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# Infrared Spectra of Carbon Monoxide as a Solid and in Solid Matrices

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The fundamental infrared absorption frequency of several isotopes of CO has been observed in solid carbon monoxide and in the solid matrices N<sub>2</sub>, Ar, and CH<sub>4</sub>. In addition, the overtone in solid carbon monoxide has been measured. It is shown that frequency shifts due to isotopic substitution in the solid state follow the formulas developed for the gas phase only when molecules of the same isotopic species are not adjacent to each other, i.e., only in dilute solutions.

## INTRODUCTION

THE examination of the infrared spectrum of solid materials is becoming more and more common; still, certain aspects of the effect of the environment upon the infrared spectrum are not well understood. The solid state affords a variety of possible ways in which the spectra might be made to deviate from that expected of an isolated molecule. A number of papers<sup>1-6</sup> have shown various ways in which spectra might differ from the predictions for isolated molecules. There is, however, a great deal of uncertainty regarding the importance of these effects. In fact most treatments completely ignore all effects except the splitting of degenerate modes due to crystal symmetry.

As yet, few precise frequency studies of solid-state infrared spectra have been made. This is partly due to the large natural linewidths encountered in solids, and partly due to the comparative dearth of instruments of sufficient resolving power.

It is well known that the linewidths of solids are greatly reduced upon lowering the temperature. In our studies we have found that in some cases the natural linewidth at low temperatures becomes smaller than 0.9 cm<sup>-1</sup>. With such sharp lines it is possible to obtain quite precise measurements of the frequencies of absorption bands.

In an effort to determine both the reliability of isotope rules for solids and the extent of change which the potential function undergoes upon going from the gas to solid phase, we have made a study of the fundamental and overtone regions of carbon monoxide in the solid state around 20°K. In this study, the overtone and fundamental of the normal C<sup>12</sup>O<sup>16</sup> molecule have been measured, as well as the fundamental vibrational frequencies of C<sup>12</sup>O<sup>17</sup>, C<sup>13</sup>O<sup>16</sup>, and C<sup>12</sup>O<sup>18</sup> in their normal isotopic abundances, which are, respectively 0.039%, 1.1%, and 0.204%. A study of the fundamentals in various matrices was also made.

The carbon monoxide molecule was chosen as the subject of this study for several reasons. (a) It is one of the simplest molecules. The simplicity of the vibrational spectrum removes all likelihood of interactions between different vibrational modes. (b) The gas phase spectrum is very well known. (c) The small dipole moment and other evidence indicates that CO is not very likely to interact with its neighbors in the solid, and hence is a rather unfavorable case for any interactions arising from the proximity of molecules in the solid state. (d) The similarity of CO to N<sub>2</sub> with respect to size and crystal structure makes CO an ideal molecule to use in a nitrogen matrix. (e) The small size of the CO molecule is also expected to allow it to fit readily into other host lattices such as argon.

## EXPERIMENTAL

The spectrometer used in this work was a Perkin-Elmer 112-G grating instrument with a 1875 lines/in. grating and a NaCl fore-prism. The low-temperature cell was a Dewar of standard design with a liquid nitrogen radiation shield. The sample window was a CsBr crystal clamped to the cold block with indium metal gaskets to insure good thermal contact. The gases used in this work were obtained from The Matheson Company, Inc., and were used without further purification. Initial experiments were made using a liquid air trap in the gas manifold line, but since this had no effect upon the spectra it was not used in subsequent experiments.

Due to the uncertain geometry of the apparatus, it is not possible to give a very accurate estimate of the film thicknesses used. In some of the figures the total amount of gas deposited is given; this deposit was not evenly distributed over the entire window and probably only 60 to 30% was actually deposited in the light beam. The rate of deposition of the films was varied somewhat but was kept within the range of 50-500 micromoles of CO per hour. In the solid solution or matrix work, various solvent-to-solute ratios were used ranging from 100/1 to 600/1.

The method of calibration used in this work was very simple and yet quite accurate. Fortunately, the gas phase spectrum of carbon monoxide has been very

<sup>1</sup> R. S. Halford, J. Chem. Phys. **14**, 8 (1946).

<sup>2</sup> D. F. Hornig, J. Chem. Phys. **16**, 1063 (1948).

<sup>3</sup> H. Winston and R. S. Halford, J. Chem. Phys. **17**, 607 (1949).

<sup>4</sup> T. H. Walnut, J. Chem. Phys. **20**, 58 (1952).

<sup>5</sup> R. M. Hexter and D. A. Dows, J. Chem. Phys. **25**, 504 (1956).

<sup>6</sup> J. C. Decius, J. Chem. Phys. **23**, 1290 (1955).

TABLE I. Fundamental infrared absorption frequencies for different species of CO.

Molecule	Matrix	Calculated frequency ( $\text{cm}^{-1}$ ) (using $x_p\omega_p = 12.07 \text{ cm}^{-1}$ )	Observed frequency ( $\text{cm}^{-1}$ )
$\text{C}^{12}\text{O}^{16}$	$\text{N}_2$	2139.58	$2139.56 \pm 0.06$
$\text{C}^{13}\text{O}^{16}$	$\text{N}_2$	2092.41	$2092.34 \pm 0.10$
$\text{C}^{12}\text{O}^{18}$	$\text{N}_2$	2088.46	$2088.56 \pm 0.15$
$\text{C}^{12}\text{O}^{16}$	CO	2139.38	$2138.44 \pm 0.09$
$\text{C}^{12}\text{O}^{17}$	CO	2112.43	$2112.41 \pm 0.06$
$\text{C}^{13}\text{O}^{16}$	CO	2092.22	$2092.19 \pm 0.05$
$\text{C}^{12}\text{O}^{18}$	CO	2088.27	$2088.32 \pm 0.06$

accurately measured<sup>7</sup> and could be used to determine wavelengths in the fundamental region. The procedure used consisted of bracketing the sample absorption with a CO gas spectrum without stopping the wavelength drive mechanism. The wavelength of the sample absorption was then found by interpolation. This process was repeated 3–10 times and the results averaged. The reproducibility of this measuring procedure was very good, giving standard deviations of the order of  $0.02$  to  $0.08 \text{ cm}^{-1}$ . In determining the probable errors reported, these standard deviations were combined with an estimated error due to other sources.

Although the absorption lines measured had a half-intensity width of  $1.0 \text{ cm}^{-1}$  or greater, the symmetry of many of the bands made it easy to determine the band centers to within a few hundredths of a wave number. The reproducibility of the measurements substantiates this claim.

The overtone region was calibrated in a similar way using the  $6\text{-}\mu$  atmospheric water band as measured by Plyler *et al.*<sup>8</sup> The grating was used in second order for this while it was used in fifth order for the sample. A simple adjustment of the fore-prism allowed rapid shifting of orders without stopping the wavelength drive mechanism.

## RESULTS

### CO in a Nitrogen Matrix

Carbon monoxide in a matrix of solid nitrogen at  $20^\circ\text{K}$  displays one sharp, strong band at  $2139.56 \text{ cm}^{-1}$  which may be attributed to the vibration fundamental of the  $\text{C}^{12}\text{O}^{16}$  molecule. This band is displaced to a frequency about  $4 \text{ cm}^{-1}$  below the normal gas phase frequency. For rather large film thicknesses, a band about one hundredth as strong as the  $\text{C}^{12}\text{O}^{16}$  fundamental shows up at  $2092.34 \text{ cm}^{-1}$ . This band is attributed to the  $\text{C}^{13}\text{O}^{16}$  molecule. About  $4 \text{ cm}^{-1}$  below this band is

another which is about a fifth as strong and must be due to  $\text{C}^{12}\text{O}^{18}$ . The absorption due to  $\text{C}^{12}\text{O}^{17}$  would be even weaker and has not been found in a nitrogen matrix. These assignments are substantiated not only by the relative band intensities but also by agreement with the calculated frequencies (see Table I).

It is unfortunate that in this work it was not possible to observe the overtone in any of the matrices because light scattering prevented observations on sufficiently thick films. The scattering was of course not such a problem for the longer wavelength region around the fundamental.

In addition to the above listed absorption bands, a very weak absorption was found at a frequency  $7.30 \text{ cm}^{-1}$  greater than the fundamental for  $\text{C}^{12}\text{O}^{16}$  (see Fig. 1). This band probably can not be attributed to any reflection phenomena as was done by Dows<sup>9</sup> in the case of the  $670 \text{ cm}^{-1}$  band in solid  $\text{CO}_2$ . With the very low concentration of CO in the solid nitrogen matrix, the contribution of the CO to the refractive index of the solid solution would be too small to noticeably affect the reflection properties of the matrix. This band may be due to a lattice vibration of translational or librational character. It might also arise from intermolecular coupling between CO pairs which happen to be situated on adjoining sites within the crystal. Even at the largest  $\text{N}_2/\text{CO}$  ratios used in this work, 1% of the molecules will be on adjacent sites. However, since no change in the relative intensity of this satellite band was observed upon varying the  $\text{N}_2/\text{CO}$  ratio from 600/1 to 160/1, the latter explanation seems to be incorrect.

Nitrogen has a very interesting phase change at  $35^\circ\text{K}$ . This phase change is believed to be accompanied by a rather large decrease in the barrier to rotation of the  $\text{N}_2$  molecules.<sup>10</sup> Since CO is very similar to  $\text{N}_2$  it was hoped that the substitution of CO in a  $\text{N}_2$  crystal might provide a means of studying this transition. Unfortunately, with our apparatus it is not possible to hold the matrix at fixed temperatures other than  $5^\circ$ ,  $20^\circ$ , and  $77^\circ\text{K}$ . It was, however, possible to observe the changes in the spectrum as the material slowly warmed up from a low temperature. The CO absorption remained relatively unchanged as the temperature was raised from  $5^\circ\text{K}$  to about  $35^\circ\text{K}$ . At about  $35^\circ\text{K}$  a

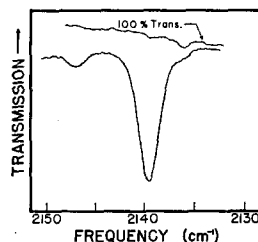


Fig. 1. CO in a nitrogen matrix at  $20^\circ\text{K}$ .  $\text{N}_2/\text{CO} = 590$ ;  $110 \mu$  moles CO.

<sup>7</sup> E. K. Plyler, L. R. Blaine, and W. S. Connor, J. Opt. Soc. Am. **45**, 102 (1955).

<sup>8</sup> E. K. Plyler, A. Danti, L. R. Blaine, and E. D. Tidwell, Natl. Bur. Standards monograph 16.

<sup>9</sup> D. A. Dows, Spectrochim. Acta **13**, 308 (1959).

<sup>10</sup> L. H. Bolz, M. E. Boyd, F. A. Mauer, and H. S. Peiser, Acta. Cryst. **12**, 247 (1959).

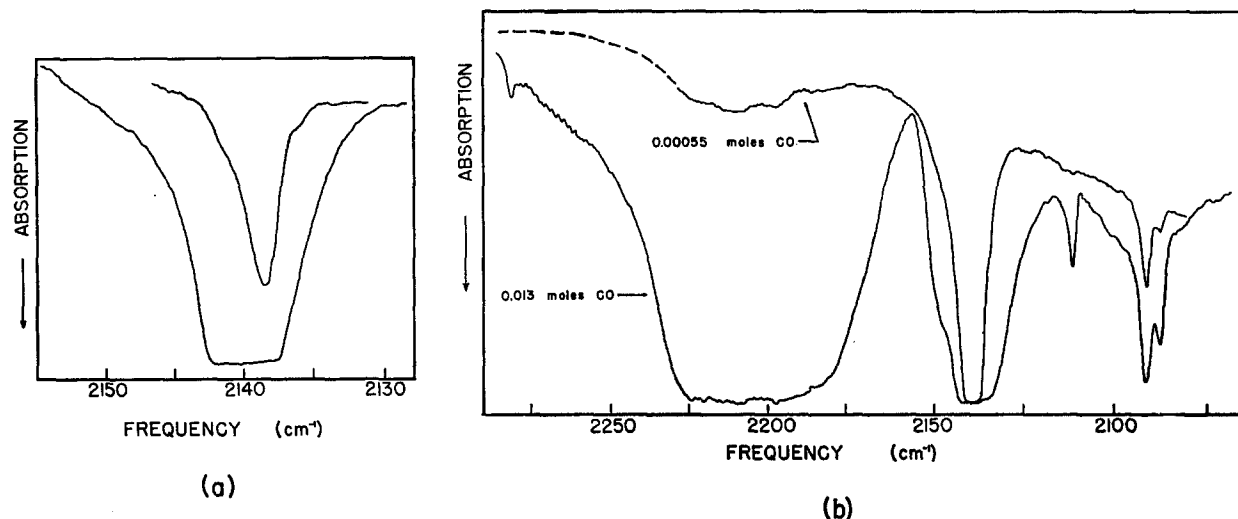


FIG. 2. Solid carbon monoxide at 20°K.

very sudden increase in bandwidth and a concomitant increase in background absorption was found. Further increases in temperature resulted in increased bandwidth and a very rapid increase in light scattering. All attempts to detect any possibility of fine structure failed. This may indicate that any fine structure is too broad or too closely spaced to be observable; or it may be a result of increased light scattering due to the phase change. Sublimation difficulties and consequent loss of thermal insulation in the apparatus prevented going to temperatures above 50°K.

### Solid Carbon Monoxide

The infrared spectrum of solid CO is very similar to that of a nitrogen matrix containing CO. There is, however, no weak, sharp absorption band at a frequency slightly higher than the  $C^{12}O^{16}$  fundamental. Moreover, the fundamental  $C^{12}O^{16}$  absorption band is asymmetrical as may be seen in Fig. 2(a). This asymmetry, which consists of a tailing off of absorption toward higher frequencies, may be a consequence of the unisolated character of the  $C^{12}O^{16}$  molecule in solid CO. All the other isotope bands are symmetrically shaped. This asymmetry of line shape could be attributed to reflection scattering. This would explain the absence of an asymmetry in the isotopic bands. Such scattering is, however, expected to cause the apparent absorption to taper off in the direction of increasing wavelength,<sup>11</sup> whereas the opposite behavior is observed.

Since thicker effective CO films were possible with pure CO, the  $C^{12}O^{17}$  fundamental was observed; also the overtone of the  $C^{12}O^{16}$  molecule was measured at 4252.7  $cm^{-1}$ . This yields an anharmonicity constant slightly smaller than that found in the gas phase. It was not possible to observe the overtones of the other isotopic bands due to light scattering difficulties.

<sup>11</sup> W. C. Price and K. S. Tetlow, *J. Chem. Phys.* **16**, 1157 (1948).

In the very heavy films of CO, the presence of a very broad absorption around 2210  $cm^{-1}$  and a very sharp absorption at about 2281  $cm^{-1}$  was observed as shown in Fig. 2(b). The latter band is due to a small amount of carbon dioxide which is expected to be one of the principal impurities in the sample. The forbidden  $Q$  branch of  $C^{13}O_2^{16}$  is located at about 2283  $cm^{-1}$  in the gas phase. Pimentel and Ewing discuss the nature of the broad band in a paper appearing elsewhere in this issue.

### CO in an Argon Matrix

Carbon monoxide trapped in an argon matrix at 5°K was found to have a rather asymmetric absorption band (see Fig. 3). As the temperature was increased, the absorption frequency seemed to decrease slightly and a subsidiary absorption appeared at a position 10.8  $cm^{-1}$  from the main band in the direction of increasing frequency.

### CO in a Methane Matrix

Methane has a strange phase transition at 20°K, the nature of which has been the subject of numerous papers.<sup>12-15</sup> This transition was originally thought to involve a sudden change in rotational freedom. However, the inability of both x ray<sup>13</sup> and NMR<sup>14</sup> to detect any changes seems to indicate that this is a transition involving the orientation of the hydrogen atoms.<sup>15</sup> The infrared spectrum of CO in a  $CH_4$  matrix likewise fails to show any change in passing from 5° to 30°K, so that it seems unlikely that the transition involves any

<sup>12</sup> K. Clusius, *Z. physik. Chem. (Leipzig)* **B3**, 41 (1929).

<sup>13</sup> H. H. Mooy, *Commun. Phys. Lab. Univ. Leiden* **19**, 216a (1931).

<sup>14</sup> J. T. Thomas, N. L. Alpert, and H. C. Torrey, *J. Chem. Phys.* **18**, 1511 (1950).

<sup>15</sup> H. M. James and T. A. Keenan, *J. Chem. Phys.* **31**, 12 (1959).

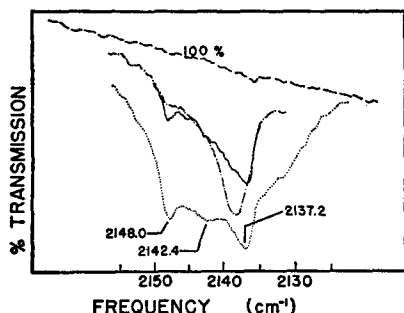


FIG. 3. CO in an argon matrix, Ar/CO=500; — 16.5  $\mu$  moles CO at 20°K; --- 21.6  $\mu$  moles CO at 5°K; .... 104  $\mu$  moles CO at 20°K.

sudden increased rotational freedom. A sudden broadening or change in fine structure would be expected in such an event.

Even at the lowest temperature observed, there is, however, an inexplicable complexity of the absorption spectrum. In Fig. 4 the absorption of CO in methane is shown and a definite shoulder may be seen at 5.2 and 3.7  $\text{cm}^{-1}$  above and below the absorption maximum respectively.

### DISCUSSION

Although  $^{12}\text{CO}$  is not expected to be very greatly perturbed by neighboring molecules in the solid state, it is evident that in solid carbon monoxide the fundamental of the most abundant molecule,  $\text{C}^{12}\text{O}^{16}$ , is displaced to a lower frequency by about 1  $\text{cm}^{-1}$ . This displacement has been determined (see Table I) by calculating the unperturbed frequency from the other isotopically substituted molecules which are assumed to be unperturbed. These calculations have been made by using the relations

$$x_e' \omega_e' / x_e \omega_e = (\omega_e' / \omega_e)^2 = \mu / \mu' \quad (1)$$

and

$$\nu_0 = \omega_e - 2x_e \omega_e, \quad (2)$$

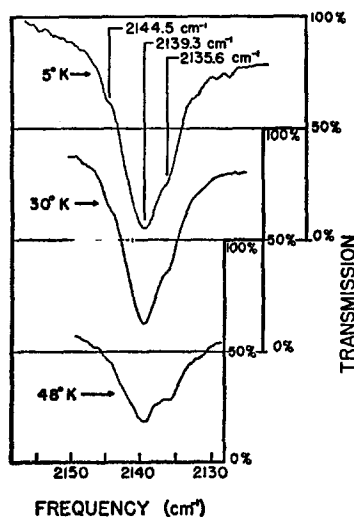


FIG. 4. CO in methane at 5°, 30°, and 48°K;  $\text{CH}_4/\text{CO}=217$ ; 29.2  $\mu$  moles CO.

where  $\mu$  is the reduced mass and  $\nu_0$  is the observed frequency. The prime indicates the value for another isotopic species. The column labeled "Calc. Freq." gives the best fit obtainable from the observed data.

The displacement of the  $\text{C}^{12}\text{O}^{16}$  fundamental from the calculated position is evidently due to a coupling between the vibrations of neighboring molecules. Since the less abundant isotopic species have vibrational frequencies quite different from the most abundant species, they are effectively decoupled and their observed frequencies are essentially those of the molecule completely isolated in a matrix.

The agreement between all observed and calculated frequencies for the nitrogen matrix substantiates this explanation. In the  $\text{N}_2$  matrix all isotopic species are isolated; consequently, the isotopic shift is correctly predicted for even the most abundant species  $\text{C}^{12}\text{O}^{16}$ .

In going from the gas to the solid state, the fundamental frequency of CO is only changed by about 0.5%, whereas the anharmonicity constant is changed by ten times this proportion (see Table II). However,

TABLE II. Infrared absorption frequencies of carbon monoxide in various matrices.

Phase	Fundamental ( $\text{cm}^{-1}$ )	Overtone ( $\text{cm}^{-1}$ )	$x_e \omega_e$ ( $\text{cm}^{-1}$ )
Gas	2143.274	4260.06	13.24
Solid	$2138.44 \pm 0.09$	$4252.74 \pm 0.40$	$12.07 \pm 0.30$
$\text{N}_2$ matrix	$2139.56 \pm 0.06$	...	...
Ar matrix at 5°K	$2138.67 \pm 0.30$	...	...
Ar matrix at 20°K	$2137.17 \pm 0.30$	...	...
$\text{CH}_4$ matrix	$2139.3 \pm 0.4$	...	...

if we calculate the anharmonicity constant from the calculated unperturbed fundamental frequency, the anharmonicity constant is found to nearly coincide with that of the gas. It is unfortunate that no anharmonicity constant could be measured for an unperturbed molecule in order to determine whether the anharmonicity constant is also affected by the coupling.

The evidence presented by these measurements seems to indicate that there are at least two different mechanisms by which the frequencies of molecules in the solid state are perturbed. First there is a coupling between the vibrations of different molecules. Since the coupling is at least in part selective with respect to isotopic species, it is apparently restricted to molecules with the same vibrational frequencies. This is probably a dipole-dipole coupling similar to that treated by Decius<sup>6</sup> in the case of nitrate and carbonate salts. This coupling must contribute only a small part of the total energy of the solid and thus would not necessarily be expected to be related to the forces involved in any translational or librational type of lattice vibrations. If this were not so, then one would expect to find a

strong rejection of other isotopic species upon formation of the solid. Furthermore, since such a strong fractionation of isotopic species is not found in going to the solid state, it seems reasonable to conclude that the forces responsible for translational and librational crystal modes must be relatively independent of isotopic species.

The other perturbation is the well-known solvent effect. Every host crystal studied here produced nearly the same frequency displacement; consequently, one may conclude that the same factors are responsible in all cases. This means that interactions with the dipole or quadrupole moments of the host may be eliminated, because only CO is polar and argon has no quadrupole moment outside of the nucleus. As a consequence, only certain induction and dispersion terms in the potential energy of the solute molecule may be responsible for the frequency shifts. This, of course, neglects repulsion terms which would give a blue shift. Both Buckingham<sup>16</sup> and Pullin<sup>17</sup> have used these terms in deriving equations which relate the dielectric properties of a solvent to the frequency shifts of the solute. Buckingham's equation predicts an approximately linear relationship between frequency shift and  $(\epsilon-1)/a^3(2\epsilon+1)$ , where  $a$  is often considered to be the radius of the cavity in which the solute is located. Our data fits this relationship, but the small number of points and the inaccuracy of all constants involved are such that this agreement can be considered little more than fortuitous.

The presence of some fine structure and the broadness of the absorption band in argon and methane matrices may be due to several causes either individually or collectively. For instance, the CO molecule may have several possible orientations or different types of lattice and/or interstitial sites which would

give rise to differing frequency shifts. In addition, a number of lattice vibrational or librational modes may be responsible for the fine structure. Hexter<sup>18</sup> has found a great deal of fine structure in the infrared absorption of GeH<sub>4</sub>, CH<sub>4</sub> and NH<sub>3</sub> in various solid solutions which seems to be due to rotation in the solid. Rotation has similarly been shown for H<sub>2</sub>O in solid matrices.<sup>19</sup>

The small size of the CO molecule makes it quite possible that the barrier to rotation in a methane or argon matrix is rather low. On the other hand, it is known that molecules in solid CO and N<sub>2</sub> have a rather high rotational barrier at 20°K. This may account for the marked difference in bandwidth for these two types of matrices. It must be remembered, however, that the band envelope of CO in methane is virtually unchanged in breadth and shape in going from 5° to 30°K. This would not be expected if any low-frequency modes were responsible for the bandwidth and fine structure.

### CONCLUSIONS

In dealing with solids where the interatomic distances and the relative orientation of molecules are well known, it is to be hoped that frequency shifts such as are found here for the CO molecule may be quantitatively explained and predicted. Although this is not yet possible, this work does at least show that the isotopic shifts in vibrational frequency which are calculated from the gas phase or isolated molecule formulas are valid in the case of dilute solid solutions. This is important for the calculation of force constants where the number of force constants exceeds the number of vibrations as in the case of the XYZ linear molecule.

<sup>16</sup> A. D. Buckingham, Proc. Roy. Soc. (London) **A255**, 32 (1960); *ibid.* **A248**, 169 (1958).

<sup>17</sup> A. D. E. Pullin, Proc. Roy. Soc. (London) **A255**, 39 (1960).

<sup>18</sup> R. M. Hexter and D. E. Milligan, Fourth International Symposium on Free Radical Stabilization, Washington, D. C., September 1959.

<sup>19</sup> E. Catalano and D. E. Milligan, J. Chem. Phys. **30**, 45 (1959).