

The Vibrational Spectrum and Thermodynamic Properties of Nickel Carbonyl

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alloy the central force picture is untenable. He finds that the atoms do not interact directly in pairs and that the major part of the energy of the superlattice arises from electrostatic interactions between the Cu and Zn atoms, which are unequally charged. This difference in charge depends upon the manner of occupation of the neighboring sites of each of the two atoms; it is greatest when they are occupied as in a super-

lattice and least when each atom is surrounded by neighbors of its own species, the atom tending in the latter case to be neutral as in the pure metal. Thus the interaction between any two atoms depends very considerably upon the other atoms which surround them and this is a complete refutation of the central force picture. Mott has suggested an interpretation of the high specific heat of β -brass on this basis.

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The Vibrational Spectrum and Thermodynamic Properties of Nickel Carbonyl

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The infra-red absorption spectrum of nickel carbonyl has been measured in the gas phase from 4 to 23μ , and in the liquid phase from 1 to 8μ . Normal coordinate treatments of both the square and tetrahedral models of the AB_4C_4 molecule have been applied to the infra-red and Raman data; the results give further evidence of the tetrahedral structure of nickel carbonyl. An analysis of the vibrational spectrum has been made, based on the tetrahedral model, and has been applied to the statistical calculation of the entropy, heat capacity, and free energy function.

INTRODUCTION

THE theory of directed valence predicts a tetrahedral structure for a nickel carbonyl molecule consisting of four carbonyl groups singly bonded to a neutral nickel atom.¹ Electron diffraction studies² appear to confirm this structure. However, the observed nickel-carbon distance indicates strong resonance with a structure involving nickel-carbon double bonds, which may or may not tend to alter the tetrahedral configuration. A square configuration has frequently been proposed, in analogy with the known square configuration of quadri-covalent compounds of bivalent nickel.² A qualitative analysis of the Raman spectrum of nickel carbonyl was interpreted as favoring the

square structure;³ however, it has been shown that the selection rules were violated in this analysis.⁴

We have therefore undertaken a quantitative analysis of the vibrational spectrum, including infra-red data, considering both the square and tetrahedral models. It was our hope to obtain a new and independent determination of the structure; indications favoring the tetrahedral configuration were found, but the square con-

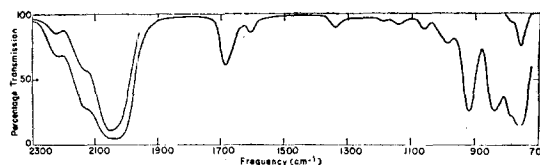


FIG. 1. Absorption spectrum of nickel carbonyl vapor, rocksalt region (20 cm path length, 300 mm pressure).

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¹ L. Pauling, *J. Am. Chem. Soc.* **53**, 1367 (1931).

² L. O. Brockway and P. C. Cross, *J. Chem. Phys.* **3**, 828 (1935).

³ A. B. F. Duncan and J. W. Murray, *J. Chem. Phys.* **2**, 636 (1934).

⁴ E. B. Wilson, Jr., *J. Chem. Phys.* **3**, 59 (1935).

TABLE I. Observed and calculated infra-red active frequencies.

OBSERVED (CM ⁻¹)	INTENSITY	CALCULATED (CM ⁻¹)	ASSIGNMENT	OBSERVED (CM ⁻¹)	INTENSITY	CALCULATED (CM ⁻¹)	ASSIGNMENT
		90	ω_5 (δ)	920	50	920	$\omega_1 + \omega_7$ (ν)
		160	$\omega_3 + \omega_5$ (δ)			960	$\omega_7 + \omega_9$ (δ)
		180	$2\omega_5$ (δ)	990	4	990	$\omega_1 + \omega_3 + \omega_7$
		300	ω_6 (ν)			1000	$\omega_4 + \omega_7$ (δ)
		370	$\omega_3 + \omega_8$ (ν)	1060	1	1060	$\omega_1 + 2\omega_3 + \omega_7$
		390	$\omega_5 + \omega_6$ (ν)			1080	$2\omega_7$ (δ)
475	20	470	$\omega_1 + \omega_5$ (ν)	1140	0	1130	$\omega_1 + 3\omega_3 + \omega_7$
		490	$\omega_3 + \omega_9$ (δ)			1150	$\omega_3 + 2\omega_7$
545	60	510	$\omega_5 + \omega_9$ (δ)	1340	1	1340	$2\omega_4 + \omega_9$
		540	ω_7 (δ)	1590	(liquid)	1590	$\omega_8 - \omega_4$
595	0	550	$\omega_4 + \omega_5$ (ν)	1610	0	1620	$3\omega_7$
		600	$2\omega_6$ (ν)			1630	$\omega_8 - \omega_9$
		610	$\omega_3 + \omega_7$ (δ)	1660	(liquid)		
		630	$\omega_5 + \omega_7$ (δ)	1682	20	1670	$\omega_8 - \omega_1$
680	10	680	$\omega_1 + \omega_6$ (ν)	1740	(liquid)	1750	$\omega_8 - \omega_8$
		720	$\omega_6 + \omega_9$ (ν)			1960	$\omega_8 - \omega_8$
760	70	760	$\omega_4 + \omega_6$ (ν)			1980	$\omega_8 - \omega_3$
790	10	800	$\omega_1 + \omega_9$ (ν)	2050	100	2050	ω_8 (ν)
840	50	840	$\omega_6 + \omega_7$ (ν)			2120	$\omega_3 + \omega_8$ (ν)
		840	$2\omega_9$ (δ)	2150	20	2140	$\omega_5 + \omega_5$ (ν)
		880	$\omega_4 + \omega_9$ (δ)	2230	4	2230	$2\omega_5 + \omega_8$

TABLE II. Assignment of observed Raman active frequencies.

OBSERVED (CM ⁻¹)	INTENSITY	CALCULATED (CM ⁻¹)	ASSIGNMENT
82	100 p	70	ω_3
		90	ω_5
382	20 P	380	ω_1
463	8 D	460	ω_4
601	4	600	$2\omega_6$
718	0	720	$\omega_6 + \omega_9$
833	2	840	$\omega_1 + \omega_4$
872	2	880	$\omega_4 + \omega_9$
913	2	920	$2\omega_4$
1609	0	1620	$\omega_2 - \omega_9$
2043	30 p	2040	ω_2
2132	5	2130	$\omega_2 + \omega_5$
2223	1	2220	$\omega_2 + 2\omega_5$

Data from reference 3; D=depolarized, P=polarized, p=partly polarized.

figuration cannot be conclusively eliminated on the basis of this analysis.

Using the tetrahedral model, a satisfactory assignment of fundamental frequencies was made, and thermodynamic properties calculated.

EXPERIMENTAL

The infra-red absorption in the rocksalt region was studied using the spectrometer at the University of Wisconsin.⁵ The absorption of the liquid was studied from 1 to 8 μ ; that of the

⁵ P. C. Cross and F. Daniels, J. Chem. Phys. 1, 48 (1933). These measurements were made by P. C. Cross, who wishes to express his gratitude to Professor Daniels and to the Wisconsin Alumni Research Corporation for the grant which made possible this study.

vapor from 4 to 14 μ . The absorption of the vapor in the region from 12 to 23 μ was also studied, using the spectrometer at Harvard University.⁶ The absorption curves are given in Figs. 1 to 3. The frequencies of the maxima of the bands are given in Table I; the Raman data of Duncan and Murray³ are summarized in Table II.

After our measurements had been completed, a report of a similar study by Bailey and Gordon appeared.⁷ The agreement between their observations and ours is very satisfactory, although there are some differences. Several of the weak bands which we found are not given by Bailey and Gordon, and their relative intensities for certain bands do not agree with ours. They resolved the band at 680 cm⁻¹ into three components; in our measurements we find some

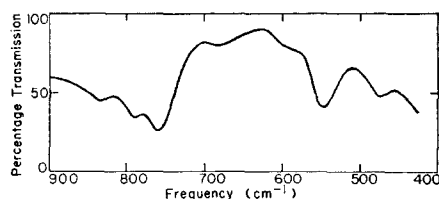


FIG. 2. Absorption spectrum of nickel carbonyl vapor, KBr region (20 cm path length, 200 mm pressure).

⁶ H. Gershinowitz and E. B. Wilson, Jr., J. Chem. Phys. 6, 197 (1938). These measurements were made by B. L. Crawford, Jr., who wishes to thank Professor Wilson and Dr. Gershinowitz for the use of this instrument and for their continued interest in this work.

⁷ Bailey and Gordon, J. Chem. Phys. 6, 225 (1938).

indication of such structure, but of such an uncertain nature that we can attach no significance to it. Certainly the possible side-components are not comparable in intensity to the peak at 680 cm^{-1} .

NORMAL COORDINATE TREATMENT

Both the square and tetrahedral configurations of the molecule AB_4C_4 were treated, using the methods of group theory⁸ in finding the normal coordinates and selection rules. The reduced representations for the internal vibrations were found to be, for the square model (D_{4h}),

$$\Gamma = 2A_{1g} + A_{2g} + 2B_{1g} + 2B_{2g} + E_g + 2A_{2u} + 2B_{2u} + 4E_u.$$

and for the tetrahedral model (T_d),

$$\Gamma = 2A_1 + 2E + 4T_2 + T_1.$$

The normal coordinates for the two models are sketched approximately in Figs. 4 and 5; the selection rules for the fundamentals are also indicated.

Frequency expressions, based upon valence-force type potential energy expressions, were calculated for both models. For the tetrahedral model, the following five-constant potential function was used:

$$2V = K_1 \sum (\Delta R_i)^2 + K_2 \sum (\Delta r_i)^2 + H_1 R^2 \sum (\Delta \alpha_{ij})^2 + H_2 r^2 \sum (\Delta \beta_i)^2 + h R^2 \sum (\Delta \alpha_{ij})(\Delta \alpha_{kl}).$$

Here R_i is the distance from the nickel to the i th carbon atom, r_i the carbon-oxygen distance in the i th CO group, α_{ij} the angle between the i th and j th nickel-carbon bonds ($\alpha_{ij}^0 = 109^\circ 28'$) and β_i the angle between the i th nickel-carbon

and carbon-oxygen bonds ($\beta_i^0 = 180^\circ$). K_1 and K_2 are the force constants for stretching of the nickel-carbon and carbon-oxygen bonds, respectively; H_1 and H_2 are force constants for distortion of the valence angles; h is the constant for interactions between opposite valence angles of the nickel atom, the last summation being taken over the three pairs of opposite angles α_{ij} .

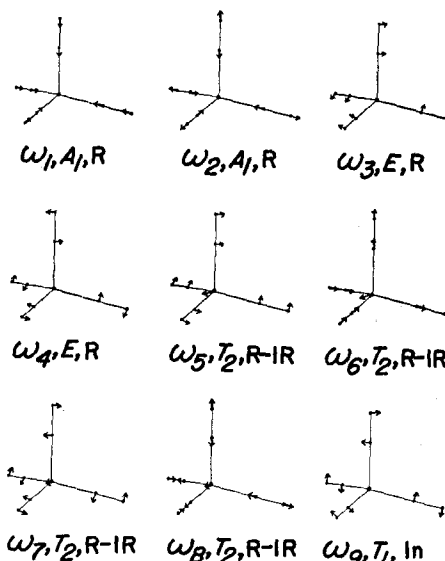


FIG. 4. Approximate modes of vibration of the tetrahedral AB_4C_4 type molecule, T_d .

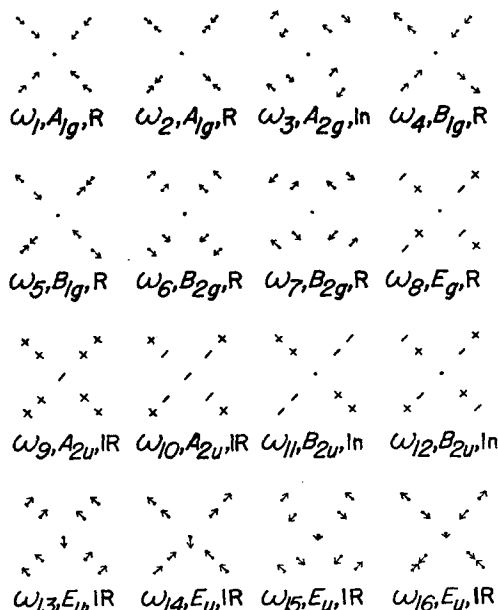


FIG. 5. Approximate modes of vibration of the square AB_4C_4 type molecule, D_{4h} .

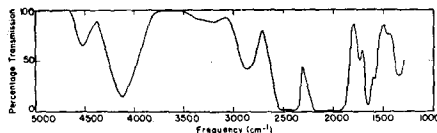


FIG. 3. Absorption of liquid nickel carbonyl (2 mm path length).

⁸ E. Wigner, *Göttinger Nachrichten* (1930), p. 133; E. B. Wilson, Jr., *Phys. Rev.* **45**, 706 (1934); J. E. Rosenthal and G. M. Murphy, *Rev. Mod. Phys.* **8**, 317 (1936). We are grateful to Professor Wilson for making available to us some preliminary work on the AB_4C_4 molecule, and for his suggestions and criticisms.

This potential function leads to the frequency expressions given below, in which $\lambda_i = 4\pi^2 c^2 \omega_i^2$. Fundamentals marked *R* are Raman active, those marked *IR* are infra-red active, and those marked *In*, inactive in both Raman and infra-red.

$2A_1; \omega_1, \omega_2; R(\rho \leq \frac{3}{4})$:

$$\lambda^2 - \lambda[(K_2/m) + (K_1 + K_2)/M] + K_1 K_2 / m M = 0$$

$2E; \omega_3, \omega_4; R$:

$$\lambda^2 - \lambda[(H_2/m) + (3H_1' + f^2 H_2)/M] + 3H_1' H_2 / m M = 0$$

$4T_2; \omega_5, \omega_6, \omega_7, \omega_8; R-IR$:

$$\begin{vmatrix} -3MS\lambda & 2(K_1 - 2H_1'') & -(K_1 + 4H_1'') & QH_2 \\ + (K_1 + 4H_1'') & -QH_2 & -QUH_2 & \\ + NQH_2 & & & \\ \\ (K_1 - 2H_1'') & -3M\lambda & -(K_1 - 2H_1'') & -(2K_2 + H_2) \\ + (K_2 - NH_2) & + 2(K_1 + H_1'') & -U(K_2 - H_2) & \\ \\ W(K_1 + 4H_1'') & -3M\lambda & -W(K_1 + 4H_1'') & 2(K_2 - PH_2) \\ - (K_2 + 2NPH_2) & 2W(K_1 - 2H_1'') & + U(K_2 + 2PH_2) & \\ \\ - (K_2 - NH_2) & - (2K_2 + H_2) & U(K_2 - H_2) & -3m\lambda \\ & & & + 2K_2 + H_2 \end{vmatrix} = 0$$

$T_1; \omega_9; In$:

$$\lambda = H_2(M + mf^2) / m M$$

where

$$\begin{aligned} H_1' &= H_1 + (h/2) & P &= 1 - Wg \\ H_1'' &= H_1 - (h/2) & Q &= 2gSUW \\ f &= (R + r)/R & U &= (M + m)/m \\ S &= M_0/(M_0 + 4M + 4m) & W &= 4m/M_0 \\ N &= 1 + (4MSr/M_0R) \end{aligned}$$

and M_0 , M and m refer to the masses of the *A*, *B*, and *C* atoms, respectively.

Frequency expressions were also calculated for the square model, using a similar potential function (seven constants). Since this model was rejected, it does not seem worth while to give these expressions in detail. Fig. 6, which shows the relation between the frequencies of the tetrahedral and square models, plotted qualitatively on an energy scale, will serve to show approximately the relative magnitudes of the frequencies. It is to be emphasized that this figure is a qualitative one; the actual separations of the levels in the square model will depend on the relative magnitudes of the bending force constants for distortion in the plane of the molecule and perpendicular to this plane.

VIBRATIONAL ANALYSIS

Consideration of the square model

While we have not found conclusive evidence from this analysis against the square configuration, there are certain features of the spectrum which are difficult to reconcile with this model. The strong Raman line at 82 cm^{-1} appears to be, as Duncan and Murray³ describe it, "very broad, unsymmetrical, and of unusually great intensity which suggests that it is complex." This would require, on the basis of the square model, two *g* type frequencies lying near 80 cm^{-1} . This is supported by the appearance of two series of bands; one occurring in the infra-red at 920 ,

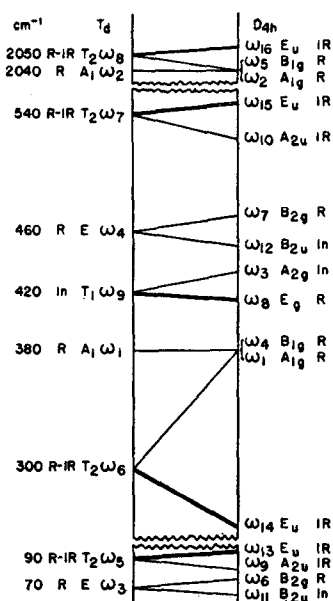


FIG. 6. Relation between the fundamental frequencies of the tetrahedral and square models for nickel carbonyl. The frequencies are located on an energy scale; the magnitudes are noted, in cm^{-1} , for the tetrahedral model; the locations for the square model are *qualitative* only.

990, and 1060 cm^{-1} , and most satisfactorily assigned to combinations involving a g type frequency of 70 cm^{-1} ; and the other occurring in both the infra-red and the Raman spectra, at 2040, 2130, and 2220 cm^{-1} (Raman frequencies), and similarly suggesting a g type frequency of 90 cm^{-1} .

There can be, however, but one g type frequency of this magnitude. The discussion of the Raman data given below in connection with the tetrahedral model applies also to the square configuration; thus the polarized lines at 382 and 2043 cm^{-1} must be assigned to ω_1 and ω_2 , and the low lying frequency of about 80 cm^{-1} to ω_6 . Several choices may be made as to the other assignments of the g type frequencies; we have been unable, however, to find a set of assignments which would give reasonable force constants and yield another g type frequency near 80 cm^{-1} . (See Fig. 6.)

These indications, together with the electron-diffraction evidence, and the satisfactory assignment obtained with the tetrahedral model, have led us to abandon further consideration of the square configuration.

Consideration of the tetrahedral model

The totally symmetric radial frequencies ω_1 and ω_2 should appear in the Raman effect as strong, polarized lines; they must therefore be assigned to 382 and 2043 cm^{-1} . We may regard the broad 82 cm^{-1} line as composed of two components at 70 and 90 cm^{-1} , the frequencies indicated by the series mentioned above. The frequency expressions then favor the assignment $\omega_3 = 70$, $\omega_5 = 90 \text{ cm}^{-1}$. We may then assign ω_4 to the next strongest Raman line, at 463 cm^{-1} ; or we may regard this line as a combination of $\omega_1 + \omega_3$ and assign ω_4 to 601 cm^{-1} . From either assignment we may calculate K_1 , K_2 , H_1' , and H_2 , and hence should be able to calculate the other five frequencies, adjusting the interaction constant h to fit the infra-red spectrum. If we take $\omega_4 = 601$, then we must adjust h to make $\omega_7 = 760$, since the frequency expressions are such that ω_7 must lie above ω_4 (see Fig. 6), and no infra-red band between 600 and 760 cm^{-1} is sufficiently intense to encourage the assignment of a fundamental within that region. This would lead to a value of about 220 cm^{-1} for ω_6 and about 580 cm^{-1} for ω_9 ; these values give no possible fundamental or binary combination for the intense band at 545 cm^{-1} , and hence must be rejected. If we take $\omega_4 = 463 \text{ cm}^{-1}$, on the other hand, we are led to the following force constants:

$$\begin{aligned} K_1 &= 2.52 (10^5) \text{ dynes/cm.} \\ K_2 &= 15.89 \\ H_1 &= 0.089 \\ H_2 &= 0.377 \\ h &= -0.010. \end{aligned}$$

Table III gives the values of the fundamental frequencies thus calculated, and also the assigned values, which are used in the calculation of com-

TABLE III. Fundamental frequencies.

	CALCULATED (cm^{-1})	ASSIGNED (cm^{-1})
ω_1	(382)	380
ω_2	(2043)	2040
ω_3	(70)	70
ω_4	(463)	460
ω_5	110	90
ω_6	310	300
ω_7	(545)	540
ω_8	2050	2050
ω_9	430	420

Frequencies in parentheses were used to determine force constants.

bination frequencies and are to be regarded as the "true" fundamental frequencies of the molecule. The agreement is satisfactory when the approximate nature of the potential function is considered.

TABLE IV. *Thermodynamic values.*

TEMP. (°K)	S^*	$-(F^0 - E_0^0)/T$	C_v
298.1	97.0	73.4	32.8
316.1	99.1	74.8	33.5
350.0	102.7	77.4	34.5
400.0	107.7	80.8	35.8
450.0	112.2	84.1	36.8
500.0	116.4	87.1	37.7

The calculated values for all infra-red active fundamentals, first overtones, and binary combinations which lie below 2250 cm^{-1} are given in Table I, compared with the observed spectrum. (The table also contains calculated values and assignments for certain higher combinations and difference tones, which are needed to completely fit the observations.) If we divide the nine fundamental frequencies approximately into those of "valence" type ($\omega_1, \omega_2, \omega_6, \omega_8$) and those of "deformation" type ($\omega_3, \omega_4, \omega_5, \omega_7, \omega_9$) we find an interesting intensity pattern exhibited in Table I. The combinations which involve at least one valence type component (marked ν in Table I) are more strongly infra-red active than the pure deformation type combinations (marked δ), which indeed are so weak as not to appear. The single real exception to this generalization is the fact that no band is found at 720 cm^{-1} , the calculated value of $\omega_8 + \omega_9$. The possible significance of this intensity pattern is an interesting subject; however, in view of our present inadequate knowledge concerning vibrational intensities, we prefer not to attempt any interpretation.

It will be noted that the difference tones arising from the two low lying fundamentals, with calculated frequencies at 1960 and 1980 cm^{-1} , are not found. This is rather surprising in view of the appearance of other difference tones. It should be pointed out, however, that this is not to be regarded as disagreeing with the particular assignment of frequencies given here; any assignment must include a Raman active frequency

near 80 cm^{-1} , which should give a difference frequency at about 1970 cm^{-1} .

The assignments and calculated frequencies, which account for the Raman spectrum, are given in Table II, together with the observed frequencies.³

The value found for the C—O bond stretching force constant, 15.89×10^5 dyne/cm, lies between the value⁹ associated with the C—O double bond, 12.3×10^5 , and that associated with the C—O triple bond, 18.6×10^5 ; it is very close to the value found in carbon dioxide, 15.24×10^5 . This is in agreement with the resonance hybrid character of the bond suggested by Brockway and Cross² on the basis of the interatomic distances.

Both the C—O and the Ni—C bond force constants, when used in Badger's relation¹⁰ between force constants and interatomic distance, give fairly good agreement: Ni—C distance, calculated 1.85 \AA , observed 1.82 \AA ; C—O distance, calculated 1.17 \AA , observed 1.15 \AA .

THERMODYNAMICS

By standard methods of statistical mechanics, the virtual entropy, free energy function, and heat capacity of nickel carbonyl (perfect gas at 1 atmos. pressure) have been calculated for the temperatures $298.1, 316.1$ (boiling point) $350, 400, 450$, and 500°K . The moments of inertia were calculated from the interatomic distances² Ni—C = 1.82 \AA , C—O = 1.15 \AA ; the product $(ABC) = 5.03 (10^{-112})\text{ g}^3\text{ cm}^6$. The thermodynamic values are given in Table IV.

In view of the fact that several of the fundamentals, including the low lying frequencies, were not directly observed, but assigned on the basis of combination assignments and frequency calculations, these thermodynamic values cannot be taken as highly accurate. After considering the effects of various frequency changes, however, we believe that the error is not greater than 2 percent in the entropy and free energy function, and somewhat less in the heat capacity.

⁹ H. W. Thompson and J. W. Linnett, J. Chem. Soc. 1384 (1937).

¹⁰ R. M. Badger, J. Chem. Phys. 3, 710 (1935).