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should be slightly larger than  $(\partial E/\partial V)_T$  which at zero pressure is equal to  $T(\partial p/\partial T)_V$ . Now the value of  $dE_p/dV$  used is only slightly larger than  $T(\partial p/\partial T)_V$ ; it seems likely that  $dE_p/dV$  should be increased rather than decreased, and this would actually increase  $|\delta C_p|$ , so that  $|\eta|$  would have to be increased less. The use of values at the normal melting temperatures and volumes gives a slight overestimate for  $|\delta C_p|$ , which might mean that  $|\eta|$  should be increased by a little more than 40 percent, but this effect is not very great.

Another quantity which occurs in the deriva-

tives of  $\eta$  which is not entirely directly determined experimentally is  $E_{t.c.}$ . We have also used the calculated rather than the experimentally determined value of  $C_{v.c.}$ . However, it does not appear that any possible change in these quantities could clear up the discrepancy.

On the other hand, it appears likely that the discrepancy is too great to be accounted for on the basis of deviations from the law of corresponding states.

We are, therefore, forced to leave the question of the quantum correction for neon in a somewhat unsatisfactory state.

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## The Raman Spectrum and Structure of Nickel Carbonyl\*

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A redetermination of the depolarization factors of the Raman lines of nickel carbonyl shows the presence of only two polarized lines instead of three, as previously reported by other investigators. The data obtained not only eliminate the only evidence against the tetrahedral structure for this molecule but supply additional evidence in its favor.

ALTHOUGH the molecular structure of nickel carbonyl has been investigated several times, no clear-cut decision as to its configuration has been arrived at. The present status of the problem is well summarized by Herzberg,<sup>1</sup> who lists the structure of this molecule as tetrahedral, but adds in a footnote, "It must be mentioned that there is a serious discrepancy between this structure and the observed Raman spectrum in that the three strongest Raman lines are polarized whereas on the tetrahedral model there are only two totally symmetrical vibrations."

Raman spectra of nickel carbonyl were obtained by Dadiou and Schneider<sup>2</sup> and by Ander-

son,<sup>3</sup> but the only conclusion that could be reached from the evidence of these investigations was that the intact carbon monoxide group was present in nickel carbonyl rather than the organic carbonyl group. A more complete investigation of the Raman spectrum was performed by Duncan and Murray.<sup>4</sup> The data were interpreted on the basis of a planar square structure, a structure which these authors incorrectly ascribed to Pauling.<sup>5</sup> On the basis of the directed theory of valence, Pauling predicted that the complexes of *bivalent* nickel should have a planar configuration, but on the basis of the same theory complexes of *neutral* nickel should have a tetrahedral structure. Not only was the theoretical basis for the planar structure as used by Duncan and Murray incorrect, but, as Wilson<sup>6</sup> pointed out shortly afterwards, the assignment was invalid since they had

\* A portion of the thesis submitted by William Horwitz in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Minnesota, August 1947.

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<sup>1</sup> G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945), p. 356.

<sup>2</sup> A. Dadiou and F. A. Schneider, *Akad. Wiss. Wein* **68**, 191 (1931).

<sup>3</sup> J. S. Anderson, *Nature* **130**, 1002 (1932).

<sup>4</sup> A. B. F. Duncan and J. W. Murray, *J. Chem. Phys.* **2**, 536 (1934).

<sup>5</sup> L. Pauling, *J. Am. Chem. Soc.* **53**, 1367 (1931).

<sup>6</sup> E. B. Wilson, Jr., *J. Chem. Phys.* **3**, 59 (1935).

TABLE I. The Raman data of nickel carbonyl.\*

Frequency cm <sup>-1</sup>	Relative intensity	Depolarization factor	Assign- ment**
79±1 (10)	100	0.86±0.07 (18)	$\begin{cases} \omega_3 \\ \omega_5 \end{cases}$
381±4 (8)	25	~0.01 (17)	$\omega_1$
461±3 (4)	10	0.83±0.11 (5)	$\omega_4$
598 (2)	3	<0.4 (1)	$2\omega_6$
2039±5 (9)	47	0.73±0.06 (18)	$\begin{cases} \omega_2 \\ \omega_8 \end{cases}$
2121±7 (4)	3	<0.4 (1)	$\omega_8 + \omega_5$

\* Number of observations in parentheses.

\*\* From Crawford and Cross (see reference 8). The assignment of 2121 cm<sup>-1</sup> has been changed from  $\omega_2 + \omega_8$ .

violated the selection rules for the Raman effect. Their conclusion that nickel carbonyl was planar was, therefore, also invalid. Actually their experimental data do not agree with either the tetrahedral or the square model, since either of these structures should have only two polarized Raman lines while Duncan and Murray reported the presence of three.

Brockway and Cross,<sup>7</sup> using electron-diffraction methods, found evidence clearly favoring a tetrahedral structure, but a surprisingly small value was found for the nickel-to-carbon distance which may tend to alter the tetrahedral structure. Crawford and Cross<sup>8</sup> performed an infra-red absorption study and a quantitative vibrational analysis on this molecule and found that a reasonable assignment of frequencies could not be made on the basis of the square model; a satisfactory assignment could be obtained for the tetrahedral model only if the Raman polarization data of Duncan and Murray were in error. The purpose of this investigation was to re-examine the state of polarization of the Raman lines of nickel carbonyl to determine whether Crawford and Cross were justified in rejecting the polarization data of Duncan and Murray which represent the only evidence against the tetrahedral structure for nickel carbonyl.

#### APPARATUS AND MATERIALS

Nickel carbonyl<sup>9</sup> of commercial grade was purified by several vacuum distillations. The

Raman spectra and depolarization factors were obtained with the apparatus described in a previous publication.<sup>10</sup>

Wave-length measurements were obtained by comparison with a bracketing iron reference spectrum. Ordinary nails were used for the arc in order to supplement the iron spectrum with manganese lines in the 2000-cm<sup>-1</sup> region. Measurements were made with a Bausch and Lomb spectrum measuring microscope or with a Leeds and Northrup recording microphotometer. The wave numbers (vacuum) were obtained by a linear interpolation over a limited region or by the use of the Hartmann formula over the entire spectrum. The frequencies and standard deviations are listed in Table I. The relatively low precision of these observations is the result of the use of a large number of different methods of measuring and calculating the spectra in an attempt to determine the most accurate and convenient method of frequency determinations.

The exposure time required to obtain a density of one unit for the strongest line (79 cm<sup>-1</sup>) of nickel carbonyl was 2.1 minutes as compared with 30 minutes for the 459-cm<sup>-1</sup> line of carbon tetrachloride and 13 minutes for the 992-cm<sup>-1</sup> line of benzene. This line is one of the most intense Raman lines which has been reported, but despite this fortunate circumstance the depolarization factor is difficult to measure because it lies on the "wing" of the exciting line as shown in the microphotometer tracing of Fig. 1. When the "minimum adjacent background" method for correcting for background which was developed for the lines of carbon tetrachloride<sup>10</sup> was applied to this line, the impossible values for  $\rho$  of greater than 1 were obtained. The background for this line was obtained by extrapolating the estimated contour of the exciting line and taking the intersection of this curve with the position of the peak as the background density. The "minimum adjacent background" was used for the correction with the 381-cm<sup>-1</sup> and 461-cm<sup>-1</sup> lines while no background correction was required for the 2039-cm<sup>-1</sup> line.

<sup>7</sup> L. O. Brockway and P. C. Cross, J. Chem. Phys. 3, 828 (1935).

<sup>8</sup> B. L. Crawford, Jr. and P. C. Cross, J. Chem. Phys. 6, 525 (1938).

<sup>9</sup> We are indebted to Mr. O. B. J. Fraser of the International Nickel Company, Inc. for this material.

<sup>10</sup> B. L. Crawford, Jr. and W. Horwitz, J. Chem. Phys. 15, 268 (1947).

## RESULTS

The only Raman polarization data on this compound available hitherto are the qualitative results of Duncan and Murray,<sup>4</sup> who report the following: the  $463\text{-cm}^{-1}$  line, depolarized; the  $382\text{-cm}^{-1}$  line, polarized; the  $82\text{-}$  and  $2043\text{-cm}^{-1}$  lines, partly polarized. The quantitative depolarization factors, as determined in this investigation, are presented in Table I together with the standard deviations and the number of observations. There is no question that the  $381\text{-cm}^{-1}$  line is highly polarized. On 16 of 17 observations there was no trace of a parallel component; on only one tracing was there any suggestion of a parallel component, and this was only a slight jog in the tracing, of the same magnitude as several other jogs of no significance (i.e., arising from grain fluctuations, spots, dust, etc.). Even if this parallel component is considered significant, the estimated degree of depolarization of this line is about 0.01, or as close to zero as it is possible to demonstrate experimentally.

These data also show that the  $79\text{-cm}^{-1}$  line is depolarized. The fact that this line actually lies on the "wing" of the Rayleigh line with substantially different background densities on its two sides may have led Duncan and Murray<sup>4</sup> to the conclusion that it was partially polarized. Even under high microphotometer magnification we have been unable to confirm Duncan and Murray's classification of this line as unsymmetrical. An unsuccessful attempt was made to resolve this line into the two lines postulated by Crawford and Cross,<sup>8</sup> using the long focal length camera of the Steinheil spectrograph which is capable of resolving doublets with a spacing of  $10\text{ cm}^{-1}$ .

The  $461\text{-cm}^{-1}$  and the  $2039\text{-cm}^{-1}$  lines were found to be depolarized and partially polarized, respectively, as reported by Duncan and Murray.<sup>4</sup> The latter is unsymmetrical. It too is a postulated doublet which could not be resolved with the long focal length camera.

A single measurement of the degree of depolarization of the weak lines at  $598\text{ cm}^{-1}$  and  $2121\text{ cm}^{-1}$  showed them to be at least partially polarized. No attempt was made to study the still weaker lines reported by Duncan and Murray,<sup>4</sup> since the continuous background was approaching

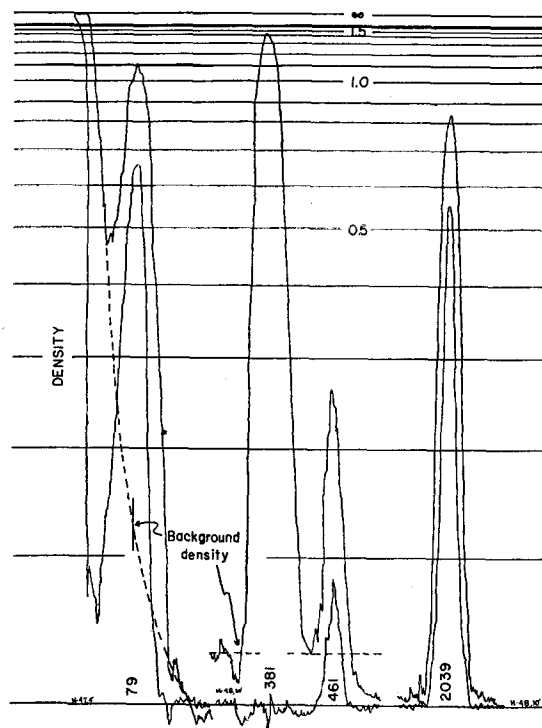


FIG. 1. Microphotometer tracing of the polarized Raman spectrum of nickel carbonyl (upper—perpendicular; lower—parallel). The Raman lines are from different plates.

substantial levels with the exposure time required.

The relative intensities found in this study, as shown in Table I, are in good agreement with those reported by Duncan and Murray.<sup>4</sup>

## DISCUSSION

The present investigation reveals the presence of only two strong polarized lines, which agrees with the selection rules for either the tetrahedral or the square configuration for nickel carbonyl. The partially polarized line reported by Duncan and Murray at  $82\text{ cm}^{-1}$  is actually depolarized. As pointed out by Crawford and Cross,<sup>8</sup> a polarized line in this region is unaccountable by either model. The fact that the  $381\text{-cm}^{-1}$  line is completely polarized is in itself very strong evidence in favor of the tetrahedral structure since complete polarization is expected theoretically only for molecules of the cubic point groups. For all non-cubic point groups, which includes the planar square, the degree of depolarization of the totally symmetric Raman lines is intermediate between 0 and  $6/7$ .

The vibrational analysis of Crawford and Cross<sup>10</sup> which rejected the polarization data of Duncan and Murray for the  $82\text{-cm}^{-1}$  line, is shown, on the basis of the data presented here, to be completely justified. As a result of polarization measurements on the two weak overtone and combination lines at  $598\text{ cm}^{-1}$  and  $2121\text{ cm}^{-1}$  it has been necessary to change the assignment of the latter from  $\omega_2 + \omega_5$  to  $\omega_8 + \omega_5$  in order to allow for a polarized combination. The original assignment of  $598\text{ cm}^{-1}$  as  $2\omega_8$  remains unchanged, since this overtone may have a polarized component.

The tetrahedral structure for nickel carbonyl may be considered as established on the basis of the following evidence:

1. The theory of directed valence predicts a tetrahedral structure for quadricovalent neutral nickel complexes.
2. The electron-diffraction study of Brockway and Cross<sup>7</sup> clearly favors the tetrahedral structure.
3. As shown by Crawford and Cross,<sup>8</sup> a satisfactory vibrational analysis of the molecule can only be made on the basis of the tetrahedral model.
4. The present investigation supplies the Raman polarization data which indicate a tetrahedral structure and which justify the previous vibrational analysis.