

## Determination of the Rotational Constant $A_0$ and the Bending Angle $\angle CNC$ For $CH_3NC$ and $CH_3^{15}NC$ Molecules

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**ABSTRACT:** The rotational constant,  $A_0$ , for the ground state of  $CH_3NC$  and  $CH_3^{15}NC$  isotopomers is calculated using a technique which was used earlier for  $CH_3CCH$  [9],  $CH_3CN$  [10] and  $SiH_3CCH$  [11]. This technique is based on calculating the moment of inertia tensors in the bent configuration due to the  $\nu_8$  vibrational state, which is associated with the  $CNC$  bending vibration. These values of the moments of inertia are fitted with the values calculated from the rotational constant  $B_v$ , found experimentally by measuring the rotational frequencies in the microwave and infrared regions. From the fitting, the rotational constant  $A_0$ , the bending angle  $\angle CNC$  and the asymmetry parameter  $\kappa$  are determined for  $\nu_8=1, 2$ , and  $3$  bending vibrational states. The effect of the isotopic substitution of  $^{13}C$ ,  $^{15}N$  and Deuterium on the angle  $\alpha$  is studied, which is found to be negligible.

**Key Words :** Methyl-isocyanides; Rotational constants; Bending angle; Asymmetric parameter; Moment of inertia tensors .

### 1. Introduction

Methyl-isocyanide ( $CH_3NC$ ) is a prolate symmetric top molecule with  $C_{3v}$  symmetry [1]. The rotational constant of the ground state  $A_0$  about the axis of highest symmetry cannot be easily obtained to a high accuracy by direct measurements in symmetric top molecules due to the fact that this constant vanishes from the frequency equation. The disappearance of  $A_0$  is a result of the application of the selection rule  $\Delta K=0$  in calculating the frequency of a rotational component in the ground vibrational state [2, 3]. If the symmetric top molecule is excited to the first few excited vibrational states, the rotational constant  $A_v$  does appear in the frequency equation and a set of experimental rotational constants can be determined from the fitting between the experimental and the theoretical values of the frequency for the  $CH_3NC$  and  $CH_3^{15}NC$  isotopomers [4-8]. These results are used to obtain the trend of the rotational constant  $A_v$  over the  $\nu_8=1, 2$  and  $3$  vibrational states and through extrapolation of these values to get  $A_0$ .

Bauer and Godon [4] have studied the microwave spectra in the  $\nu_8=1$  and the ground vibrational states for  $CH_3CN$  and  $CH_3NC$  isotopomers. Chen He and Bernheim [5] have studied the infrared spectra of  $CH_3NC$  in the  $\nu_8=1$  and the ground vibrational state. Plíva *et*

*al.* [6] have studied the spectra of the hot bands  $\nu_7+\nu_8-\nu_8$  and  $\nu_4+2\nu_8-\nu_8$  for  $\text{CH}_3\text{NC}$  molecule. Godon and Bauer [7] have studied the spectra in the  $\nu_8=1$  and the  $\nu_8=2$  vibrational states of  $\text{CH}_3\text{NC}$  and its  $^{15}\text{N}$  isotopomers. Bauer *et al.* [8] have studied the microwave spectra of  $\text{CH}_3^{14}\text{NC}$  and  $\text{CH}_3^{15}\text{NC}$  isotopomers in the  $\nu_8=3$  vibrational state. Tam and Roberts [9] have outlined a method of using the rotational constant  $B_V$  in the ground and the  $\nu_{10}=1, 2, 3,$  and  $4$  excited vibrational states of  $\text{CH}_3\text{CCH}$  to determine the ground rotational constant  $A_0$ . The method consists of determining a trend in each rotational constant over a range of the vibrational states available and using this trend to determine the value of  $A_0$  in the limiting case for the ground state ( $\nu_{10}=0$ ). This method has been used to determine the rotational constant  $A_0$  for the  $\text{CH}_3\text{CN}$  molecule and its  $^{13}\text{C}$  and  $^{15}\text{N}$  tagged isotopomers [10], and for  $\text{SiH}_3\text{CCH}$  Molecule [11].

The aim of this work is to extend this method to determine the rotational constants  $A_0$ , the rotational constant  $C_v$  and the bending angle  $\angle\text{CNC}$  of the  $\nu_8$  vibration and its overtones for  $\text{CH}_3\text{NC}$  and  $\text{CH}_3^{15}\text{NC}$  isotopomers. The  $\nu_8$  is associated with the CNC bending vibration [12]. Also, to study the effect of isotopic substitution of  $^{13}\text{C}$ ,  $^{15}\text{N}$  and Deuterium atoms on the angle  $\alpha$ , which is the angle between the figure axis of  $\text{CH}_3$  group and the  $\text{C}-\text{H}$  bonds, for eight isotopomers of  $\text{CH}_3\text{CN}$  (see Figure 1).

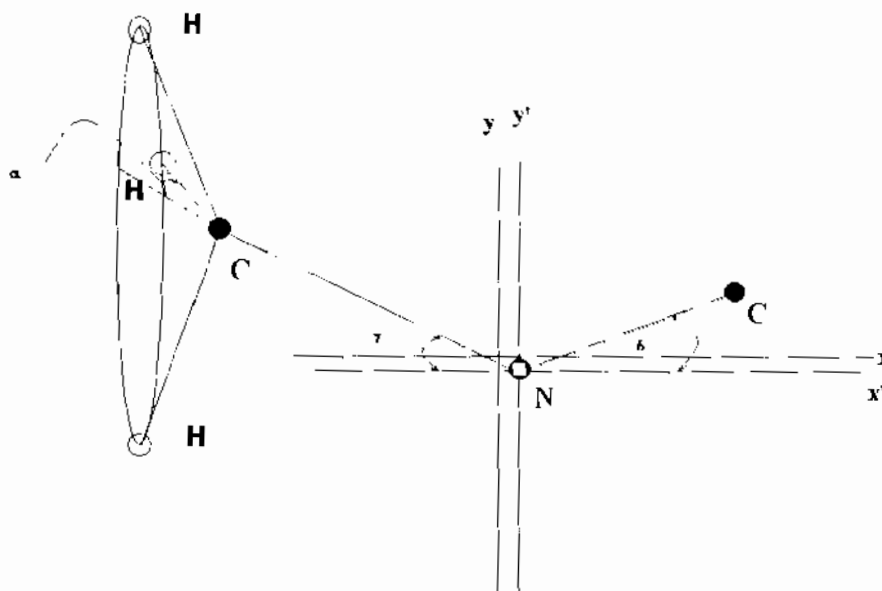


Fig. (1). The coordinate configuration chosen for the broken symmetry of the  $\text{CH}_3\text{NC}$  molecule in the  $\nu_8$  bending vibration.

## 2. Outline of The Method

The rotational constant  $B_v$  for  $\text{CH}_3\text{NC}$  and  $\text{CH}_3^{15}\text{NC}$  isotopic species is experimentally determined using data from microwave and infrared spectra for these isotopic species [4-8]. The moment of inertia in the bent configuration of  $\text{CH}_3\text{NC}$  molecule, as shown in Figure 1, can be obtained with respect to the two coordinates systems  $(x, y, z)$  and  $(x', y', z')$  which are the center of mass coordinates before and after the  $C_{3v}$  symmetry is broken by the  $\nu_8$  vibration and its overtones respectively. The origin

is located at the center of mass of the molecule. From basic considerations, the equations used to calculate the moments of inertia tensors about the x-axis and the z-axis for  $C_{3v}$  symmetric top molecule were developed by Kesler *et al.* [13] before the symmetry is broken by the  $\nu_8$  vibrational state, where the  $\angle CNC$  bending angle ( $\delta = \gamma = 0^\circ$ ) (Figure 1). These equations must be modified for the configuration of broken symmetry due to the  $\nu_8=1$ ,  $\nu_8=2$  and  $\nu_8=3$  bending vibrational states, and to take into consideration the non-point-mass distribution of the three hydrogen atoms in the methyl group. The formulas for the components of the inertia tensor for an arbitrary axis of rotation are [13-15].

$$I_{xx} = \sum_{i=1}^N m_i (y_i^2 + z_i^2) - \frac{1}{M} \left\{ \left( \sum_{i=1}^N m_i y_i \right)^2 + \left( \sum_{i=1}^N m_i z_i \right)^2 \right\} \quad (1)$$

$$I_{yy} = \sum_{i=1}^N m_i (x_i^2 + z_i^2) - \frac{1}{M} \left\{ \left( \sum_{i=1}^N m_i x_i \right)^2 + \left( \sum_{i=1}^N m_i z_i \right)^2 \right\} \quad (2)$$

$$I_{zz} = \sum_{i=1}^N m_i (x_i^2 + y_i^2) - \frac{1}{M} \left\{ \left( \sum_{i=1}^N m_i x_i \right)^2 + \left( \sum_{i=1}^N m_i y_i \right)^2 \right\} \quad (3)$$

$$I_{xy} = -\sum_{i=1}^N m_i (x_i y_i) + \frac{1}{M} \left( \sum_{i=1}^N m_i x_i \right) \left( \sum_{i=1}^N m_i y_i \right) = I_{yx} \quad (4)$$

$$I_{xz} = -\sum_{i=1}^N m_i (x_i z_i) + \frac{1}{M} \left( \sum_{i=1}^N m_i x_i \right) \left( \sum_{i=1}^N m_i z_i \right) = I_{zx} \quad (5)$$

$$I_{yz} = -\sum_{i=1}^N m_i (z_i y_i) + \frac{1}{M} \left( \sum_{i=1}^N m_i z_i \right) \left( \sum_{i=1}^N m_i y_i \right) = I_{zy} \quad (6)$$

The total mass  $M$  is

$$M = \sum_{i=1}^N m_i \quad (7)$$

Although these equations (1-6) lack accuracy when the coordinates are not taken with respect to the center of mass of the molecule. It is possible to use them if the products of inertia (equations 4-6) vanish [10, 11]. It is convenient as well to utilize the symmetry in the molecule to simplify the calculations of these inertia tensors for the broken symmetry configuration. The plane described by one hydrogen, the carbon and the isocyanide group ( $N=C$ ) are chosen for the projection plane, the  $x'z'$  plane, for one set of the calculations. The inertia tensors can, now, be expressed in an explicit form for the coordinate set ( $x'$ ,  $y'$ ,  $z'$ ). In the bent configuration (Figure 1) where the angle of bending for the  $\nu_8$  vibrational state is characterized by the angle  $\angle CNC$ . The orientation of the bending of each section of the molecule with respect to the "fixed"  $z$ -axis is determined by two angles  $\delta$  and  $\gamma$ . The  $N=C$  group is assumed to deviate by the angle  $\delta$  and the  $CH_3$  group to deviate from the original symmetry axis by the angle  $\gamma$  (Figure 1). Although this procedure is equivalent to consider, only, the bending of the  $C-N=C$  group by an angle of  $(\delta + \gamma)$ , it seems easier to visualize the projection of each component of the inertia tensor by two separate angles  $\delta$  and  $\gamma$  [10]. The inertia tensors are, then, given by

$$\begin{aligned}
I_{xx} = & 1.5m_H[d_{CH} \sin \alpha \cos \gamma]^2 + \frac{1}{M}(d_{NC'} \cos \delta)^2(m_{C'})(M - m_{C'}) + \\
& \frac{1}{M}(d_{CN} \cos \gamma)^2(m_N + m_{C'})(m_C + 3m_H) + \frac{6}{M}m_H(m_{C'} + m_N)d_{CN}d_{CH}(\cos^2 \gamma) \cos \alpha + \\
& \frac{3}{M}[d_{CH} \cos \gamma \cos \alpha]^2 m_H(M - 3m_H) + \frac{2}{M}d_{NC'}d_{CN}(\cos \delta) \cos \gamma(m_C + 3m_H)(m_{C'}) \\
& + \frac{6}{M}d_{NC'}(\cos \delta)d_{CH} \cos \alpha \cos \gamma(m_{C'})m_H) \quad (8)
\end{aligned}$$

$$\begin{aligned}
I_{yy} = & 1.5m_H[d_{CH} \cos \alpha \cos \gamma]^2 + \frac{1}{M}(d_{NC'} \cos \delta)^2(m_{C'})(M - m_{C'}) + \\
& \frac{1}{M}(d_{CC'} \cos \gamma)^2((m_{C'} + m_N))(m_C + 3m_H) + \frac{6}{M}m_H((m_{C'} + m_N))d_{CN}d_{CH}(\cos^2 \gamma) \sin \alpha + \\
& \frac{3}{M}[d_{CH} \cos \gamma \sin \alpha]^2 m_H(M - 3m_H) + \frac{2}{M}d_{NC'}d_{CN}(\cos \delta) \cos \gamma(m_C + 3m_H)(m_{C'}) \\
& \frac{6}{M}(d_{NC'}d_{CH} \sin \alpha(\cos \gamma)(\cos \delta)(m_{C'})m_H) \quad (9)
\end{aligned}$$

$$I_{zz} = 3m_H(d_{CH} \sin \alpha)^2 + m_C(d_{CN} \sin \gamma)^2 + (m_{C'})(d_{NC'} \sin \delta)^2 \quad (10)$$

The effect of the polar orientation of the  $\text{CH}_3$  group with respect to the  $(x', y', z')$  coordinates is studied for the  $\text{CH}_3\text{CN}$  molecule by Al-share *et al.* [10], and for  $\text{CH}_3\text{CCH}$  molecule by Tam and Roberts [9]. They showed that when the molecule is bent, the rotating  $\text{CH}_3$  group has a negligible effect on the bend angle. Also, no effect is found due to the rotation of  $\text{CH}_3$  group on the rotational constants A, B, and C of the  $\text{CH}_3\text{CN}$  molecule [16].

A function  $\mathbf{M}$  is defined such that

$$\mathbf{M} = |\mathbf{I} - \lambda \mathbf{1}| \quad (11)$$

Once the elements of the inertia tensor have been obtained, the secular equation is solved

$$|\mathbf{I} - \lambda \mathbf{1}| = 0 \quad (12)$$

and from the solutions of equation (12) the moments of inertia  $I_{xx}$ ,  $I_{yy}$  and  $I_{zz}$  are determined. Then, the values of the rotational constants A, B, and C of the molecule can be obtained using the following relations [17].

$$B = \frac{h}{8\pi^2 I_{xx}} \quad (13)$$

$$C = \frac{h}{8\pi^2 I_{yy}} \quad (14)$$

$$A = \frac{h}{8\pi^2 I_{zz}} \quad (15)$$

The experimental value of the rotational constant B is inserted in a computer program based on equations (8) and (13), then the angles  $\delta$  and  $\gamma$  are iterated over a pre-expected intervals to obtain their values which minimize  $\mathbf{M}$  to a predetermined value of

0.0001 or less between the value of  $I_{xx}$  calculated from equation (8) and the value calculated from the rotational constant  $B$  from equation (13), keeping in mind that  $B$  was obtained experimentally in the microwave and infrared spectra for each vibrational states [4-8]. The inertia tensors in equations (8-10) showed a small dependency on the angle  $\alpha$ , the angle between the figure axis of  $\text{CH}_3$  group and the  $\text{H}-\text{C}$  bonds, over the vibrations (Figure 1). The value of the angle  $\alpha$  is assumed to be constant for all the vibrations, this value is the one which minimize the function  $\mathbf{M}$  for the principal moment of inertia  $I_{xx}$  for the ground vibrational state ( $\angle \delta = \angle \gamma = 0^\circ$ ). The angle  $\alpha$  is found to be  $(70.6236^\circ)$  and  $(70.9126^\circ)$  for  $\text{CH}_3\text{NC}$  and  $\text{CH}_3^{15}\text{NC}$  isotopomers, respectively. The  $\angle \text{CNC}$  bending angle for the  $\nu_8$  vibrational state is constrained by the experimental value of each vibration and is given, in terms of the angle  $\delta$  and  $\gamma$ , by

$$\angle \text{CNC} = \Pi - (\delta + \gamma) \quad (16)$$

In order to calculate the rotational constants  $C_v$  and  $A_v$  for each vibration, the values of the angles  $\delta$  and  $\gamma$  for each vibrational state, see Table 1, are inserted into a computer program based on equations (9) and (10), then in equations (14) and (15), respectively. Finally the rotational constant  $A_v$  is plotted versus the excited vibrational quantum number  $\nu$  (Figure 2), and the curve is extrapolated to find the value  $A_0$  for the ground vibrational state. The values used in these calculations for the atomic masses of the  $^{12}\text{C}$ ,  $^{13}\text{C}$ ,  $^{14}\text{N}$ ,  $^{15}\text{N}$ , D and H atoms [18] and the values of the bond lengths [5] are reported in Table 2.

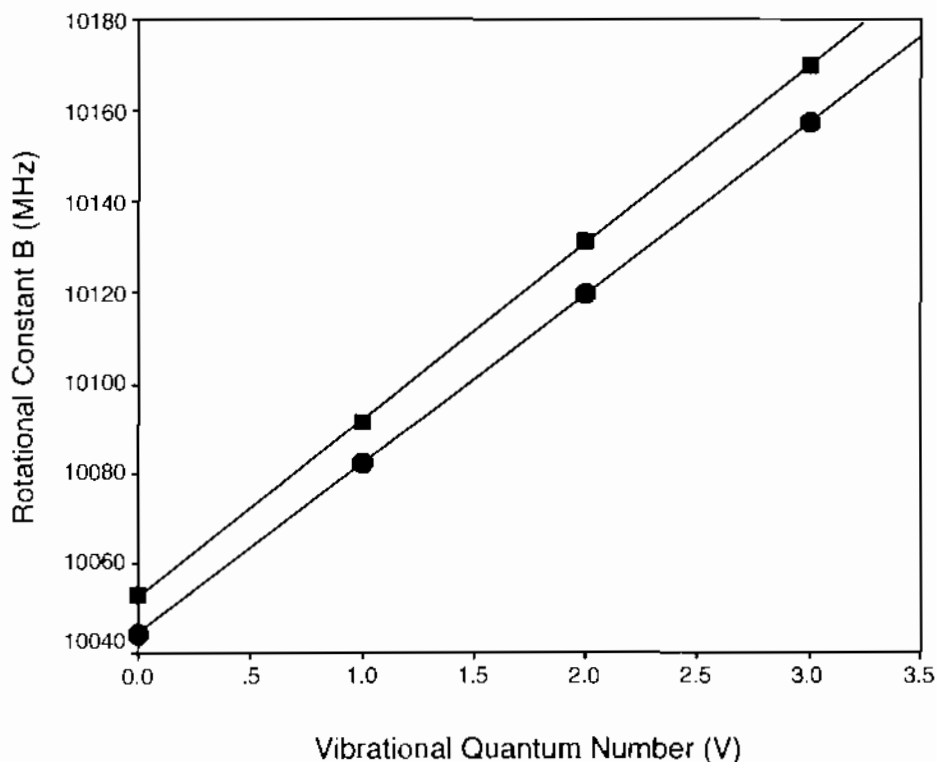


Fig. (2). The rotational constant  $B$  (MHz) versus the vibrational quantum number  $\nu$  for  $\text{CH}_3\text{NC}$  ■ and  $\text{CH}_3^{15}\text{NC}$  ●.

Table (1). Summary of the average values of the moments of inertia, the rotational constants, the asymmetry parameter  $\kappa$ , and the bending angle  $\angle CNC'$  for  $CH_3NC$  and  $CH_3^{15}NC$  isotopomers. Under line digit gives the statistical standard errors.

| <b><math>CH_3NC</math></b>      |                          |                         |                         |                         |
|---------------------------------|--------------------------|-------------------------|-------------------------|-------------------------|
| Constant                        | Ground                   | $v_s=1$                 | $v_s=2$                 | $v_s=3$                 |
| $I_{xx}$ (amu $\text{\AA}^2$ )  | 50.27377                 | 50.07921                | 49.88415                | 49.6945                 |
| $I_{yy}$ (amu $\text{\AA}^2$ )  | 50.27377                 | 50.29076                | 50.30794                | 50.3230                 |
| $I_{zz}$ (amu $\text{\AA}^2$ )  | 3.2025                   | 3.393806                | 3.63259                 | 3.86741                 |
| B (MHz)                         | 10052.79773 <sup>a</sup> | 10091.8331 <sup>a</sup> | 10131.2928 <sup>b</sup> | 10169.9594 <sup>c</sup> |
| C (MHz)                         | 10052.79773              | 10049.38                | 10045.95                | 10042.94                |
| A (MHz)                         | 157810.3                 | 148915.7                | 139126.9                | 130679.4                |
| $\kappa$                        | -1                       | -0.99939                | -0.99867                | -0.99789                |
| $\angle CNC'$ (°)               | 180                      | 175.352                 | 173.164                 | 171.5203                |
| <b><math>CH_3^{15}NC</math></b> |                          |                         |                         |                         |
| Constant                        | Ground                   | $v_s=1$                 | $v_s=2$                 | $v_s=3$                 |
| $I_{xx}$ (amu $\text{\AA}^2$ )  | 50.316                   | 50.12657                | 49.94053                | 49.7572                 |
| $I_{yy}$ (amu $\text{\AA}^2$ )  | 50.316                   | 50.33335                | 50.34968                | 50.36845                |
| $I_{zz}$ (amu $\text{\AA}^2$ )  | 3.23293                  | 3.44386                 | 3.67001                 | 3.89926                 |
| B (MHz)                         | 10044.328 <sup>d</sup>   | 10082.297 <sup>b</sup>  | 10119.8557 <sup>b</sup> | 10157.1481 <sup>e</sup> |
| C (MHz)                         | 10044.328                | 10040.85                | 10037.62                | 10033.88                |
| A (MHz)                         | 156325.9                 | 146751.3                | 137708.1                | 129612.1                |
| $\kappa$                        | -1                       | -0.99939                | -0.99871                | -0.99793                |
| $\angle CNC'$ (°)               | 180                      | 175.420                 | 173.299                 | 171.739                 |

<sup>a</sup> Ref. (6).

<sup>b</sup> Ref. (7).

<sup>c</sup> Ref. (8).

<sup>d</sup> Ref. (4).

<sup>e</sup> Ref. (5).

Table (2). Molecular constants used in basic structure of  $CH_3NC$  molecule to calculate the moment of inertia tensors.

|                                    |                 |                                    |                     |
|------------------------------------|-----------------|------------------------------------|---------------------|
| Mass of H atom <sup>a</sup>        | 1.007825 (amu)  | Mass of $^{14}N$ atom <sup>a</sup> | 15.000108 (amu)     |
| Mass of D atom <sup>a</sup>        | 2.01400 (amu)   | C-H bond <sup>b</sup>              | 1.0934 $\text{\AA}$ |
| Mass of $^{12}C$ atom <sup>a</sup> | 12.0000 (amu)   | C-N bond <sup>b</sup>              | 1.4266 $\text{\AA}$ |
| Mass of $^{13}C$ atom <sup>a</sup> | 13.003355 (amu) | N=C bond <sup>b</sup>              | 1.1665 $\text{\AA}$ |
| Mass of $^{14}N$ atom <sup>a</sup> | 14.003074 (amu) | HCH bond angle <sup>b</sup>        | 109° 32'            |

<sup>a</sup> Ref. [18].

<sup>b</sup> Ref. [15].

### 3. Results and Discussion

Table 1 gives the values of the rotational constants A, B, C, the moments of inertia ( $I_{xx}$ ,  $I_{yy}$ ,  $I_{zz}$ ), the bending angle  $\angle CNC'$  and the asymmetry parameter  $\kappa$ . These parameters are obtained, using a computer program based on equations (8-10) and equations (13-15) as mentioned above in the previous section. Each of these parameters will be discussed separately:

### 3.1 The Bending Angle $\angle CNC$

The value of the rotational constant  $B_v$  for the ground, the  $v_8=1$ ,  $v_8=2$  and  $v_8=3$  vibrational states were measured in the microwave and infrared spectra [4-8]. These constants can be used in equation (13) to give the value of  $I_{XX}$ . The values of the angles  $\delta$  and  $\gamma$  are iterated in a computer program based on equation (8) to minimize the difference between the value of  $I_{XX}$  from equation (13) and its value from equation (8) down to  $1 \times 10^{-4}$ . Although, this iteration technique gives more than one set of the angles  $\delta$  and  $\gamma$  which give the best fit between the value of  $I_{XX}$  from equation (13) and  $I_{XX}$  from equation (8), the sum of these two angles ( $\delta + \gamma$ ) exhibits very small fluctuations during the fit, which means small fluctuations in the  $\angle CNC$  bending angle. It is known that a statistical average can be obtained to give a reasonable good estimate for a particular constant, if the fluctuations associated with that constant are small [10]. From Table 1, it can be seen that the bending angle  $\angle CNC$  decreases with the increasing of the vibrational level, suggesting that the highly excited states are extremely sensitive to the degree of bending in the molecular system. The substitution of  $^{15}\text{N}$  in the  $\text{N}=\text{C}$  group has a small effect on the  $\angle CNC$  bending angle of about  $0.1^\circ$  to  $0.2^\circ$  as shown in Table 1.

Figure 2 represents a plot of the rotational constants  $B_v$  versus the vibrational quantum number  $v$  for both isotopomers, which show a linear relation. This line can be used to estimate the value of  $B_v$  for higher overtones (i.e.,  $v_8=4$ ,  $v_8=5$ ,  $v_8=6$ , and  $v_8=7$  vibrational states). This constant can be used to start the search for the rotational components for each vibrational state. After measuring these components experimentally in the microwave or infrared regions, this constant can be refined to give the best fit between the experimental and theoretical values of the frequency of these components.

### 3.2 The Rotational Constants $A$ and $C$

The value of the rotational constants  $A_v$  are calculated for each excited vibrational state, by inserting the value of the angles  $\delta$  and  $\gamma$  found before for the corresponding vibrational state into a computer program based on equation (10) to calculate the moment of inertia  $I_{ZZ}$ , then equation (15) to calculate  $A_v$ . These values are reported in Table 1 for the first time in this work for the  $v_8=2$  and  $v_8=3$  bending vibrational states for  $\text{CH}_3\text{NC}$  and  $\text{CH}_3^{15}\text{NC}$  isotopomers. They show good agreement with the values assumed in microwave and infrared spectra [4-8], also agree with the trend found for  $\text{CH}_3\text{CN}$  molecule [10]. Figure 3 represents a plot of the rotational  $A_v$  versus the vibrational quantum number  $v$  for  $\text{CH}_3\text{NC}$  and  $\text{CH}_3^{15}\text{NC}$  isotopomers, which is a linear relation. From this figure,  $A_0$ , its value for the ground state can be obtained by extrapolating the line to intercept with the y-axis, which was found to be 157810.3 MHz and 155163.033 MHz for  $\text{CH}_3\text{NC}$  and  $\text{CH}_3^{15}\text{NC}$  isotopomers, respectively.

The value of the rotational constant  $C$  are calculated by inserting the value of the angles  $\delta$  and  $\gamma$  into a computer program based on equation (9) to calculate the moment of inertia  $I_{YY}$ . Then in equation (14) to calculate  $C_v$  for the  $v_8=1$ ,  $v_8=2$  and  $v_8=3$  bending vibrational states for  $\text{CH}_3\text{NC}$  and  $\text{CH}_3^{15}\text{NC}$  isotopomers. These values are reported in Table 1, for the first time in this work. Figure 4 represents a plot of the rotational constants  $C_v$  versus the vibrational quantum number  $v$  for both isotopes, which shows a linear relation.

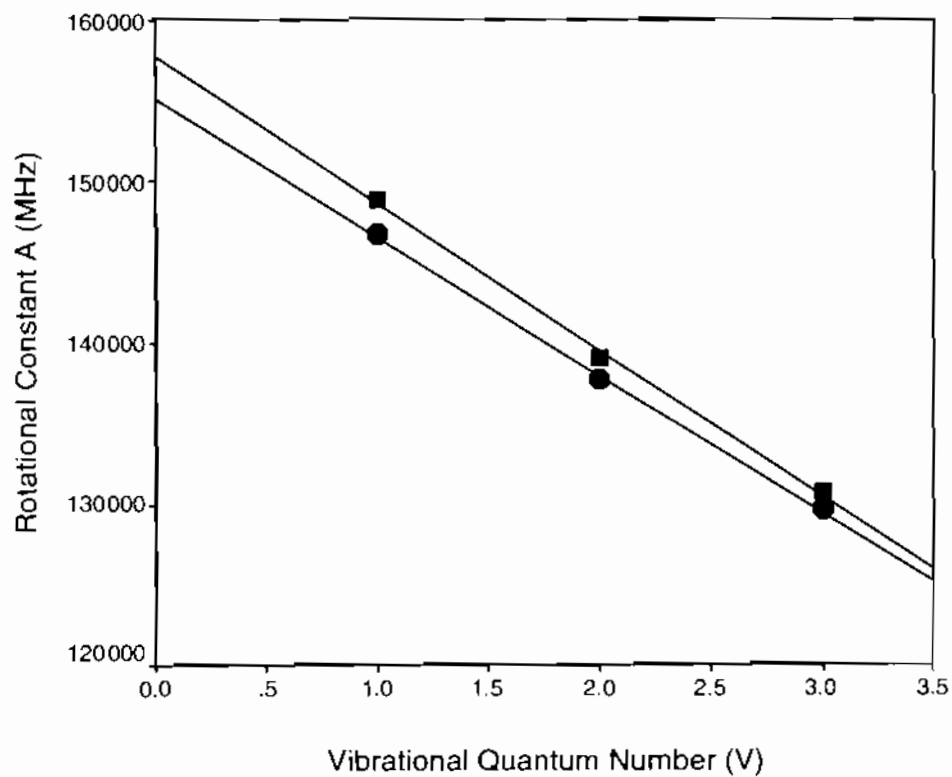


Fig. (3). The rotational constant A versus the vibrational quantum number  $v$  for CH<sub>3</sub>NC ■ and CH<sub>3</sub><sup>15</sup>NC ●

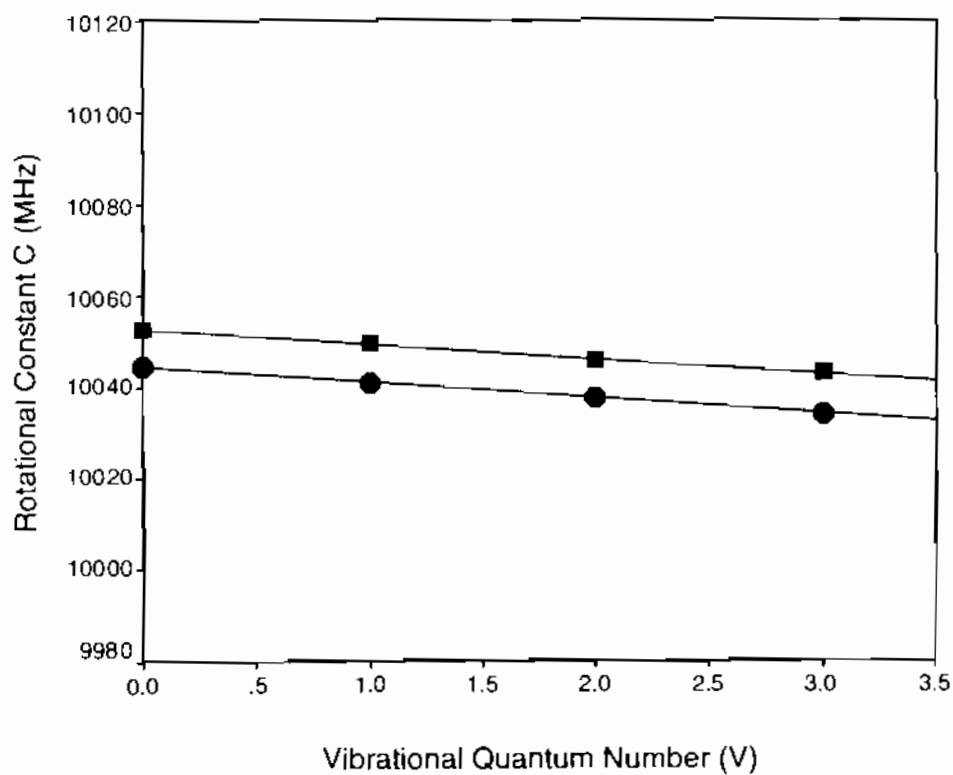


Fig. (4). The rotational constant C (MHz) versus the vibrational quantum number  $v$  for CH<sub>3</sub>NC ■ and CH<sub>3</sub><sup>15</sup>NC ●.



### 3.3 The Asymmetry Parameter $\kappa$

The asymmetry parameter  $\kappa$  is calculated from the values of the rotational constants using the following relation [19]:

$$\kappa = \frac{2B - A - C}{A - C} \quad (17)$$

The nature of the asymmetry parameter  $\kappa$  with respect to the excited vibrational levels can be observed so that the degree of the departure from that of a true symmetric top to asymmetric top molecule can be predicted. Although, the departure of the asymmetry parameter  $\kappa$  for both isotopomers from its value for the symmetric top molecule seems to be very small, see Table 1, but it shows an increase with the increase of the vibrational quantum number  $v$ . This departure is comparable to what was found for the  $\text{CH}_3\text{CCH}$  molecule [9]. The substitution of  $^{15}\text{N}$  in the  $\text{N}=\text{C}$  group does not affect the asymmetry parameter  $\kappa$  for the fundamental and the first two overtones of the  $\nu_8$  bending vibrational state as shown in Table 1.

### 3.4 The Angle $\alpha$

The value of the angle  $\alpha$ , the angle between the figure axis of  $\text{CH}_3$  group and the  $\text{C}-\text{H}$  bond (see Figure 1) is studied for eight isotopomers of  $\text{CH}_3\text{NC}$ . The effect of the isotopic substitution of  $^{13}\text{C}$ ,  $^{15}\text{N}$  and Deuterium atoms on the angle  $\alpha$  is investigated. The values of this angle reported in Table 3 are those which minimize the function  $\mathbf{M}$  for the principal moment of inertia  $I_{XX}$  for the ground state ( $\angle \delta = \angle \gamma = 0$ ). The value  $\text{C}-\text{H}$  bond for the eight isotopomers is reported in Table 3. The fluctuation in the values of  $\alpha$  are very small  $\sim 0.6^\circ$  between the value of  $\text{CH}_3\text{NC}$  and  $\text{CD}_3\text{NC}$ , while for the other isotopes are  $\sim 0.05^\circ$ . These results show that only the deuterium substitution has a small effect, whereas the substitution of the other atoms has a negligible effect. Therefore an average value of the angle  $\alpha$  can be considered as the one to describe the molecular structure for  $\text{CH}_3\text{NC}$  Molecule, which was found to be ( $70.886^\circ$ ).

Table (3). The values of the rotational constants  $B$  for the ground vibrational state, the  $\text{C}-\text{H}$  bond and  $\alpha$  angle for eight isotopes of  $\text{CH}_3\text{NC}$  molecule. ( $\text{BI}_{XX} = 505391 \text{ MHz amu } \text{\AA}^2$ ). Under line digit gives the statistical standard errors.

| Isotope                     | $I_{XX}$ ( $\text{amu } \text{\AA}^2$ ) | $B_{01}$ (MHz)             | $\text{C}-\text{H}$ bond ( $\text{\AA}$ ) | $\alpha$ (degrees) <sup>e</sup> |
|-----------------------------|---|----------------------------|---|---------------------------------|
| $\text{CH}_3\text{NC}$      | 50.2658 <sup>d</sup>                    | 10052.79773 <sup>a,d</sup> | 1.0934 <sup>e</sup>                       | 70.6238                         |
| $^{13}\text{CH}_3\text{NC}$ | 51.7203 <sup>b</sup>                    | 9771.6177 <sup>d</sup>     | 1.0982 <sup>f</sup>                       | 70.8720                         |
| $\text{CH}_3^{13}\text{C}$  | 52.1241 <sup>b</sup>                    | 9695.918 <sup>d</sup>      | 1.09822 <sup>f</sup>                      | 70.8144                         |
| $\text{CH}_3^{15}\text{NC}$ | 50.3082 <sup>b</sup>                    | 10044.328 <sup>c</sup>     | 1.1007 <sup>f</sup>                       | 70.9126                         |
| $\text{CD}_3\text{NC}$      | 58.8904 <sup>b</sup>                    | 8581.891 <sup>d</sup>      | 1.1074 <sup>f</sup>                       | 71.2818                         |
| $^{13}\text{CD}_3\text{NC}$ | 60.0926 <sup>b</sup>                    | 8410.203 <sup>d</sup>      | 1.09703 <sup>f</sup>                      | 70.8829                         |
| $\text{CD}_3^{13}\text{C}$  | 61.0484 <sup>b</sup>                    | 8278.530 <sup>d</sup>      | 1.09709 <sup>f</sup>                      | 70.8495                         |
| $\text{CD}_3^{15}\text{NC}$ | 58.9885 <sup>b</sup>                    | 8567.619 <sup>d</sup>      | 1.09704 <sup>f</sup>                      | 70.85105                        |

<sup>a</sup> Ref. [6]. <sup>b</sup> Ref. [19]. <sup>c</sup> Ref. [4]. <sup>e</sup> Ref. [5].

<sup>d</sup> Calculated using the conversion factor  $B \times I_{XX} = 505391 \text{ MHz amu } \text{\AA}^2$ .

<sup>f</sup> Calculated using the same change of  $\text{C}-\text{H}$  bond due to the isotopic substitution for  $\text{CH}_3\text{CN}$  molecule given in Re [20].

<sup>e</sup> Calculated in this work.

#### 4. Conclusion

In this work the value,  $A_0$ , of the rotational constant  $A$  for the ground state for  $\text{CH}_3\text{NC}$  and  $\text{CH}_3^{15}\text{NC}$  isotopomers is determined to be 157810.3 MHz and 155163.033 MHz, respectively. Also, the values of the rotational constants  $A_v$  and  $C_v$  for the fundamental and the first two overtones of the  $\nu_8$  bending vibrational state are determined. A trend is established for determining the rotational constants  $A$ ,  $B$  and  $C$  for higher overtones of the  $\nu_8$  vibrational state (i.e.  $\nu_8=4$ ,  $\nu_8=5$ ,  $\nu_8=6$  and  $\nu_8=7$ ). These constants can be used to start the search for the rotational components for these vibrational states. The values of the bending angle  $\angle\text{CNC}$  and the asymmetry parameter  $\kappa$  are determined for the first time which leads to more establishment of the geometry of the bending configuration of  $\text{CH}_3\text{NC}$  molecule. The substitution of  $^{15}\text{N}$  in the  $\text{N}=\text{C}$  group shows a small effect on the bending angle  $\angle\text{CNC}$ , whereas no effect on the asymmetry parameter  $\kappa$  was found. The fluctuation of the angle  $\alpha$  due to the isotopic substitution is negligible.

#### References

- [1] **J.G. Motteru and W.H. Fletcher**, *Spectrochimica Acta*, **18**, (1962) 995-1003.
- [2] **H. Burger, G. Schippel, A. Ruoff, H. Essig and S.J. Craddock**, *J. Mol. Spectrosc.*, **106**, (1984) 249.
- [3] **G. Graner, J. Demaison, G. Wlodarczak, R. Anttila, J.J. Hillman and D.E. Jennings**, *J. Mol. Phys.* **64**, (1968) 214-224.
- [4] **Bauer and M. Godon**, *Can. J. Phys.* **53**, (1975) 1154-1156.
- [5] **Chun He and R.A. Bernheim**, *J. Mol. Spectrosc.* **155**, (1992) 365-383.
- [6] **J. Plíva, L.D. Le and R.A. Bernheim**, *J. Mol. Spectrosc.* **180**, (1996) 110-115.
- [7] **M. Godon and A. Bauer**, *J. Mol. Structure*, **38**, (1977) 9-16.
- [8] **Bauer, M. Godon and S. Maes**, *J. Mol. Spectrosc.* **59**, (1976) 421-434.
- [9] **H. S. Tam and J.A. Roberts**, *Struct. Chem.* **1**, (1990) 211-216.
- [10] **M. Al-Share, J. Hajsaleh, S.W. Qian and J.A. Roberts**, *Struct. Chem.* **5 No 2**, (1994) 109-115.
- [11] **M. Al-Share**, accepted for publication at Indian Journal of pure & Applied Physics.
- [12] **J.L. Duncan, D.C. McKean, M.W. Mackenzie and J. Perez Peña**, *J. Mol. Spectrosc.* **76**, (1979) 55-70.
- [13] **M. Kessler, H. Ring, R. Trambarulo and W. Gordy**, *Phys. Rev.* **79**, (1950) 54-56.
- [14] **R. Trambarulo and W. Gordy**, *J. Chem. Phys.* **18**, (1950) 1613-1616.
- [15] **J. D. Graybeal**, "Molecular Spectroscopy" McGraw-Hill: New York p 667 (1988).
- [16] **M. Al-Share**, accepted for publication at Al-Manarah Journal, Alalbait University.
- [17] **C.H. Townes and A.L. Schawlow** "Microwave Spectroscopy", Dover publication Inc., New York, USA, (1975) PP 50.
- [18] **D.R. Lide, Ed.**, "Handbook of Chemistry and Physics", 71<sup>st</sup> ed (1990).
- [19] **C.H. Townes and A.L. Schawlow**, "Microwave Spectroscopy", Dover publication Inc., New York, USA, (1975) PP 84.
- [20] **D.C. McKean, J.L. Duncan and M.W. Mackenzie**, *J. Mol. Structure*, **42**, (1977) 77-83.
- [21] **M. Al-Share**, *Acta Cienica Indica*, **28 (P) No. 3**, 133-136 (2002).

## تعيين الثابت الدوراني $A_0$ وزاوية الانحناء CNC لمركبي $\text{CH}_3^{15}\text{NC}$ و $\text{CH}_3\text{NC}$

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المستخلص. لقد تم حساب الثابت الدوراني للمستوى الطاقى الأرضي لمركبي  $\text{CH}_3\text{NC}$  و  $\text{CH}_3^{15}\text{NC}$  من خلال استخدام آلية طبقت في السابق على مركبات أخرى هي  $\text{CH}_3\text{CCH}$  و  $\text{CH}_3\text{CN}$ . هذه الآلية تعتمد بالأساس على حساب عزوم القصور الذاتي في هيئة الانحناء للجزيء نتيجة الحركة الاهتزازية المرتبطة بحركة الانحناء الاهتزازي.

لقد تم مطابقة قيم هذه العزوم المحسوبة بهذه الطريقة مع القيم المحسوبة من خلال قيم الثابت الدوراني  $B_0$  والمحسوب تجريبيا من خلال قياس الطيف الدوراني لهذا الجزيء ضمن منطقة ترددات الأشعة تحت الحمراء والميكرووية. بعد إجراء مطابقة بين القيمتين تم حساب كل من الثابت الدوراني  $A_0$  وزاوية الانحناء CNC ومعامل عدم التماثل  $\kappa$  للمستويات الطاقية الاهتزازية.

