

Scheinbar müßte nach (A 19)  $\mathbf{A}(\mathbf{r}, \mathbf{r}')$  selbst HERMITESCH sein. Die Summe über  $n$  ist aber in Wirklichkeit ein Integral über ein kontinuierliches

Spektrum von  $\nu_{n0}$ , wobei der Nenner des ersten Gliedes durch  $\nu_{n0} - \nu + i b$  mit einem kleinen Imaginärteil  $b$  ersetzt werden muß (s. MOLIÈRE<sup>26</sup>).

### Anhang 3. Orthogonalität und Normierung von Blochschen Funktionen im unendlichen Gitter

1) BLOCHSche Funktionen mit unterschiedlichen  $\mathbf{f}$ -Werten sind orthogonal. Denn es gilt nach (5)

$$\int_{\infty} (\mathbf{B}^{(i)}(\mathbf{r}, \mathbf{f})^* \mathbf{B}^{(j)}(\mathbf{r}, \mathbf{f}')) d\mathbf{r} = \sum_{\mathbf{f}} \exp \{ -2\pi i (\mathbf{f} - \mathbf{f}', \mathbf{R}_l) \} \int_v (\mathbf{B}^{(i)}(\mathbf{r}, \mathbf{f})^* \mathbf{B}^{(j)}(\mathbf{r}, \mathbf{f}')) d\mathbf{r} \\ = \frac{1}{v} \delta(\mathbf{f} - \mathbf{f}') \int_v (\mathbf{B}^{(i)}(\mathbf{r}, \mathbf{f})^* \mathbf{B}^{(j)}(\mathbf{r}, \mathbf{f}')) d\mathbf{r}. \quad (\text{A 27})$$

2) BLOCHSche Funktionen mit gleichen  $\mathbf{f}$ -Werten und unterschiedlichen Bandindizes ( $i$ ) sind in einer Einheitszelle orthogonal. Dies kann man aus der HERMITESchen Eigenschaft des Operators  $\text{rot} \text{rot} + u$  unmittelbar folgern.

Es gilt also

$$\int_v (\mathbf{B}^{(j)*} \mathbf{B}^{(i)}) d\mathbf{r} = 0, \quad \text{wenn } \nu^{(i)}(\mathbf{f})^2 \neq \nu^{(j)}(\mathbf{f})^2. \quad (\text{A 28})$$

Im Falle der Entartung, d. h. wenn  $\nu^{(i)}(\mathbf{f})^2 = \nu^{(j)}(\mathbf{f})^2$  für  $(i) \neq (j)$ , kann man, wie üblich, durch eine lineare Kombination orthogonale Funktionen bilden.

3) (A 27) und (A 28) zusammenfassend kann man schreiben

$$\int_{\infty} (\mathbf{B}^{(j)}(\mathbf{r}, \mathbf{f})^* \mathbf{B}^{(i)}(\mathbf{r}, \mathbf{f}')) d\mathbf{r} = \delta_{ij} \delta(\mathbf{f} - \mathbf{f}') \frac{1}{v} \int_v (\mathbf{B}^{(i)}(\mathbf{r}, \mathbf{f})^* \mathbf{B}^{(i)}(\mathbf{r}, \mathbf{f})) d\mathbf{r}. \quad (\text{A 29})$$

Zur Normierung kann man über den Wert des Integrals auf der rechten Seite verfügen.

### Anhang 4. Entwicklung der Wannierschen Gleichung nach Potenzen von $(2\pi i \zeta_0)^{-1}$

Wir setzen (81) in (82) ein und berücksichtigen nur die Glieder mit den Potenzen  $(2\pi i \zeta_0)^0$  und  $(2\pi i \zeta_0)^{-1}$ . Es ist unmittelbar klar, daß die Glieder mit  $(2\pi i \zeta_0)^0$  von  $\delta\hat{E} F$  durch  $\delta\hat{E}(\nabla_{\mathbf{r}} \hat{S}_0, \mathbf{r}) F$  gegeben sind. Die Glieder mit  $(2\pi i \zeta_0)^{-1}$  von  $\delta\hat{E} F$  werden vernachlässigt (s. Text). Deshalb haben wir nur noch die Glieder mit  $(2\pi i \zeta_0)^{-1}$  von  $\hat{E} F$  aufzusuchen.

Nach (60) ist

$$\hat{E} \left( \frac{1}{2\pi i \zeta_0} \nabla_{\mathbf{r}}, \mathbf{r} \right) = \sum_{n=0}^{\infty} \frac{1}{n!} \left( \frac{1}{2\pi i \zeta_0} \nabla_{\mathbf{r}} - \hat{\mathbf{f}}_0, \nabla_{\hat{\mathbf{f}}} \right)^n \hat{E}(\hat{\mathbf{f}}, \mathbf{r})_{(\hat{\mathbf{f}}_0)}. \quad (\text{A 30})$$

Mit (81) folgt

$$\hat{E} F = \left\{ \sum_{n=0}^{\infty} \frac{1}{n!} \left( \nabla_{\mathbf{r}} \hat{S}_0 + \frac{1}{2\pi i \zeta_0} \nabla_{\mathbf{r}} \hat{S}_1 - \hat{\mathbf{f}}_0, \nabla_{\hat{\mathbf{f}}} \right)^n \hat{E}(\hat{\mathbf{f}}, \mathbf{r})_{(\hat{\mathbf{f}}_0)} \right. \\ \left. + \sum_{n=2}^{\infty} \frac{1}{n!} \frac{n(n-1)}{2} \left( \nabla_{\mathbf{r}} \hat{S}_0 - \hat{\mathbf{f}}_0, \nabla_{\hat{\mathbf{f}}} \right)^{n-2} \left[ \left( \frac{1}{2\pi i \zeta_0} \nabla_{\mathbf{r}} \nabla_{\hat{\mathbf{f}}} \right) (\nabla_{\mathbf{r}} \hat{S}_0 \nabla_{\hat{\mathbf{f}}}) \right] \hat{E}(\hat{\mathbf{f}}, \mathbf{r})_{(\hat{\mathbf{f}}_0)} \right. \\ \left. + O((2\pi i \zeta_0)^{-2}) \right\} F. \quad (\text{A 31})$$

Durch sukzessive Anwendung der Operation  $(1/2\pi i \zeta_0 \cdot \nabla_{\mathbf{r}} - \hat{\mathbf{f}}_0, \nabla_{\hat{\mathbf{f}}})$  von (A 30) ergibt sich die erste Summe von (A 31), wenn alle Operatoren  $\nabla_{\mathbf{r}}$  auf  $F$  wirken. Die zweite Summe entsteht, wenn ein Operator nicht auf  $F$ , sondern auf einen der durch die vorherige Operation entstandenen Faktoren  $(\nabla_{\mathbf{r}} \hat{S}_0 - \hat{\mathbf{f}}_0, \nabla_{\hat{\mathbf{f}}})$  wirkt. Die Zahl solcher Glieder ist durch  $n(n-1)/2$  gegeben. Das Glied  $(2\pi i \zeta_0)^{-1} \nabla_{\mathbf{r}} \hat{S}_1$  wird aus der zweiten Summe fortgelassen, weil es die Potenz  $(2\pi i \zeta_0)^{-2}$  ergibt.



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Durch Entwicklung der  $n$ -ten Potenz in der ersten Zeile von (A 31) entsteht

$$\begin{aligned} \hat{E} F = & \left\{ \sum_{n=0}^{\infty} \frac{1}{n!} (\nabla_{\mathbf{r}} \hat{S}_0 - \hat{\mathbf{f}}_0, \nabla_{\hat{\mathbf{f}}})^n \hat{E}(\hat{\mathbf{f}}, \mathbf{r})_{(\hat{\mathbf{f}}_0)} \right. \\ & + \sum_{n=1}^{\infty} \frac{1}{(n-1)!} (\nabla_{\mathbf{r}} \hat{S}_0 - \hat{\mathbf{f}}_0, \nabla_{\hat{\mathbf{f}}})^{n-1} \left( \frac{1}{2\pi i \varkappa_0} \nabla_{\mathbf{r}} \hat{S}_1 \nabla_{\hat{\mathbf{f}}} \right) \hat{E}(\hat{\mathbf{f}}, \mathbf{r})_{(\hat{\mathbf{f}}_0)} \\ & + \frac{1}{2} \sum_{n=2}^{\infty} \frac{1}{(n-2)!} (\nabla_{\mathbf{r}} \hat{S}_0 - \hat{\mathbf{f}}_0, \nabla_{\hat{\mathbf{f}}})^{n-2} \left[ \frac{1}{2\pi i \varkappa_0} (\nabla_{\mathbf{r}} \nabla_{\hat{\mathbf{f}}}) (\nabla_{\mathbf{r}} \hat{S}_0 \triangle_{\hat{\mathbf{f}}}) \right] \hat{E}(\hat{\mathbf{f}}, \mathbf{r})_{(\hat{\mathbf{f}}_0)} \\ & \left. + O((2\pi i \varkappa_0)^{-2}) \right\} F. \end{aligned} \quad (\text{A 32})$$

Mit der Definition von  $E(\mathbf{f}, \mathbf{r})$  [ähnlich wie (A 30)] ergibt sich

$$\begin{aligned} \hat{E} F = & \left\{ \hat{E}(\nabla_{\mathbf{r}} \hat{S}_0, \mathbf{r}) + \frac{1}{2\pi i \varkappa_0} (\nabla_{\mathbf{r}} \hat{S}_1 \nabla_{\hat{\mathbf{f}}}) \hat{E}(\hat{\mathbf{f}}, \mathbf{r})_{(\hat{\mathbf{f}} = \nabla_{\mathbf{r}} \hat{S}_0)} \right. \\ & \left. + \frac{1}{2\pi i \varkappa_0} \frac{1}{2} (\nabla_{\mathbf{r}} \nabla_{\hat{\mathbf{f}}})^2 \hat{S}_0 \hat{E}(\hat{\mathbf{f}}, \mathbf{r})_{(\hat{\mathbf{f}} = \nabla_{\mathbf{r}} \hat{S}_0)} + O((2\pi i \varkappa_0)^{-2}) \right\} F, \end{aligned} \quad (\text{A 33})$$

wobei die Ausdrucksweise

$$[(\nabla_{\mathbf{r}} \nabla_{\hat{\mathbf{f}}}) (\nabla_{\mathbf{r}} \hat{S}_0 \nabla_{\hat{\mathbf{f}}})] \hat{E}(\hat{\mathbf{f}}, \mathbf{r}) = (\nabla_{\mathbf{r}} \nabla_{\hat{\mathbf{f}}})^2 \hat{S}_0 \hat{E}(\hat{\mathbf{f}}, \mathbf{r}) \quad (\text{A 34})$$

benutzt wurde.

### Anhang 5. Aufbau und Bewegung von Wellenpaketen nach der Strahlenoptik

Nach (99) und (100) hat man

$$F(t, \mathbf{r}) = \exp \{2\pi i (S_0(\mathbf{r}) - \nu_0 t)\}. \quad (\text{A 35})$$

Das vollständige Integral<sup>28</sup> der Eikonalgleichung (65) bzw. (86) sei durch  $S_0(\mathbf{r} a_1 a_2 \nu_0) + a_3$  gegeben. Die beiden Konstanten  $a_1$  und  $a_2$  sind etwa durch die Einstrahlungsbedingungen bestimmt. Man nehme z. B. an, daß eine ebene Welle auf eine ebene Eintrittsfläche des Kristalls einfällt. Dann sind  $a_1$  und  $a_2$  die beiden zur Oberfläche parallelen Komponenten des Wellenvektors der einfallenden Welle.

Man bildet aus den einfallenden ebenen Wellen mit verschiedenen Werten von  $a_1$ ,  $a_2$  und  $\nu_0$  ein Wellenpaket. Dieses nimmt nach Eintritt in den Kristall die Form an:

$$F(t, \mathbf{r}) = \iiint A(a_1 a_2 \nu_0) \exp \{2\pi i \varphi(a_1 a_2 \nu_0)\} \exp \{2\pi i [S_0(\mathbf{r} a_1 a_2 \nu_0) - \nu_0 t + a_3]\} da_1 da_2 d\nu_0. \quad (\text{A 36})$$

$A(a_1 a_2 \nu_0)$  und  $\varphi(a_1 a_2 \nu_0)$  sind aus der Konstruktion des Paketes im Vakuum bestimmt.

Das Zentrum des Paketes befindet sich dort, wo die Phasen der Komponentenwellen übereinstimmen. Dies bedeutet, daß die Phase des Integranden von (A 36) als Funktion der Parameter  $a_1$ ,  $a_2$  und  $\nu_0$  stationär wird. Wenn man setzt

$$\Phi = \varphi(a_1 a_2 \nu_0) + S_0(\mathbf{r} a_1 a_2 \nu_0) - \nu_0 t + a_3, \quad (\text{A 37})$$

$$\text{dann soll gelten} \quad \frac{\partial \Phi}{\partial a_1} = 0, \quad \frac{\partial \Phi}{\partial a_2} = 0, \quad \frac{\partial \Phi}{\partial \nu_0} = 0. \quad (\text{A 38})$$

$$\text{Daraus folgt} \quad \frac{\partial S_0}{\partial a_1} = -\frac{\partial \varphi}{\partial a_1}, \quad \frac{\partial S_0}{\partial a_2} = -\frac{\partial \varphi}{\partial a_2}, \quad \frac{\partial S_0}{\partial \nu_0} - t = -\frac{\partial \varphi}{\partial \nu_0}. \quad (\text{A 39})$$

$\partial \varphi / \partial a_1$ ,  $\partial \varphi / \partial a_2$  und  $\partial \varphi / \partial \nu_0$  sind Konstanten, die durch die Einstrahlungsbedingungen, d. h. in unserem Beispiel durch die Anfangswerte der beiden Ortskoordinaten und der Zeit am Durchgangspunkt auf der Eintrittsfläche vorgegeben sind.

<sup>28</sup> Zum Beispiel A. SOMMERFELD, Vorlesungen über theoretische Physik, Band I, Mechanik, 7. Aufl., Akadem. Verlagsges. Leipzig 1964, Kap. 8.

Nach dem bekannten JACOBISCHEN Satz<sup>28</sup> sind die Werte von  $t$ ,  $r$  und  $f = \nabla_r S_0$ , die (A 39) erfüllen, d. h. die Bewegung des Paketes beschreiben, gerade die Lösungen der kanonischen Gln. (102) und (103).

Dieser unmittelbare Zusammenhang zwischen dem JACOBISCHEN Satz und der Vorstellung des Paket-zentrums als dem Punkt der stationären Phase scheint bisher nicht richtig erkannt worden zu sein<sup>29</sup>.

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<sup>28</sup> Vgl. The Mathematical Papers of Sir W. R. HAMILTON, Vol. I, Geometrical Optics (ed. A. W. CONWAY u. J. L.

SYNGE), Cambridge Univ. Press, Cambridge 1931, S. 500 (Editor's Appendix, Note 20).

## Mean Amplitudes of Vibration, Thermodynamic Functions, Molecular Polarizability and Absolute Raman Intensities of $\Sigma_g^+$ Modes in Carbon Subnitride\*

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Vibrational and structural informations for carbon subnitride, a molecule possessing a linear symmetrical structure with the point group  $D_{\infty h}$ , have been used to determine the mean-square amplitude quantities and mean amplitudes of vibration for the bonded and nonbonded atom pairs at the temperatures  $T=0$  and  $T=298$  °K by the CVIN method. The molar thermodynamic functions have been computed for the temperature range 100—6000 °K on the basis of a rigid rotator, harmonic oscillator model. Bond polarizabilities, molecular polarizability and polarizability derivatives corresponding to absolute RAMAN intensities of  $\Sigma_g^+$  modes in the ground electronic state have been calculated by the LIPPINCOTT-STUTMAN method employing the delta-function potentials.

Carbon subnitride has a system of three conjugated triple bonds and was first reported by MOUREU and BONGRAND<sup>1</sup> and later by BLOMQUIST and WINSLOW<sup>2</sup>. One may find its physical and chemical properties described in a review form by MOUREU and BONGRAND<sup>3</sup>. An X-ray diffraction study of the crystal structure by HANNAN and COLLIN<sup>4</sup> has established that carbon subnitride has a linear symmetrical configuration with the symmetry point group  $D_{\infty h}$ . MILLER and HANNAN<sup>5</sup> studied both the infrared absorption and RAMAN spectra of this molecule in the liquid and gaseous states, assigned on the

basis of a  $D_{\infty h}$  symmetry eight of the nine fundamental frequencies and carried out a normal coordinate treatment. The same investigations were later repeated by MILLER, HANNAN and COUSINS<sup>6</sup>, all but one of the fundamentals were directly observed by locating many more RAMAN lines and infrared bands and the vibrational assignments were revised. The near ultraviolet spectrum of this molecule in solution and vapour phase was studied and a vibrational analysis of one of the two band systems was made by MILLER and HANNAN<sup>7</sup>. Carbon subnitride has the same conjugated bond system as dimethyl-

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<sup>1</sup> C. MOUREU and J. C. BONGRAND, Bull. Soc. Chim. Belges **5**, 846 [1909].

<sup>2</sup> A. T. BLOMQUIST and E. C. WINSLOW, J. Org. Chem. **10**, 149 [1945].

<sup>3</sup> C. MOUREU and J. C. BONGRAND, Ann. Chem. **14**, 5 [1920].

<sup>4</sup> R. B. HANNAN, JR. and R. L. COLLIN, Acta Cryst. **6**, 350 [1953].

<sup>5</sup> F. A. MILLER and R. B. HANNAN, JR., J. Chem. Phys. **21**, 110 [1953].

<sup>6</sup> F. A. MILLER, R. B. HANNAN, JR., and L. R. COUSINS, J. Chem. Phys. **23**, 2127 [1955].

<sup>7</sup> F. A. MILLER and R. B. HANNAN, JR., Spectrochim. Acta **12**, 321 [1958].

triacetylene<sup>8</sup>, plus a pair of nonbonding electrons with opposite spins on each nitrogen atom and should therefore exhibit all the  $\pi$ - $\pi$  transitions of dimethyltriacetylene in addition to the n- $\pi$  transitions<sup>9</sup>. MILLER and HANNAN<sup>7</sup> explained the two observed band systems and made a new vibrational assignments for the ground and upper states in conjunction with the earlier investigations<sup>5, 6</sup>. The results favour a linear conformation in both the ground and upper states. The fundamental frequencies in  $\text{cm}^{-1}$  for carbon subnitride in the ground state are given in Table 1.

| Symmetry Species | Frequency | Schematic Description of the Mode | Assignment |
|------------------|-----------|-----------------------------------|------------|
| $\Sigma_g^+$     | $\nu_1$   | Symmetrical C≡N stretching        | 2290       |
|                  | $\nu_2$   | Symmetrical C≡N stretching        | 2129       |
|                  | $\nu_3$   | Symmetrical C-C stretching        | 692        |
| $\Sigma_u^+$     | $\nu_4$   | Asymmetrical C≡N stretching       | 2241       |
|                  | $\nu_5$   | Asymmetrical C-C stretching       | 1154       |
| $\pi_g$          | $\nu_6$   | Asymmetrical C-C≡N bending        | 504        |
|                  | $\nu_7$   | Asymmetrical C-C≡C bending        | 263        |
| $\pi_u$          | $\nu_8$   | Symmetrical C-C≡N bending         | 472        |
|                  | $\nu_9$   | Symmetrical C-C≡C bending         | 107        |

Table 1. The observed fundamental frequencies in  $\text{cm}^{-1}$  for carbon subnitride.

It is the aim of the present investigation to evaluate the mean amplitudes of vibration by the CYVIN method<sup>10</sup> with the recent vibrational and structural data<sup>4, 7</sup>, compute the statistical thermodynamic functions on the basis of a rigid rotator, harmonic oscillator model and calculate the molecular polarizability and derived polarizabilities by the LIPPINCOTT-STUTMAN method<sup>11</sup> employing the delta-function potential for carbon subnitride.

## Mean Amplitudes of Vibration

The carbon subnitride molecule having a point group  $D_{\infty h}$  gives rise to thirteen vibrational degrees of freedom constituting nine fundamental frequencies which are distributed under the various irreducible representations as follows:

$$3 \Sigma_g^+(R, p) + 2 \Sigma_u^+(I, \parallel) + 2 \pi_g(R, dp) + 2 \pi_u(I, \perp)$$

where R, I, p, dp,  $\parallel$  and  $\perp$  stand for RAMAN active, infrared active, polarized, depolarized, parallel and perpendicular, respectively. On the basis of its structure one could expect a resonance between the two C-C vibrations because of mechanical coupling provided by the connecting C≡C bond and a consequence of which the energy levels would repel one another resulting in one being abnormally high and the other abnormally low. This is evidently seen from 692  $\text{cm}^{-1}$  as the frequency of the C-C symmetrical stretching vibration and 1154  $\text{cm}^{-1}$  as the C-C asymmetrical stretching vibration. A similar situation may be observed in the case of dimethyltriacetylene<sup>12</sup>. This gives an additional support to MILLER and HANNAN<sup>6, 7</sup> for their choice of 692  $\text{cm}^{-1}$  as the frequency of the C-C symmetrical stretching vibration.

Thirteen internal coordinates have been selected here to describe the thirteen vibrational degrees of freedom and they are given as follows:  $r_1$  and  $r_2$  are the C≡N stretching coordinates;  $t$  is the C≡C stretching coordinate;  $d_1$  and  $d_2$  are the C-C stretching coordinates;  $\theta_1$  and  $\theta_2$  designate the C-C≡N bending coordinates in the  $xz$  plane while  $\theta'_1$  and  $\theta'_2$  designate the same in the  $yz$  plane;  $\phi_1$ ,  $\phi_2$ ,  $\phi'_1$  and  $\phi'_2$  designate the C-C≡C bending coordinates in the  $xz$  and  $yz$  planes as those of

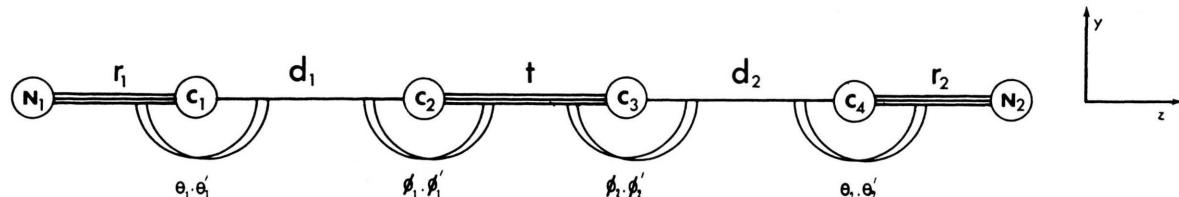


Fig. 1. Geometric illustration of the internal coordinates for carbon subnitride. The symbols denote the deviations from the equilibrium values. The equilibrium C≡N, C-C and C≡C bond lengths are identified by the symbols R, D and T, respectively.

<sup>8</sup> M. BEER, J. Chem. Phys. **25**, 745 [1956].

<sup>9</sup> J. R. PLATT, J. Opt. Soc. Amer. **43**, 252 [1953].

<sup>10</sup> S. J. CYVIN, Spectrochim. Acta **15**, 828 [1959].

<sup>11</sup> E. R. LIPPINCOTT and J. M. STUTMAN, J. Phys. Chem. **68**, 2926 [1964].

<sup>12</sup> I. M. MILLS and H. W. THOMPSON, Proc. Roy. Soc., Lond. A **226**, 306 [1954].

$\theta$ 's (see Fig. 1). The equilibrium interbond distances  $C\equiv N$ ,  $C\equiv C$  and  $C-C$  are being represented here by the symbols  $R$ ,  $T$  and  $D$ , respectively. On the basis of the principle outlined by WILSON<sup>13</sup>, a set of symmetry coordinates satisfying the conditions of normalization, orthogonality and transformations of the concerned irreducible representations has been constructed with the help of the internal coordinates described above and given in the following:

$$\begin{aligned} S_1(\Sigma_g^+) &= (r_1 + r_2)/\sqrt{2}; \\ S_2(\Sigma_g^+) &= t; \\ S_3(\Sigma_g^+) &= (d_1 + d_2)/\sqrt{2}; \\ S_4(\Sigma_u^+) &= (r_1 - r_2)/\sqrt{2}; \\ S_5(\Sigma_u^+) &= (d_1 - d_2)/\sqrt{2}; \\ S_{6a}(\pi_g) &= (R D)^{1/2}(\theta_1 - \theta_2)/\sqrt{2}; \\ S_{6b}(\pi_g) &= (R D)^{1/2}(\theta_1' - \theta_2')/\sqrt{2}; \\ S_{7a}(\pi_g) &= (D T)^{1/2}(\phi_1 - \phi_2)/\sqrt{2}; \\ S_{7b}(\pi_g) &= (D T)^{1/2}(\phi_1' - \phi_2')/\sqrt{2}; \\ S_{8a}(\pi_u) &= (R D)^{1/2}(\theta_1 + \theta_2)/\sqrt{2}; \\ S_{8b}(\pi_u) &= (R D)^{1/2}(\theta_1' + \theta_2')/\sqrt{2}; \\ S_{9a}(\pi_u) &= (D T)^{1/2}(\phi_1 + \phi_2)/\sqrt{2} \end{aligned}$$

and  $S_{9b}(\pi_u) = (D T)^{1/2}(\phi_1' + \phi_2')/\sqrt{2}$ .

Here the angle displacements are multiplied by the equilibrium bond lengths  $R(C\equiv N)$ ,  $T(C\equiv C)$  and  $D(C-C)$  in order to keep the dimensions of the mean-square amplitude quantities referring to the angle bending the same as those of the quantities due to the bonded atom pairs. On the basis of the principle postulated by WILSON<sup>13</sup> and FERIGLE and MEISTER<sup>14</sup>, the  $G$  matrix elements related to the kinetic energy have been obtained in terms of the above set of symmetry coordinates. One would normally expect twenty five mean-square amplitude quantities for a molecule of the present investigation, but the high symmetry of the molecular system reduces these to fifteen. Since the parallel and perpendicular vibrations do not occur in the same symmetry species, the mean-square amplitude quantities due to the interaction between the bonded atom pairs and interbond angles are not at all permitted in

this case. Following the method of CYVIN<sup>10</sup>, the symmetrized mean-square amplitude matrices in terms of the mean-square amplitude quantities were obtained by introducing the symmetry coordinates.

From the secular equation  $|\Sigma G^{-1} - EA| = 0$  postulated by CYVIN<sup>10</sup>, the secular equations giving the normal frequencies in terms of the mean-square amplitude quantities were constructed at the temperatures  $T = 0$  and  $T = 298$  °K with help of the  $\Sigma$  and  $G$  matrices and vibrational and structural data<sup>4, 7</sup>. Since it is not possible to evaluate all the symmetrized mean-square amplitude matrices under the symmetry species  $\Sigma_g^+$ , the off-diagonal elements were neglected for the sake of convenience to solve the diagonal elements. In the cases of other symmetry species, there are two diagonal elements and one off-diagonal element with two equations under each symmetry species. The equations resulted in imaginary values for the diagonal elements when the off-diagonal element was neglected. Hence the off-diagonal element was taken into consideration and the equations were solved under each symmetry species in the manner described by earlier investigators<sup>15-22</sup>. The calculated values of the symmetrized mean-square amplitude matrices in  $\text{\AA}^2$  are given in Table 2 at the temperatures  $T = 0$  and  $T = 298$  °K, and the calculated values of the mean-square amplitude quantities in  $\text{\AA}^2$  at these temperatures are given

| Element       | Symmetrized mean-square amplitude matrix |              |
|---------------|--|--------------|
|               | $T = 0$                                  | $T = 298$ °K |
| $\Sigma_{11}$ | 0.0009553                                | 0.0009553    |
| $\Sigma_{22}$ | 0.0012464                                | 0.0012485    |
| $\Sigma_{33}$ | 0.0013076                                | 0.0013154    |
| $\Sigma_{44}$ | 0.0014564                                | 0.0014564    |
| $\Sigma_{55}$ | 0.0021246                                | 0.0021382    |
| $\Sigma_{45}$ | -0.0008138                               | -0.0008247   |
| $\Sigma_{66}$ | 0.0078135                                | 0.0131246    |
| $\Sigma_{67}$ | 0.0021854                                | 0.0025544    |
| $\Sigma_{88}$ | 0.0039182                                | 0.0095125    |
| $\Sigma_{99}$ | 0.0035675                                | 0.0088236    |
| $\Sigma_{89}$ | -0.0009984                               | 0.0021078    |

Table 2. Symmetrized mean-square matrices in  $\text{\AA}^2$  for carbon subnitride.

<sup>13</sup> E. B. WILSON, JR., J. Chem. Phys. **7**, 1047 [1939]; **9**, 76 [1941].

<sup>14</sup> S. M. FERIGLE and A. G. MEISTER, J. Chem. Phys. **19**, 982 [1951].

<sup>15</sup> G. GLOCKLER, Rev. Mod. Phys. **15**, 111 [1943].

<sup>16</sup> G. GLOCKLER and J. TUNG, J. Chem. Phys. **13**, 388 [1945].

<sup>17</sup> P. TORKINGTON, J. Chem. Phys. **17**, 357 [1949].

<sup>18</sup> P. TORKINGTON, Proc. Roy. Soc., Lond. A **64**, 32 [1951].

<sup>19</sup> J. DUSCHESNE and L. BURNELLE, J. Chem. Phys. **19**, 1191 [1951].

<sup>20</sup> J. DUSCHESNE and A. H. NIELSEN, J. Chem. Phys. **20**, 1968 [1952].

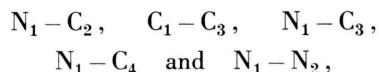
<sup>21</sup> J. W. LINNETT and D. F. HEATH, Trans. Faraday Soc. **48**, 592 [1952].

<sup>22</sup> S. SMITH and J. W. LINNETT, Trans. Faraday Soc. **52**, 891 [1956].

| Symbol                  | Mean-square amplitude quantity |                         |
|-------------------------|--------------------------------|-------------------------|
|                         | $T=0$                          | $T=298^{\circ}\text{K}$ |
| $\sigma_r$              | 0.0012059                      | 0.0012059               |
| $\sigma_{rr}$           | -0.0002506                     | -0.0002506              |
| $\sigma_d$              | 0.0017161                      | 0.0017268               |
| $\sigma_{dd}$           | -0.0004085                     | -0.0004114              |
| $\sigma_t$              | 0.0012464                      | 0.0012485               |
| $\sigma_{rd}$           | -0.0008138                     | -0.0008247              |
| $\sigma_{\theta}$       | 0.0058658                      | 0.0113186               |
| $\sigma_{\theta\theta}$ | -0.0019477                     | -0.0018061              |
| $\sigma_{\phi}$         | 0.0054331                      | 0.0104261               |
| $\sigma_{\phi\phi}$     | -0.0018656                     | -0.0016025              |
| $\sigma_{\theta\phi}$   | 0.0005935                      | 0.0023311               |
| $\sigma_{r+d}$          | 0.0021082                      | 0.0021080               |
|                         | 0.0029625                      | 0.0029753               |
| $\sigma_{r+d+t}$        | 0.0033546                      | 0.0033565               |
| $\sigma_{r+2d+t}$       | 0.0038211                      | 0.0038367               |
| $\sigma_{2r+2d+t}$      | 0.0057722                      | 0.0057899               |

Table 3. Mean-square amplitude quantities in  $\text{\AA}^2$  for carbon subnitride.

in Table 3 where  $\sigma_r$ ,  $\sigma_d$  and  $\sigma_t$  are the mean-square amplitude quantities due to the bonded atom pairs  $\text{C}\equiv\text{N}$ ,  $\text{C}-\text{C}$  and  $\text{C}\equiv\text{C}$ , respectively;  $\sigma_{\theta}$  and  $\sigma_{\phi}$  are the quantities due to the bendings  $\text{C}-\text{C}\equiv\text{N}$  and  $\text{C}-\text{C}\equiv\text{C}$ , respectively;  $\sigma_{rr}$ ,  $\sigma_{dd}$ ,  $\sigma_{rd}$ ,  $\sigma_{\theta\theta}$ ,  $\sigma_{\phi\phi}$ ,  $\sigma_{\theta\phi}$  and  $\sigma_{\theta\phi'}$  are the respective interaction quantities;  $\sigma_{r+d}$ ,  $\sigma_{d+t}$ ,  $\sigma_{r+d+t}$ ,  $\sigma_{r+2d+t}$  and  $\sigma_{2r+2d+t}$  are the quantities due to the nonbonded atom pairs



respectively. The corresponding calculated values of the mean amplitudes of vibration in  $\text{\AA}$  for the bonded as well as nonbonded atom pairs are given in Table 4.

| Distance                 | Mean amplitude of vibration |                         |
|--------------------------|-----------------------------|-------------------------|
|                          | $T=0$                       | $T=298^{\circ}\text{K}$ |
| $\text{C}\equiv\text{N}$ | 0.0347                      | 0.0347                  |
| $\text{C}-\text{C}$      | 0.0414                      | 0.0416                  |
| $\text{C}\equiv\text{C}$ | 0.0353                      | 0.0354                  |
| $\text{N}_1-\text{C}_2$  | 0.0459                      | 0.0459                  |
| $\text{C}_1-\text{C}_3$  | 0.0544                      | 0.0545                  |
| $\text{N}_1-\text{C}_3$  | 0.0579                      | 0.0579                  |
| $\text{N}_1-\text{C}_4$  | 0.0618                      | 0.0620                  |
| $\text{N}_1-\text{N}_2$  | 0.0759                      | 0.0761                  |

Table 4. Mean amplitudes of vibration in  $\text{\AA}$  for carbon subnitride.

The mean-square amplitude quantities due to the bendings are very much greater than those due to the bonded and nonbonded atom pairs. The situation is reversed for the corresponding force constants. The quantities due to the nonbonded atom pairs are very greater than those due to the bonded atom pairs. The values of the mean-square amplitudes of vibration at the two temperatures are not very different for the parallel vibrations but they are for the perpendicular vibrations. In the cases of nonbonded atom pairs, the mean amplitudes of vibration are in the increasing order as expected with the increase of interbond distances. In the cases of bonded atom pairs, the mean amplitudes of vibration are in the decreasing order with the increase of bond orders (see Table 4). Of particular interest is the fact that the interbond distances in carbon subnitride are about the same as those found in the three related molecules<sup>23-26</sup>; cyanoacetylene, hydrogen cyanide, cyanogen and diacetylene, hydrogen cyanide, cyanogen and diacetylene. The mean amplitudes of vibration at room temperature are as follows: 0.0347  $\text{\AA}$  in carbon subnitride, 0.0349  $\text{\AA}$  in cyanogen<sup>27</sup> and 0.0342  $\text{\AA}$  in hydrogen cyanide<sup>28</sup> for the  $\text{C}\equiv\text{N}$  bond; 0.0416  $\text{\AA}$  in carbon subnitride and 0.0419  $\text{\AA}$  in cyanogen<sup>27</sup> for the  $\text{C}-\text{C}$  bond; 0.0354  $\text{\AA}$  in carbon subnitride and 0.0358  $\text{\AA}$  in acetylene<sup>29</sup> for the  $\text{C}\equiv\text{C}$  bond. This clearly shows that the addition of the third triple bond to a conjugated system has only a minor effect on the structure. Hence the values of mean amplitudes of vibration are readily transferable to related systems having similar chemical bonds with nearly identical interbond distances.

### Thermodynamic Functions

The molar thermodynamic functions such as heat content, free energy, entropy and heat capacity of carbon subnitride were calculated using the vibrational and structural data<sup>4,7</sup> for the temperature range 100–6000  $^{\circ}\text{K}$ . A rigid rotator, harmonic oscillator model was assumed and all the quantities were calculated for a gas in the thermodynamic

<sup>23</sup> A. A. WESTENBERG and E. B. WILSON, JR., J. Amer. Chem. Soc. **72**, 199 [1950].

<sup>24</sup> A. LANGSETH and C. K. MOLLER, Acta Chem. Scand. **4**, 725 [1950].

<sup>25</sup> L. PAULING, H. D. SPRINGALL, and K. J. PALMER, J. Amer. Chem. Soc. **61**, 927 [1939].

<sup>26</sup> A. H. NETHERCOT, J. A. KLEIN, and C. H. TOWNES, Phys. Rev. **86**, 798 [1952].

<sup>27</sup> S. J. CYVIN and E. MEISINGSETH, Acta Chem. Scand. **15**, 1289 [1961].

<sup>28</sup> E. MEISINGSETH and S. J. CYVIN, Acta Chem. Scand. **16**, 1321 [1962].

<sup>29</sup> E. MEISINGSETH and S. J. CYVIN, Acta Chem. Scand. **15**, 2021 [1961].

standard gaseous state of unit fugacity (one atmosphere). The standard formulae and tables of functions for the harmonic oscillator contributions were used from PITZER<sup>30</sup>. The principal moments of

| <i>T</i> | $(H_0 - E_0^0)/T$ | $-(F_0 - E_0^0)/T$ | <i>S</i> <sup>0</sup> | <i>C<sub>p</sub></i> <sup>0</sup> |
|----------|-------------------|--------------------|-----------------------|-----------------------------------|
| 100      | 9.026             | 37.584             | 46.610                | 11.944                            |
| 150      | 10.481            | 41.289             | 51.770                | 14.758                            |
| 200      | 11.853            | 44.716             | 56.569                | 17.186                            |
| 273.16   | 13.671            | 48.709             | 62.380                | 19.834                            |
| 298.16   | 14.208            | 49.894             | 64.102                | 20.528                            |
| 300      | 14.261            | 50.025             | 64.286                | 20.576                            |
| 400      | 16.101            | 54.317             | 70.418                | 22.661                            |
| 500      | 17.570            | 58.093             | 75.663                | 24.153                            |
| 600      | 18.774            | 61.400             | 80.174                | 25.373                            |
| 700      | 19.796            | 64.412             | 84.208                | 26.395                            |
| 800      | 20.681            | 66.775             | 87.456                | 27.257                            |
| 900      | 21.453            | 69.625             | 91.078                | 27.997                            |
| 1000     | 22.131            | 71.950             | 94.081                | 28.616                            |
| 1100     | 22.754            | 74.062             | 96.816                | 29.140                            |
| 1200     | 23.213            | 75.939             | 99.152                | 29.583                            |
| 1300     | 23.794            | 77.878             | 101.672               | 29.953                            |
| 1400     | 24.256            | 79.724             | 103.980               | 30.273                            |
| 1500     | 24.681            | 81.564             | 106.245               | 30.543                            |
| 1600     | 25.036            | 82.854             | 107.890               | 30.773                            |
| 1700     | 25.373            | 84.540             | 109.913               | 30.968                            |
| 1800     | 25.689            | 86.173             | 111.862               | 31.142                            |
| 1900     | 25.994            | 87.421             | 113.415               | 31.298                            |
| 2000     | 26.246            | 88.563             | 114.809               | 31.423                            |
| 2200     | 26.728            | 91.257             | 117.985               | 31.636                            |
| 2400     | 27.173            | 93.877             | 121.050               | 31.816                            |
| 2600     | 27.507            | 95.623             | 123.130               | 31.947                            |
| 2800     | 27.835            | 98.068             | 125.903               | 32.056                            |
| 3000     | 28.113            | 99.724             | 127.837               | 32.145                            |
| 3200     | 28.365            | 101.361            | 129.726               | 32.221                            |
| 3400     | 28.598            | 103.018            | 131.616               | 32.283                            |
| 3600     | 28.794            | 104.975            | 133.769               | 32.334                            |
| 3800     | 28.992            | 106.530            | 135.522               | 32.381                            |
| 4000     | 29.170            | 108.029            | 137.199               | 32.420                            |
| 4200     | 29.316            | 109.139            | 138.455               | 32.453                            |
| 4400     | 29.463            | 111.182            | 140.645               | 32.482                            |
| 4600     | 29.596            | 112.502            | 142.098               | 32.508                            |
| 4800     | 29.703            | 113.367            | 143.070               | 32.530                            |
| 5000     | 29.811            | 114.246            | 144.057               | 32.551                            |
| 5200     | 29.941            | 115.863            | 145.804               | 32.569                            |
| 5400     | 30.034            | 116.722            | 146.756               | 32.584                            |
| 5600     | 30.111            | 117.482            | 147.593               | 32.597                            |
| 5800     | 30.189            | 118.611            | 148.800               | 32.608                            |
| 6000     | 30.285            | 119.698            | 149.983               | 32.621                            |

Table 5. Heat content, free energy, entropy and heat capacity of carbon subnitride for the ideal gaseous state at one atmospheric pressure. *T* is the temperature in °K; the other quantities are in cal. deg<sup>-1</sup> mole<sup>-1</sup> and  $E_0^0$  is the energy of one mole of perfect gas at absolute zero temperature.

<sup>30</sup> K. S. PITZER, Quantum Chemistry, Prentice-Hall, Inc., New York 1953.

<sup>31</sup> D. R. STULL, J. CHAO, T. E. DERGAZARIAN, S. T. HADDEN, H. PROPHET, J. A. RIZOS, and A. C. SWANSON, Joint Army-Navy-Air Force Thermochemical Data, The Advanced Research Projects Agency Programme, U.S. Air Force Contract No. AF 33(616)-6149, The Dow Chemical Company, Thermal Laboratory, Midland, Michigan, March 31, 1961.

<sup>32</sup> G. T. AMSTRONG and S. MARANTZ, J. Phys. Chem. **64**, 1776 [1960].

inertia were calculated from the X-ray diffraction study<sup>4</sup> and their values are:

$$I_{xx} = I_{yy} = 27.7126 \text{ AWU} \text{ Å}^2 (46.0342 \times 10^{-40} \text{ g cm}^2); \\ I_{zz} = 0.$$

A symmetry number of 2 was assumed in the calculations. The contributions due to the centrifugal distortion, isotopic mixing and nuclear spins were neglected in the calculations. The calculated values of the thermodynamic functions in cal. deg<sup>-1</sup>·mole<sup>-1</sup> for carbon subnitride are given in Table 5. STULL and his associates<sup>31</sup> calculated the thermodynamic quantities from the earlier vibrational data<sup>5</sup> and their values for entropy and heat capacity in cal. deg<sup>-1</sup>·mole<sup>-1</sup> at room temperature are 69.314 and 20.528, respectively. The corresponding values in cal. deg<sup>-1</sup>·mole<sup>-1</sup> from the present study are 64.102 and 20.528, respectively. Their higher value for the entropy is probably due to the unreliable vibrational assignments particularly for the deformation modes. AMSTRONG and MARANTZ<sup>32</sup> measured the heat of combustion of carbon subnitride in the liquid state and calculated the heat of formation in the gaseous state at room temperature as 120.6 kcal. mole<sup>-1</sup> from the data for the heat of vapourization given by SAGGIOMO<sup>33</sup>. No other experimental or calculated values of the thermodynamic quantities are available in the literature.

### Molecular Polarizability

On the basis of quantum mechanical models several approaches have been made in recent years and developed in many ways to compute the atomic and molecular polarizabilities in order to test how far the polarizability could be a useful criterion for testing the accuracy of wave functions chosen<sup>34-39</sup>. LIPPINCOTT and STUTMAN<sup>11</sup> developed from a delta-function potential a method of generating component polarizabilities in order to compute the molecular or average polarizabilities with  $\alpha_M = (\alpha_1 + \alpha_2 + \alpha_3)$  where  $\alpha_1$ ,  $\alpha_2$  and  $\alpha_3$  refer to the three principal

<sup>33</sup> A. J. SAGGIOMO, J. Org. Chem. **22**, 1171 [1957].

<sup>34</sup> H. R. HASSE, Proc. Cambridge Phil. Soc. **26**, 542 [1930].

<sup>35</sup> R. A. BUCKINGHAM, Proc. Roy. Soc., Lond. A **160**, 94 [1937].

<sup>36</sup> J. G. KIRKWOOD, Physik. Z. **33**, 57 [1932].

<sup>37</sup> R. P. BELL and D. A. LONG, Proc. Roy. Soc., Lond. A **203**, 364 [1950].

<sup>38</sup> J. A. ABBOTT and H. C. BOLTON, J. Chem. Phys. **20**, 762 [1952].

<sup>39</sup> H. J. KOLKER and M. KARPLUS, J. Chem. Phys. **39**, 2011 [1963].

polarizability components. The molecular polarizability is composed mainly of bond parallel components obtainable from molecular delta-function model and bond perpendicular components obtainable from the atomic delta-function polarizabilities. In addition, corrections to the parallel and perpendicular components are made to compensate for polarity effects. The contribution to the parallel component by the bond region electrons is calculated using a linear combination of atomic delta-function wave functions representing the two nuclei involved in the bond and analytically expressed as

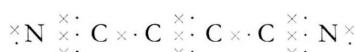
$$\alpha_{\parallel b} = 4 n A_{12} (1/a_0) (\langle x^2 \rangle)^2$$

where  $A_{12}$  is the root mean-square delta-function strength of the two nuclei,  $a_0$  the Bohr radius,  $n$  the bond order and  $\langle x^2 \rangle$  the mean-square coordinate of a bonding electron which may be expressed as

$$\langle x^2 \rangle = (R^2/4) + (1/2 c_R^2).$$

Here  $R$  is the internuclear distance at the equilibrium configuration.

The nonbond region electron contribution to the parallel bond component  $\alpha_{\parallel n}$  is calculated from the fraction of the electrons in the valence shell of each atom not involved in bonding and its respective atomic polarizability; and the basis for such calculation is the LEWIS-LANGMUIR octet rule<sup>40, 41</sup> modified by LINNETT<sup>42</sup> as a double-quartet of electrons. As an example, the electronic configuration of carbon subnitride is given according to the LINNETT electronic picture of bonding as follows



where the "dots" represent electrons with spins of  $+1/2$  and the "crosses" electrons with spins of  $-1/2$ . If each nitrogen atom has two electrons in its ground electronic or valence shell, then the nonbond region electron contribution for this molecule is  $\alpha_{\parallel n} = (4/5) \alpha_N$  since 2 of 5 electrons in the valence shell of each nitrogen atom are not involved in the bond formation according to the LINNETT electronic picture of bonding<sup>42</sup>. This may analytically be expressed as  $\Sigma \alpha_{\parallel n} = \Sigma f_j \alpha_j$  where  $f_j$  is the fraction of electrons of the  $j$ th atom not involved in the bond formation and  $\alpha_j$  the atomic polarizability of the  $j$ th

atom which would be obtainable from delta-function strength.

LIPPINCOTT and STUTMAN<sup>11</sup> assumed that the perpendicular component of a diatomic molecule is simply the sum of the two atomic polarizabilities and this assumption is partially justified by a pictorial representation of perpendicular distortion.  $\alpha = 2 \alpha_A$  for a non-polar diatomic  $A_2$  molecule. This principle was extended to polyatomics from a consideration of the structure of the molecule and the assumption that each atom if it were not bonded would possess three degrees of atomic polarizability freedom. If an atom forms one bond, one degree of freedom is lost, e. g., a diatomic molecule has 4 residual degrees of freedom. If an atom forms 2 bonds which are linear, only one degree of freedom is lost, e. g.  $n_{df}$  for  $\text{CO}_2$  is only 6. Extending this principle to the carbon subnitride molecule, the atomic degrees of freedom remaining is 12. One may refer the earlier investigation<sup>11</sup> for a more detailed description. Thus the delta-function model gives explicit expressions for the parallel and perpendicular components and the mean polarizabilities for the diatomic as well as polyatomic systems. All these are in accordance with the investigations of DENBIGH<sup>43</sup> regarding the bond refractions and bond and molecular polarizabilities.

The delta-function strengths  $A$ 's in atomic units, atomic polarizabilities  $\alpha$ 's in  $10^{-25} \text{ cm}^3$  and  $c$ 's in atomic units adopted from the earlier investigations<sup>11</sup> for the present work are as follows:

$$\begin{aligned} A_N &= 0.927, & \alpha_N &= 7.43, & c_N &= 4.146, \\ A_C &= 0.846, & \alpha_C &= 9.78, & c_C &= 3.384. \end{aligned}$$

The  $c$  value for the carbon atom has been obtained in the manner described by LIPPINCOTT and DAYHOFF<sup>44</sup> for a bond of polyatomic system. The calculated values of the polarizabilities in  $10^{-25} \text{ cm}^3$  for the  $\text{C}\equiv\text{N}$ ,  $\text{C}-\text{C}$  and  $\text{C}\equiv\text{C}$  bonds are 21.309, 13.268 and 23.034, respectively. The total value of the polarizability contribution to the parallel component from the bond region electrons is obtained as

$$\Sigma \alpha_{\parallel b} = 92.188 \times 10^{-25} \text{ cm}^3.$$

The value of the polarizability contributions to the parallel component from the bond region electrons is given as

$$\Sigma \alpha_{\parallel n} = \Sigma f_j \alpha_j = 5.944 \times 10^{-25} \text{ cm}^3.$$

<sup>40</sup> G. N. LEWIS, J. Amer. Chem. Soc. **38**, 762 [1916].

<sup>41</sup>

I. LANGMUIR, J. Amer. Chem. Soc. **38**, 2221 [1916].

<sup>42</sup>

J. W. LINNETT, J. Amer. Chem. Soc. **83**, 2643 [1961].

K. G. DENBIGH, Trans. Faraday Soc. **36**, 936 [1940].

E. R. LIPPINCOTT and M. O. DAYHOFF, Spectrochim. Acta **16**, 807 [1960].

The calculated value of the sum of the perpendicular components of all the bonds in the molecule is given as

$$\Sigma 2 \alpha_{\perp} = 107.960 \times 10^{-25} \text{ cm}^3.$$

Hence the average molecular polarizability for carbon subnitride has been obtained as follows:

$$\begin{aligned} \alpha_M &= \frac{1}{3} (\Sigma \alpha_{\parallel b} + \Sigma \alpha_{\parallel n} + \Sigma 2 \alpha_{\perp}) \\ &= 68.696 \times 10^{-25} \text{ cm}^3. \end{aligned}$$

There is no experimental value available in the literature for molar refraction of carbon subnitride to derive the molecular polarizability and make a comparison here.

### Absolute Raman Intensities of $\Sigma_g^+$ Modes

There will be a change in the electron distribution and in the forces binding the nuclei when there are changes in the internuclear distances within the molecule; consequently, there will also be a change in the value of the electron polarizability. Much work has so far not been done on this aspect. There is an increase of the polarizability of the covalent bond as the bond goes from lower to a higher vibrational state. If the polarizability is a sensitive measure of the distortion of an electronic distribution under an applied electro-magnetic field, then the change in the polarizability with respect to the internuclear distance between the two atoms should be an effective criterion for the covalency of a chemical bond. This quantity  $\alpha' = (\delta \alpha / \delta R)$  on which the absolute intensity of the RAMAN scattering depends is experimentally measurable from RAMAN spectroscopic techniques. Absolute RAMAN intensities are determined by the derivatives of molecular polarizability with respect to elongations of the various bonds within the molecule. When a bond stretches, the major change in the molecular polarizability is localized in that bond and so the derivative is a bond property indirectly related to the force constant. The value of the polarizability derivative depends on the bond type<sup>45</sup>. It is exceedingly small for a pure ionic bond and very much larger for a pure covalent bond. The recent investigations on the group IV tetrahalides<sup>46</sup> show that it has been assumed to be proportional to the percent covalency and to the sum of

the atomic numbers of the central and peripheral atoms. It is directly proportional to the bond order for the hydrocarbon gases<sup>47</sup>. The observed intensity of a RAMAN line is given by

$$I_p = \frac{K M (v_0 - v_p)^4}{v_p [1 - \exp(-h v_0 / k T)]} \cdot 45 \left( \frac{\delta \alpha}{\delta Q_p} \right)^2 \left( \frac{6}{6 - 7 \varrho} \right)$$

where  $K$  is a constant,  $M$  the molar concentration of the scattering species,  $v_p$  the vibrational frequency of the  $p$ th normal mode  $Q_p$ ,  $k$  the BOLTZMANN constant,  $T$  the temperature in  $^{\circ}\text{K}$ ,  $\alpha$  the average molecular polarizability and  $\varrho$  the degree of depolarization of the observed spectral line. Hence measurement of the intensity of a RAMAN line provides an immediate calculation for the experimental value of  $(\delta \alpha / \delta Q)$  through well defined transformation,  $(\delta \alpha / \delta R)$ . It is aimed here to derive a functional form  $(\delta \alpha / \delta R)$  for the symmetrical stretching mode of a diatomic and polyatomic systems from the delta-function potential and apply this to the  $\Sigma_g^+$  modes of oscillation in carbon subnitride.

The polarizability contribution from the bond region electrons to the bond parallel component for a polyatomic system is directly given here from the delta-function potential as follows:

$$\alpha_{\parallel b} = 4 n A_{12} (1/a_0) [ (R^2/4) + (1/2 c_R^2) ]^2.$$

On differentiating this with respect to the internuclear distance  $R$  and neglecting terms of small magnitude, we have the following:

$$(\delta \alpha_{\parallel b} / \delta R) = n A_{12} (1/a_0) (R^3).$$

The molecular polarizability of a diatomic molecule is written as follows:

$$\alpha = (1/3) (\alpha_{\parallel} + 2 \alpha_{\perp}).$$

The necessary desired quantity is the change in the molecular polarizability due to the symmetrical stretching of the bond and the following approximation may be satisfied:

$$(\delta \alpha / \delta R) = (\delta \alpha_{\parallel b} / \delta R).$$

The quantity  $(\delta \alpha_{\parallel b} / \delta R)^2$  is assumed to be directly proportional to the absolute RAMAN intensity of the stretching mode in the ground electronic state. Hence we have

$$\begin{aligned} (\delta \alpha / \delta R) &= (1/3) (\delta \alpha_{\parallel} / \delta R) \\ &= (1/3) (\delta \alpha_{\parallel b} / \delta R) = n A_{12} (1/3 a_0) (R^3). \end{aligned}$$

<sup>45</sup> D. A. LONG, Proc. Roy. Soc., Lond. A **217**, 203 [1953].

<sup>46</sup> L. A. WOODWARD and D. A. LONG, Trans. Faraday Soc. **45**, 1131 [1949].

<sup>47</sup> H. J. BERNSTEIN and T. YOSHINO, Paper read at the Institute of Petroleum Hydrocarbon Research Group Conference on Molecular Spectroscopy, London, February 1958.

As the absolute intensities of RAMAN lines due to the symmetrical  $\text{C}\equiv\text{N}$ ,  $\text{C}-\text{C}$  and  $\text{C}\equiv\text{C}$  stretching vibrations depend on the derivatives of the polarizabilities of the respective bonds, such calculations have been made here from the above derived equation using the internuclear distances, delta-function strengths, BOHR radius, etc. given earlier for carbon subnitride. The calculated values of the polarizability derivatives in  $\text{\AA}^2$  for the  $\text{C}\equiv\text{N}$ ,  $\text{C}-\text{C}$  and  $\text{C}\equiv\text{C}$  bonds are 2.347, 1.227 and 2.411, respectively. These values compare well with those measured experimentally in other related systems having similar chemical bonds. They are  $2.61 \text{\AA}^2$  for the  $\text{C}\equiv\text{N}$  bond in acetonitrile<sup>48</sup>,

<sup>48</sup> G. W. CHANTRY and R. A. PLANE, J. Chem. Phys. **35**, 1027 [1961].

$1.37 \text{\AA}^2$  for the  $\text{C}-\text{C}$  bond in ethane<sup>49</sup> and  $2.92 \text{\AA}^2$  for the  $\text{C}\equiv\text{C}$  bond in acetylene<sup>49</sup>. The bond region electrons alone are involved in the calculation of polarizability derivatives and the nonbond region electrons do not have any influence on the polarizability derivative. As in the case of polarizability, polarizability derivatives also increase with the increase in the bond order. From the results of the present investigation it is seen that the derivatives of polarizabilities are in general transferable from one molecular system to another with similar chemical bonds with nearly identical internuclear distances.

<sup>49</sup> T. YOSHINO and H. J. BERNSTEIN, Spectrochim. Acta **14**, 127 [1959].

## Light Mixing and the Generation of the Second Harmonic in a Plasma in an External Magnetic Field<sup>1</sup>

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(Z. Naturforschg. **20 a**, 793—800 [1965]; received 9 February 1965)

The theory of light scattering in a plasma is extended by including an external electric field (e.g. the field of a laser beam) in calculating the density fluctuations. It is shown that in the presence of a time constant homogeneous magnetic field there arise density fluctuations with the frequency and the wave number of the external electric field. Expansions of the general expressions are obtained for the case that the frequency is large compared to the electron gyrofrequency. The special case that the external electric field is a transverse wave is discussed in detail.

The light of a second beam may be scattered by these forced density fluctuations. The scattered light has the sum and the difference frequency of the two light beams, i.e. light mixing occurs. In the framework of this theory the effect occurs only if the two beams are parallel. — If one considers the scattering of the same beam that forces the density fluctuations, the scattered light is the second harmonic.

In the past few years several papers have been published dealing with the problem of the scattering of electromagnetic waves in a plasma. The radiation energy  $dI_2(\omega_2, \mathbf{k}_2)$  with the frequency  $\omega_2$  and the wavevector  $\mathbf{k}_2$  that is scattered per second into a given solid angle  $d\Omega$  is given by

$$dI_2(\omega_2, \mathbf{k}_2) = \lim_{T \rightarrow \infty} \frac{1}{T} J_1(\omega_1, \mathbf{k}_1) \langle |n(\mathbf{k}, \omega)|^2 \rangle \frac{d\omega_2}{2\pi} \sigma_e d\Omega \quad (1)$$

where  $J_1(\omega_1, \mathbf{k}_1)$  is the primary intensity with the frequency  $\omega_1$ , and the wave vector  $\mathbf{k}_1$ ,  $\sigma_e$  is the scattering crosssection for a single electron and  $T$  is

the duration of observation. The ensemble average is denoted by  $\langle \rangle$  and  $n(\mathbf{k}, \omega)$  is the FOURIER transform of the electron density, where  $\mathbf{k}$  and  $\omega$  are given by

$$\mathbf{k}_2 = \mathbf{k}_1 + \mathbf{k} \quad \text{and} \quad \omega_2 = \omega_1 + \omega \quad (2a)$$

$$\text{or} \quad \mathbf{k}_2 = \mathbf{k}_1 - \mathbf{k} \quad \text{and} \quad \omega_2 = \omega_1 - \omega. \quad (2b)$$

These conditions mean that in general the  $\mathbf{k}$ -vectors must form a triangle.

From eq. (1) and (2) follows that the spectral distribution of the scattered radiation represents the spectral distribution of the electron density fluctuations, if the primary radiation is monochromatic. By this the problem of calculating the spectrum of the scattered radiation is reduced to the problem of calculating the density fluctuations. This problem has

<sup>1</sup> The basic ideas of this paper were reported in Proc. VI<sup>th</sup> Intern. Conf. Ionization Phenomena in Gases, Vol. III, p. 189, Paris 1963.