Anomalous absorption in 202-111 transition of methanimine

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Abstract: The methanimine molecule is of great interest for astronomers and astrophysicists. It is considered as a prebiotic molecule as it is a potential precursor of Glycine, the simplest amino acid. The reaction of CH2NH with HCN in interstellar medium makes aminoacetonitrile (NH2CH2CN) which further reacts with H2O to make glycine (NH2CH2COOH). The amino-acids like Glycine are building blocks of proteins that are essential for life to occur. Earlier, we have calculated the radiative lifetimes and Einstein A-coefficients for transitions between 69 lowest rotational energy levels of methanimine. In the present study, we have obtained the anomalous absorption in 202 – 111 transition of methanimine at 33.705893 GHz. We have solved the statistical equilibrium equations coupled with the equations of radiative transfer. The brightness temperature is found to be minimum around the hydrogen molecular density of 10^{4.5} cm^{-3} and it rises on both sides of this density.

1. Introduction

The methanimine(CH2NH) molecule was firstly detected in the molecular cloud Sgr B2 towards the Galactic center [1] by using microwave spectroscopy. It was predicted in the interstellar medium because similar molecules like formaldehyde [2] and thioformaldehyde [3] were already observed there. The presence of CH2NH in the molecular cloud Sgr B2 was further confirmed in subsequent studies [4–10]. A number of transitions of CH2NH were detected in molecular clouds Orion KL, W51, W49, Ori 3N (Orion Ridge), TMC-1, L134N and G34.3+0.15 [11], in dark molecular cloud L183 [12], Orion-KL [13], Arp220 galaxy [14], in molecular cloud G19.61-0.23 [15] and in circumstellar envelope of IRC+10216 [16].

2. Methanimine: A Prebiotic Molecule

The CH2NH molecule is a planar asymmetric top type having components of dipole moment along a and b axis as μa = 1.340 Debye and μb = 1.446 Debye [17]. The laboratory spectrum of CH2NH in the gas phase was first obtained by Johnson & Lovas [18] in the range of 60 GHz to 123 GHz. Further, its laboratory spectrum was obtained in various frequency ranges [19–23].

The methanimine is considered as a prebiotic molecule as it is a potential precursor of aminoacetonitrile (NH2CH2CN) [24,25] which is a key molecule in the formation of glycine (NH2CH2COOH), the simplest amino acid [26,27]. The amino-acids make proteins, which are necessary for life to occur. The methanimine (CH2NH) molecule is a precursor of aminoacetonitrile formed by the reaction CH2NH + HCN → NH2CH2CN.

The aminoacetonitrile (NH2CH2CN) participates in Strecker type synthesis to form glycine by the reaction NH2CH2CN + 2H2O → NH2CH2COOH + NH3. The presence of glycine is given by Kuan...
et al. [28] but is not confirmed in a subsequent study [29]. The aminoacetonitrile has also been detected by Belloche et al. [27] in Sgr B2.

3. Computational Details

For rotational energy levels of Methanimine, both the collisional and radiative transitions are possible. The radiative transitions obey selection rules but the collisional transitions do not obey such rules. The first step is to optimize the co-ordinates of CH$_2$NH which is done with the help of software GAUSSIAN (2003) [30].

For the transitions occurring between rotational energy levels of CH$_2$NH, we can write a set of equations of statistical equilibrium coupled with the equations of radiative transfer [31], as given below:

\[
n_i = \sum_{j=1}^{N} n_i P_{ij} = \sum_{j=1}^{N} n_j P_{ij}
\]

where the level $i = 1,2,3, \ldots, N$ and $n_i$ is the population density of $i$th energy level. Also, $P_{ij}$ is defined as

(i) For radiatively allowed transitions:

\[
P_{ij} = \begin{cases} 
(A_{ij} + B_{ij}I_{\nu bg}) \beta_{ij} + n_{H_2} C_{ij} & i > j \\
B_{ij} I_{\nu bg} \beta_{ij} + n_{H_2} C_{ij} & i < j
\end{cases}
\]

(ii) For collisional only (radiatively forbidden) transitions

\[
P_{ij} = n_{H_2} C_{ij}
\]

Here, $A_{ij}$ and $B_{ij}$ represent Einstein coefficients (for radiative transitions) whereas $C_{ij}$ is the collisional rate coefficients. Also, $n_{H_2}$ is the molecular hydrogen density and the escape probability $\beta$ is related to optical thickness $\tau_{\nu}$ as

\[
\beta_{ij} = \beta_{ji} = \frac{1 - e^{-\tau_{\nu}}}{\tau_{\nu}}
\]

and the optical thickness is expressed as

\[
\tau_{\nu} = \frac{hv}{4\pi(dv/dr)}(B_{ij} n_i - B_{ji} n_j)
\]

Here, $(dv/dr)$ represents the velocity gradient in the molecular cloud (Cosmic object). For the molecular cloud under consideration, we have considered the cosmic microwave background (CMB) behind it. So the external radiations falling on the cloud are cosmic microwave background which is at a temperature ($T_{bg}$) of 2.73 K.

For the lowest 69 levels, with energies up to 141 cm$^{-1}$, the energies and radiative lifetimes are calculated using software ASROT [32] and are reported in our previous work [33]. Hence, the set of statistical equilibrium equations are solved using the radiative and collisional transition probabilities. Also, the thermal populations are taken as initial populations here.

In interstellar medium, the intensity of a spectral line produced with homogeneous excitation condition is given by
\[ I_\nu - I_{\nu, bg} = (S_\nu - I_{\nu, bg})(1 - e^{-\tau_\nu}) \]

For optically thin \((\tau_\nu \approx 0)\) case, \(T_B = T_{bg}\) where \(T_{bg} = 2.73\) Kelvin. In the R-J limit \([\nu(\text{GHz}) \ll 21 T(\text{Kelvin})]\), we will have

\[ T_B = T_{ex} + (T_{bg} - T_{ex})e^{-\tau_\nu} \]

For anomalous absorption \((I_\nu < I_{\nu, bg} ; T_B < T_{bg})\) with \(\tau_\nu > 0\), we have positive value of \(T_{ex}\) but still less than \(T_{bg}\), i.e. \((0 < T_{ex} < T_{bg})\) and thus \(T_B > T_{ex}\).

Hence, for anomalous absorption in a transition, we have

\[ 0 < T_{ex} < T_B < T_{bg}. \]

### 4. Transitions between rotational levels in Methanimine

For radiative transitions, in addition to the selection rule \(\Delta J = \pm 1\), the transitions are classified into 4 groups which are exclusive from each other. For a-type transitions, we have

- \(k_a, k_c\) : Group I: odd, even ↔ odd, odd
- Group II: even, even ↔ even, odd

The two groups behave as independent entities so no radiative or collisional transition occurs between these groups. Also, for the b-type transitions, the selection rules are

- \(k_a, k_c\) : Group III: odd, even ↔ even, odd
- Group IV: even, even ↔ odd, odd

Here, also there are no radiative or collisional transitions between the levels of group III and IV. Based on the above discussion, the first 15 rotational energy levels are classified into four groups which are exclusive of each other.

Group I: \((1_{11}, 1_{10}, 2_{12}, 2_{11}, 3_{13}, 3_{12}, 4_{14}, 4_{13})\)

Group II: \((0_{00}, 0_{01}, 2_{02}, 3_{03}, 4_{04}, 2_{21}, 2_{20})\)

Group III: \((1_{01}, 1_{10}, 2_{12}, 3_{03}, 3_{12}, 4_{14}, 2_{21})\)

Group IV: \((0_{00}, 2_{02}, 1_{11}, 2_{11}, 3_{13}, 4_{04}, 4_{13}, 2_{20})\)

The radiative, as well as collisional transitions, are individually confined within each group. The transitions due to collisions do not obey selection rules unlike radiative transitions, but they are still confined within a group, individually.

The collisional rate coefficients are required to solve the set of equations of statistical equilibrium equations coupled with the radiative transfer equations. But unlike radiative transitions, the collisional transitions are not governed by any selection rules. If the colliding partner has sufficient energy, the transition can occur between all the levels in a particular group of energy levels. The collisional coefficients of CH$_2$NH colliding with H$_2$ calculated by Faure et al. [34] are used here. Also, for the cold interstellar medium, the calculations are limited to para H$_2$.

### 5. Results and Discussion
We have optimized the co-ordinates of methanimine molecule using the software GAUSSIAN (2003) [30]. Table 1 shows the obtained optimized co-ordinates of CH$_2$NH. In these calculations, the Becke 3-parameter hybrid functional in conjunction with the Lee-Yang-Perr non-local correlation functional (B3LYP) [35,36] is used along with basis sets aug-cc-pVDZ and aug-c-pVTZ. The obtained values of rotation and centrifugal constants are shown in table 2.

**Table 1. The optimized space co-ordinates of CH$_2$NH.**

| Atom | X       | Y       | z       |
|------|---------|---------|---------|
| C    | 0.062372| 0.778497| 0.000000|
| H    | -0.982293| 1.102381| 0.000000|
| H    | 0.926145| -1.015310| 0.000000|
| N    | 0.062372| -0.523198| 0.000000|
| H    | -0.754690| -1.095667| 0.000000|

**Table 2. The rotational and centrifugal distortion constants for CH$_2$NH.**

| Constant | aug-cc-pVDZ | aug-cc-pVTZ |
|----------|-------------|-------------|
| $A \times 10^5$ | 2.085912975 | 2.115576292 |
| $B \times 10^4$ | 3.41547219 | 3.45064373 |
| $C \times 10^4$ | 2.93491023 | 2.96674771 |
| $D_J \times 10^3$ | 60.866127 | 62.932642 |
| $D_{JK} \times 10^3$ | 732.047923 | 741.932689 |
| $D_K$ | 5.839960126 | 6.09387395 |
| $d_1 \times 10^3$ | -9.531309 | -9.792946 |
| $d_2 \times 10^3$ | -1.773163 | -1.789099 |
| $H_J \times 10^6$ | -0.02763731158 | -0.03026010471 |
| $H_{JK} \times 10^6$ | 8.449668321 | 8.352378839 |
| $H_{KL} \times 10^6$ | 680.6931766 | 730.4186343 |
| $H_K \times 10^6$ | 4.933638227 | 4.950073983 |
| $h_1 \times 10^8$ | 21.18656635 | 21.85239675 |
| $h_2 \times 10^8$ | 30.03815910 | 30.50159818 |
| $h_3 \times 10^8$ | 6.960776290 | 7.059300501 |

The Einstein A-coefficients and collisional rate coefficients are input parameters for solution of the set of statistical equilibrium equations. These non-linear equations are solved for a given value of $\gamma$ and hydrogen molecular density. The parameter $\gamma$ is given by $\gamma = n_{\text{mol}} / (dv_r/dr)$, where (dv$_r$/dr) gives the velocity gradient in an object and $n_{\text{mol}}$ represents the density of CH$_2$NH.

For the transition 2$_{02}$ - 1$_{11}$ between rotational energy levels in CH$_2$NH molecule, a plot of brightness temperature (T$_B$) with molecular hydrogen density (n$_{H_2}$) is obtained as shown in figure 1. The calculations are done for a variety of parameters so that the maximum number of cosmic objects are included that may contain CH$_2$NH. The variation is studied at kinetic temperatures 10K, 15K, 20K, 25K and 30K, which is the expected temperature in cold objects. Also, n$_{H_2}$ is varied in the range $10^2$ cm$^{-3}$ and $10^6$ cm$^{-3}$ so that log(n$_{H_2}$) varies from 2 to 6. Here, solid line is drawn for $\gamma = 10^{-5}$ cm$^{-3}$(km/s)$^{-1}$ pc and the dashed line for $\gamma = 10^{-6}$ cm$^{-3}$(km/s)$^{-1}$ pc.

For the transition 2$_{02}$-1$_{11}$, T$_B$ is found to be less than T$_{bg}$ indicating absorption feature. The brightness temperature is minimum around the density n$_{H_2} = 10^{4.5}$ cm$^{-3}$ and it rises on both sides of this density. Also, the minima shift towards low-density region when $\gamma$ is increased by an order of magnitude. Thus,
anomalous absorption is predicted in $2_{02}-1_{11}$ transition. Also, the contribution of collisional rate coefficients is found to be very small as compared to radiative rate coefficients.

![Figure 1](image.png)

**Figure 1.** The variation of $T_B$ vs. log($n_{H_2}$) for the transition $2_{02}-1_{11}$ at kinetic temperatures of 10K, 15K, 20K, 25K and 30K.

6. Conclusion
The anomalous absorption in $2_{02}-1_{11}$ transition is predicted by the investigation of the lowest 15 rotational energy levels of methanimine. The anomalous absorption of $2_{02}-1_{11}$ transition is found to be maximum around the density of $10^{4.5}$ cm$^{-3}$, and it diminishes on both sides of this density. Also, it is observed that the collisional rate coefficients have little significance as compared to radiative coefficients.

7. References
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