 and 3 was wrongly assessed; it was corrected by the authors of ref 4 and 5.

(7) T. C. DeVore, *Inorg. Chem.*, **15**, 1315 (1976).

(8) A. J. Rest, *J. Organomet. Chem.*, **40**, C76 (1972).

(9) E. P. Kündig, M. Moskovits, and G. A. Ozin, *Can. J. Chem.*, **51**, 2737 (1973).

(10) Experiments were easiest to perform with the molybdenum system because of favorable overlap between UV/visible absorption maxima of the reagents and the output of the mercury lamp used for the Raman photolysis experiments.

(11) J. K. Burdett, M. A. Graham, J. J. Turner, and R. F. Turner, unpublished results.

(12) A. J. Downs and G. P. Gaskill, unpublished results.

(13) W. J. Chambers and N. J. Fitzpatrick, *Proc. R. Ir. Acad., Sect. B*, **71**, 97 (1971).

(14) J. Nasielski, private communication; M. Wyart, Thèse, Bruxelles, 1976.

(15) R. N. Perutz and J. J. Turner, *Inorg. Chem.*, **14**, 262 (1975). A report (E. P. Kündig and G. A. Ozin, *J. Am. Chem. Soc.*, **96**, 3820 (1974)) postulating a trigonal bipyramid for the skeleton of the matrix-trapped $M(CO)_5$ species has been shown to be a false alarm (J. K. Burdett, M. A. Graham, R. N. Perutz, M. Poliakoff, A. J. Rest, J. J. Turner, and R. F. Turner, *ibid.*, **97**, 4805 (1975)).

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

(17) M. A. Graham, M. Poliakoff, and J. J. Turner, *J. Chem. Soc. A*, 2939 (1971).

(18) J. K. Burdett, R. N. Perutz, M. Poliakoff, and J. J. Turner, *Pure Appl. Chem.*, **49**, 271 (1977).

(19) R. Poilblanc and M. Bigorgne, *Bull. Soc. Chim. Fr.*, 1301 (1962); R. J. H. Clark and B. C. Crosse, *J. Chem. Soc. A*, 224 (1969); C. Jeanne, R. Pince, and R. Poilblanc, *Spectrochim. Acta, Part A*, **31**, 819 (1975); S. F. A. Kettle, I. Paul, and P. J. Stamper, *J. Chem. Soc., Dalton Trans.*, 2413 (1972).

(20) J. K. Burdett, M. Poliakoff, J. A. Timney, and J. J. Turner, to be submitted for publication.

(21) There is plenty of evidence substantiating the "reversible" and "irreversible" formation of $M(CO)_y$ fragments. See ref 32 for example.

(22) R. N. Perutz, Ph.D. Thesis, University of Cambridge, 1974.

(23) J. K. Burdett and J. J. Turner, "Cryochemistry", M. Moskovits and G. A. Ozin, Ed., Wiley, New York, N.Y., 1976, p 493.

(24) P. Kündig, M. Moskovits, and G. A. Ozin, *J. Mol. Struct.*, **14**, 137 (1972); E. P. Kündig, D. McIntosh, M. Moskovits, and G. A. Ozin, *J. Am. Chem. Soc.*, **95**, 7234 (1973); L. A. Hanlan, H. Huber, E. P. Kündig, B. R. McGarvey, and G. A. Ozin, *ibid.*, **97**, 7054 (1975).

(25) M. Poliakoff and J. J. Turner, *J. Chem. Soc., Dalton Trans.*, 1351 (1973).

(26) D. Sellmann, *Angew. Chem., Int. Ed. Engl.*, **13**, 639 (1974); A. D. Allen, R. O. Harris, B. R. Loescher, J. R. Stevens, and R. N. Whiteley, *Chem. Rev.*, **73**, 11 (1973).

(27) See for example M. S. Quinby and R. D. Feltham, *Inorg. Chem.*, **11**, 2468 (1972); S. Pell, R. H. Mann, H. Taube, and J. N. Armor, *ibid.*, **13**, 479 (1974).

(28) G. A. Ozin and A. Vander Voet, *Can. J. Chem.*, **51**, 3332 (1973).

(29) D. M. Kurtz, Jr., D. F. Shriver, and I. M. Klotz, *J. Am. Chem. Soc.*, **98**, 5033 (1976).

(30) L. H. Jones, R. S. McDowell, and M. Goldblatt, *Inorg. Chem.*, **8**, 2349 (1969).

(31) See footnote 12 in ref 7 correcting the earlier claim (G. A. Ozin and A. Vander Voet, *Can. J. Chem.*, **51**, 637 (1973)). We are indebted to a reviewer for disclosing that the origin of the spectroscopic features formerly attributed to CoN_2 is now thought to be Co_2N_2, a species which may well embody simultaneous "side-on" coordination of both metal atoms by the N_2 ligand.

(32) J. K. Burdett, M. Poliakoff, J. J. Turner, and H. Dubost, "Advances in Infrared and Raman Spectroscopy", Vol. 2, R. J. H. Clark and R. E. Hester, Ed., Heyden, London, 1976.

(33) This is a slightly more complex task than with $Mo(CO)_5$ itself since many of the bands were split; accordingly average frequencies of split bands were used in the analysis. No advantage was gained by annealing the matrix.

(34) J. K. Burdett and J. J. Turner, to be submitted for publication.

(35) Inclusion of one of these molecules in the refinement process is essential to ensure that all the carbonyl force constants are well determined.

(36) M. Bigorgne, *Spectrochim. Acta, Part A*, **32**, 1365 (1976).

(37) W. F. Edgell, *Spectrochim. Acta, Part A*, **31**, 1623 (1975).

(38) M. Poliakoff and J. J. Turner, *J. Chem. Soc., Dalton Trans.*, 2276 (1974).

(39) R. F. Turner, Ph.D. Thesis, University of Newcastle upon Tyne, 1976.

(40) M. Poliakoff, private communication.

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

(42) J. K. Burdett, J. M. Grzybowski, M. Poliakoff, J. J. Turner, and R. F. Turner, to be submitted for publication.

(43) See for example H. E. Hallam, Ed., "Vibrational Spectroscopy of Trapped Species", Wiley, London, 1973.

(44) R. N. Perutz and J. J. Turner, *J. Chem. Soc., Faraday Trans. 2*, **69**, 452 (1973).