The Molecular Structure of Isocyanic Acid from Microwave and InfraRed Absorption Spectra

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where I_{mn} is the unit matrix of mn rows and columns and $L_m(x)$ is a matrix:

$$L_m(x)=\begin{matrix}(1)\\(2)\\(3)\\ \cdot\\ \cdot\\ \cdot\\(m-1)\\(m)\end{matrix}\begin{Vmatrix}M_n(x)&I_n&&&\\I_n&M_n(x)&I_n&&\\&I_n&M_n(x)&&\\&&&\cdot&\\&&&&\cdot\\&&&&M_n(x)&I_n\\&&&&I_n&M_n(x)\end{Vmatrix},$$

and similarly $M_n(x)$ is a matrix:

$$M_n(x)=\begin{matrix}(1)\\(2)\\(3)\\ \cdot\\ \cdot\\ \cdot\\(n-1)\\(n)\end{matrix}\begin{Vmatrix}x&1&&&\\1&x&1&&\\&1&x&&\\&&&\cdot&\\&&&&\cdot\\&&&&x&1\\&&&&1&x\end{Vmatrix}$$

Here x is, in the case of neglected overlap integrals,

$$x=W/\beta=(Q-E)/\beta,$$

where Q is the Coulomb integral and β the exchange integral of two neighboring atoms,[1] and E is the energy eigenvalue. If we do not neglect the overlap integrals of two neighboring atoms, S, we have

$$x=W/\beta'=(Q-E)/(\beta-SE).$$

Applying Rutherfords results,[2] we obtain for the roots of the determinant equation

$$x=2\left(\cos\frac{\lambda\pi}{l+1}+\cos\frac{\mu\pi}{m+1}+\cos\frac{\nu\pi}{n+1}\right)$$

$(\lambda=1, 2, \cdots, l;\ \mu=1, 2, \cdots, m;\ \nu=1, 2, \cdots, n)$. Thus in the case of neglected overlap integrals we have

$$E=Q-2\beta\left(\cos\frac{\lambda\pi}{l+1}+\cos\frac{\mu\pi}{m+1}+\cos\frac{\nu\pi}{n+1}\right),$$

and with the overlap integral S:

$$E=\frac{Q-2\beta\left(\cos\frac{\lambda\pi}{l+1}+\cos\frac{\mu\pi}{m+1}+\cos\frac{\nu\pi}{n+1}\right)}{1-2S\left(\cos\frac{\lambda\pi}{l+1}+\cos\frac{\mu\pi}{m+1}+\cos\frac{\nu\pi}{n+1}\right)}.$$

In the case of $S=0$ one can see that—treating metals with one valence electron only—the filled part of the band of width 12β are those states in which

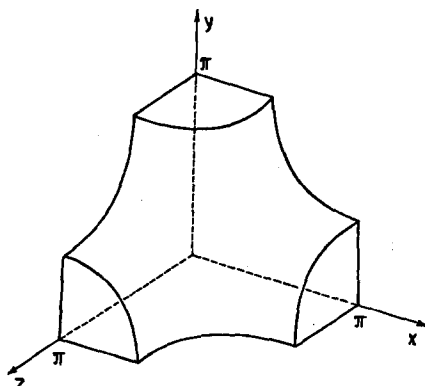$$\cos\frac{\lambda\pi}{l+1}+\cos\frac{\mu\pi}{m+1}+\cos\frac{\nu\pi}{n+1}<0.$$

FIG. 1. Space covered by the range of integration.

If l, m, $n \rightarrow \infty$, we have a continuous band from $Q+6\beta$ to $Q-6\beta$ which is filled from $Q+6\beta$ to Q. One can obtain the average energy, if one integrates

$$\frac{2}{\pi^3}[Q+2\beta(\cos x+\cos y+\cos z)]$$

in the (x, y, z)-space closed by the six planes $x=0$, $y=0$, $z=0$, $x=\pi$, $y=\pi$, $z=\pi$, further by the surface

$$\cos x+\cos y+\cos z=0.$$

The space which is covered by this integration is sketched in Fig. 1.

We can transform this integral finally to an integral which involves in the integrand the normal elliptic integral of the first kind. This integral can be simply evaluated and so we get

$$\bar{E}_{sp}=Q+1945\beta.$$

This means a considerable gain in stability against the linear chain,[1] which gives

$$\bar{E}_{lin}=Q+1273\beta.$$

In a similar way one can calculate the plane structure too, which gives

$$\bar{E}_{pl}=Q+1621\beta.$$

The increasing stability as the structure becomes of more dimensions gives a rough explanation of Kossel's theory concerning crystal growth, namely, if on the surface of a crystal there is begun a new row or a new plane, there will be no atom beginning another row or plane until the first row or plane is accomplished in the neighborhood of the point considered, since the more condensed (more dimensional) structures are energetically favorized.

The calculations are somewhat more tedious if we take into account the overlap integral. In this case we treat only the case $S<\frac{1}{6}$.

The average energy for one electron will be in this case

$$\bar{E}=(\beta/S)+[Q-(\beta/S)]f(S),$$

where $f(S)$ is a function of the overlap integral only, it is the average of

$$1/[1-2S(\cos x+\cos y+\cos z)].$$

This average as a series in S begins

$$f(S)=1-1945S+\cdots.$$

The calculation of $f(S)$ makes necessary the evaluation of integrals involving certain elliptic normal integrals. $f(S)$ can be given in integral form or in a table.

Detailed investigations and applications of the preceding theory will be published in a forthcoming paper in the *Hungarica Acta Physica*.

[1] T. A. Hoffmann and A. Kónya, J. Chem. Phys. 16, 1172 (1948); Hungarica Acta Physica (to be published).
[2] D. E. Rutherford, Proc. Roy. Soc. Edinburgh 62A, 229 (1947).

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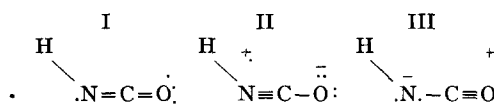May 22, 1950

EXPERIMENTAL investigations of the infra-red† and microwave spectra of the slightly asymmetric rotor, HNCO, have been made, and the structure of the molecule has been determined. The molecular constants computed from the microwave absorption frequencies of the $J=0\rightarrow1$ rotational transitions in the ground vibrational state, and from the resolved infra-red hybrid band of

TABLE I. Rotational molecular constants for HNCO.

	Microwave absorption frequencies $(J=0\rightarrow1)$ Mc/sec.	$B_0+C_0/2$ cm^{-1} from microwaves	$A_0-B_0+C_0/2$ cm^{-1} from the infra-red
H^{1}N^{14}C^{12}O^{16}	21,981.7	0.36664	30.30 ±0.1
H^{1}N^{15}C^{12}O^{16}	21,323.5	0.35566	
H^{2}N^{14}C^{12}O^{16}	20,394.7	0.34017	

the first overtone of the N—H stretching vibration, ν_1, are listed in Table I.

On the assumption that the —NCO group is linear and that the molecule is HNCO and not HOCN, the four remaining structural parameters (three interatomic distances and one angle) have been evaluated. The linearity of the —NCO group is shown by the electron diffraction investigation of Eyster, Gillette, and Brockway,[1] which yielded equal N—C and C—O distances of 1.19A in accord with the following reasonable resonating structures, all of which contribute to a linear configuration.

$$
\begin{array}{ccc}
\text{I} & \text{II} & \text{III} \\
\text{H} & \text{H} & \text{H} \\
\diagdown & \diagdown \; + & \diagdown \qquad + \\
.\ddot{N}=C=\ddot{O}. & .N\equiv C-\ddot{O}: & .\ddot{N}.-C\equiv O
\end{array}
$$

Measured values of the stretching frequencies associated with hydrogen valence forces in HNCO and HNCS are listed in Table II, along with characteristic values for other relevant bonds. Although the hydrogen valence frequency in isocyanic acid is high in comparison with the value usually attributed to N—H vibrations, the practical identity of this frequency in HNCO and HNCS can leave little doubt but that in both cases it results from an NH vibration, and that isocyanic and isothiocyanic acids are predominantly, if not exclusively, present.

TABLE II. Hydrogen stretching frequencies.

	Fundamental cm^{-1}	First overtone cm^{-1}
HNCO	3538	6915
HNCS	3530	6903
H—N<	3350[a]	—
H—O—	3680[a]	—
H—S—	2750[a]	—

[a] See reference 2, p. 195.

Since the force constant for the NH bond is unusually high in isocyanic acid, as shown by the stretching frequency, Badger's rule suggests that the length of the bond will be shortened from the value of 1.014A found in NH$_3$[2] to 0.987A. This is indeed found to be the case.

Effective values of the calculated structural parameters in the ground vibrational state are listed in Table III.

Equations expressing A_0 and C_0 for the various isotopic species in terms of the molecular parameters were solved numerically by the Newton-Raphson approximation method to the nearest 0.001A. The isotopic substitutions of deuterium for hydrogen and N^{15} in place of N^{14} lead to an uncertainty of about 0.005A in the N—O distance and 0.01A in the N—H distance. In spite of

TABLE III. Structural parameters for HNCO.

	Spectroscopic HNCO parameters distances in A	Electron[a] diffraction values distances in A
C—O distance	1.171 ±0.01	1.19 ±0.03
N—C distance	1.207 ±0.01	1.19 ±0.03
N—H distance	0.987 ±0.01	1.01 (estimated)
N—O distance	2.378 ±0.005	2.38 ±0.03
H—N—C angle	128° 5' ±30'	125° (estimated)

[a] See reference 1.

the accuracy of the N—O distance there is an uncertainty of 0.01A in the N—C and C—O distances, because the proximity of the carbon to the center of mass makes the calculation insensitive to its exact position. Excellent agreement is obtained with the total N—O distance determined by electron diffraction.

We wish to thank Professors W. H. Pickering, and H. V. Neher, and Mr. Bart Locanthi for invaluable counsel concerning electronic problems. We also greatly appreciate several very helpful discussions with Professor R. M. Badger. The work was supported in part by a grant from the Research Corporation, to whom we wish to express our gratitude here.

* AEC Predoctoral Fellow.
** AEC Postdoctoral Fellow.
† In some of the infra-red bands interesting perturbations were observed which will be discussed in a later paper.
[1] Eyster, Gillette, and Brockway, J. Am. Chem. Soc. 62, 3236 (1940).
[2] G. Herzberg, Infra-Red and Raman Spectra (D. Van Nostrand Company, Inc., New York, 1947), third printing, p. 439.

Remarks on the Surface Tension of Small Droplets

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IN two recent communications to this Journal, LaMer and Pound[1,2] have reported estimates of the surface tension of very small drops based upon the Becker-Döring[3] theory of nucleation and measurements of the critical supersaturation pressure leading to the rapid production of a fog in certain vapors. Using the data of Volmer and Flood,[4] they concluded that the surface tension is independent of radius, in apparent conflict with predictions of Tolman's[5] quasi-thermodynamic theory and our statistical mechanical theory[6] of surface phases. Later calculations based on the data of Sander and Damköhler[7] yielded values of the surface tension which decreased with increasing drop curvature, in agreement with the predictions of both theories.

It is our purpose in the present note to make a few critical remarks concerning the significance of calculations of the sort carried out by LaMer and Pound. The conclusion that surface tension decreases with increasing curvature, reached both by Tolman and by us, does not seem to be open to doubt. However, it must be emphasized that the magnitude of the predicted effect becomes significant only for drops so small that the application of macroscopic thermodynamic concepts becomes ambiguous. In other words, the theory states that there is no sensible effect of curvature on surface tension in the macroscopic domain. Since the critical "droplet" of nucleation theory is in representative cases a cluster of about 100 molecules of radius of the order of 10A, it is definitely outside the domain of applicability of macroscopic thermodynamic concepts, and it is with the "surface tension" of such droplets that LaMer and Pound are concerned.

The Becker-Döring theory of the dynamics of nucleation extrapolates macroscopic concepts into the microscopic domain and is therefore subject to the ambiguities to which we have called attention. By this remark, we do not intend to depreciate the value of the Becker-Döring theory as an extraordinarily useful approximation. On the contrary, we believe that it should be exploited to the fullest extent. We are, however, inclined to doubt whether it is sufficiently refined to decide the rather delicate point in question, that is the dependence of surface tension on radius of curvature. We shall discuss some of the ambiguities which arise when it is used for this purpose.

Nucleation in a supersaturated vapor is initiated by statistical density fluctuations giving rise to molecular clusters, which decay unless they exceed a critical size. Cluster embryos exceeding the critical size serve as nuclei for the new phase through growth by accretion of molecules from the vapor. In the Becker-Döring theory, the clusters are idealized as minute spherical droplets possessing the properties of the liquid phase in bulk with a vapor pressure determined by the Gibbs-Thompson formula. The work of