I. Importance of Collisional Rates

Calculation of rate coefficients for collisional transitions between energy levels is the most difficult task in the study of molecules in the interstellar medium. The rate coefficients for collisional transitions between rotational levels in H$_2$CS and H$_2$CC due to collision with any particle are not available in literature. In this chapter, we have understood the importance of rate coefficients for collisional transitions. We are interested in the rotational transitions due to collisions with He atom.

1. Anomalous absorption in $1_{11} - 1_{10}$ transition

This $1_{11} - 1_{10}$ transition exists in ortho specie of an $a$-type asymmetric top molecule. The molecules of our interest, H$_2$CS and H$_2$CC, are $a$-type asymmetric top molecules. The first organic molecule, H$_2$CO, first identified in the interstellar medium by Snyder et al. (1969) and Zuckerman et al. (1970) also is $a$-type asymmetric top molecule. Further, H$_2$CO was first identified through $1_{11} - 1_{10}$ transition, which has been the first transition found in anomalous absorption (i.e., the absorption against the cosmic microwave background) by Palmer et al. (1969) in the interstellar medium.

![Figure 1: Two doublets for $J = 1$ and $J = 2$ of ortho specie of $a$-type asymmetric top molecule.](image)
Importance of Collisional Rates

The anomalous absorption of a spectral line is a unique phenomenon, as the brightness temperature of radiation becomes less than the temperature 2.73 K of the cosmic microwave background. The phenomenon of anomalous absorption has not been yet produced in any terrestrial laboratory. In order to understand the anomalous absorption of $1_{11} - 1_{10}$ transition, let us consider two doublets of $J = 1$ and $J = 2$, as shown in Figure 1. For convenience, we have labeled the levels $1_{11}$, $1_{10}$, $2_{12}$, $2_{11}$ as 1, 2, 3, 4, respectively. There are four radiative transitions, shown by dotted lines in the figure.

For an optically thin atmosphere, the collisional rates are negligible in comparison to the radiative transition probabilities. That is, $n_{H_2}C_{ul} << A_{ul}$. Then, for these four levels, the statistical equilibrium equations may be expressed in the following form (Sharma et al., 2013):

$$n_1(n_{H_2}C_{13} + n_{H_2}C_{14}) = n_3A_{31}$$
$$n_2(n_{H_2}C_{23} + n_{H_2}C_{24}) = n_4A_{42}$$
$$n_3A_{31} = n_1n_{H_2}C_{13} + n_2n_{H_2}C_{23}$$
$$n_4A_{42} = n_1n_{H_2}C_{14} + n_2n_{H_2}C_{24}$$

Here, $n$'s are the population densities of the levels. These equations can be rearranged as (Sharma et al., 2013)

$$\frac{n_2}{n_1} = \frac{C_{14}}{C_{23}}$$

For anomalous absorption, the requirement is that $n_2 < n_1$. It shows that for the anomalous absorption, we should have $C_{14} < C_{23}$. This is, when $C_{14} < C_{23}$ or in turn $C_{41} < C_{32}$, the transition between the levels $1_{11}$ and $1_{10}$ has absorption against the CMB. It obviously shows that the rate coefficients for collisional transitions play important role. In chapter V, we have calculated rate coefficients for collisional transitions between rotational levels of $H_2CS$ and of $H_2CC$ colliding with He atom.

When collisional rate coefficients are not available, scientists have used scaling laws for them, with the condition that they do not favour any anomalous behaviour from their own. For example, Chandra et al., (2007) have used rate coefficients for downward transitions $J'_{k_a,k_c} \rightarrow J_{k_a,k_c}$ at a kinetic temperature $T$ as

$$C(J'_{k_a,k_c} \rightarrow J_{k_a,k_c}) = 1 \times 10^{-11} (2J + 1) \sqrt{\frac{T}{30}}$$

(1.1)

Here, the collisional rate coefficient can be understood as the product of the cross-section and thermal velocity. This relation (1.1) gives $C_{41} = C_{32}$. Thus, in view
of the above discussion, for getting anomalous absorption one has to modify either \( C_{41}, C_{32} \) or both.

Chandra et al. (2011) have carried out an investigation of \( \text{H}_2\text{CC} \) where the collisional rate coefficients for the downward transitions \( J_{k_a k_c}^{\prime} \rightarrow J_{k_a k_c} \) at kinetic temperature \( T \) have been calculated with the help of equation (1.1). The collisional rates for upward transitions were calculated with the help of the detailed equilibrium (Chandra & Kegel, 2000). Keeping in view the accuracy of collisional rate coefficients, in one set of calculations, Chandra et al. (2011) increased the collisional rate coefficients between the levels \( 1_{10} \) and \( 2_{12} \) by a factor of 2, as compared to those obtained with the help of equation (1.1). In the second set of calculations, Chandra et al. (2011) decreased the collisional rate coefficients between the levels \( 1_{11} \) and \( 2_{11} \) by a factor of 2, as compared to those obtained with the help of equation (1.1). This factor of 2 may be considered to be within the accuracy of collisional rate coefficients. Chandra et al. (2011) found that \( \text{H}_2\text{CC} \) may be identified in cool cosmic objects through its transition \( 1_{10} - 1_{11} \) at 4.85 GHz in anomalous absorption.

2. \( \text{H}_2\text{CC} \) and \( \text{H}_2\text{CO} \)

Since the structure of energy levels of \( \text{H}_2\text{CC} \) is very similar to that of \( \text{H}_2\text{CO} \), in order to understand the need of collisional rate coefficients, we (Sharma et al., 2013) have decided to use the collisional rates for downward transitions in \( \text{H}_2\text{CO} \) for the corresponding transitions in \( \text{H}_2\text{CC} \). Green et al. (1978) have calculated collisional rates between 22 levels of ortho-\( \text{H}_2\text{CO} \) colliding with \( \text{He} \) atom. Troscmont et al. (2009) have calculated collisional rates between 10 levels of ortho-\( \text{H}_2\text{CO} \) colliding with ortho-\( \text{H}_2 \) \((J = 1)\) and with para-\( \text{H}_2 \) \((J = 0)\). Using the collisional rate coefficients of Green et al. (1978) and of Troscmont et al. (2009), we (Sharma et al., 2013) have investigated the transfer of radiation in \( \text{H}_2\text{CC} \) by solving a set of statistical equilibrium equations coupled with the equations of radiative transfer.

Since the collisional rate coefficients of Green et al. (1978) are for the transitions between 22 rotational levels of ortho-\( \text{H}_2\text{CO} \), we therefore have restricted our first investigation up to 22 rotational levels in the ground vibrational and ground electronic states. In the present investigation, a set of 22 linear equations coupled with 29 equations of radiative transfer has been solved through iterative procedure for the given values of \( n_{\text{H}_2} \) and \( \gamma \). In order to include a large number of cosmic objects where \( \text{H}_2\text{CC} \) may be found, numerical calculations have been carried out
for wide ranges of physical parameters. We have taken \( \gamma = 10^{-6} \text{ cm}^{-3} \text{ (km/s)}^{-1} \) pc and \( 10^{-5} \text{ cm}^{-3} \text{ (km/s)}^{-1} \) pc. The molecular hydrogen density \( n_{H_2} \) is varied over the range from \( 10^3 \text{ cm}^{-3} \) to \( 10^7 \text{ cm}^{-3} \), and calculations have been performed for kinetic temperatures 10 K, 20 K, 30 K and 40 K, as the kinetic temperature in a cool molecular cloud would be in this range.

The results for brightness temperature \( T_B \) (column 1) and optical depth \( \tau \) (column 2) for \( 1_{10} - 1_{11} \) transition of H\(_2\)CC are shown in Figure 2. The results obviously show the anomalous absorption of the transition. Column 2 shows that optical depth of the line is quite large. In column 3, the results of Chandra et al. (2011) are shown where the collisional rate coefficients for the transitions between the levels \( 1_{10} \) and \( 2_{12} \) were increased by a factor of 2. In column 4, the results of Chandra et al. (2011) are shown where the collisional rate coefficients for the transitions between the levels \( 1_{10} \) and \( 2_{11} \) were decreased by a factor of 2.

As the data of Troscompt et al. (2009) are for 10 levels of ortho-H\(_2\)CO, we have repeated the calculations for 10 levels only. We have taken the collisional rate coefficients of Green et al. (1978) for 10 levels of ortho-H\(_2\)CO. In Figure 3, we have given the results for \( 1_{10} - 1_{11} \) transition in H\(_2\)CC for the calculations between 10 levels. Column 1 (brightness temperature) and column 2 (optical depth) are for the collisional rate coefficients of Green et al. (1978), column 3 (brightness temperature) is for the collisional rate coefficients of Troscompt et al. (2009) due to collisions with ortho-H\(_2\) (\( J = 1 \)) and column 4 (brightness temperature) is for the collisional rate coefficients of Troscompt et al. (2009) due to collisions with para-H\(_2\) (\( J = 0 \)).

In Figure 4, we have results for \( 2_{11} - 2_{12} \) transition in H\(_2\)CC for the calculations between 10 levels. Column 1 (brightness temperature) and column 2 (optical depth) are for the collisional rate coefficients of Green et al. (1978), column 3 (brightness temperature) is for the collisional rate coefficients of Troscompt et al. (2009) due to collisions with ortho-H\(_2\) (\( J = 1 \)) and column 4 (brightness temperature) is for the collisional rate coefficients of Troscompt et al. (2009) due to collisions with para-H\(_2\) (\( J = 0 \)).

### 2.1 Need for collisional rate coefficients

By using the collisional rate coefficients of Green et al. (1978) and of Troscompt et al. (2009), we have found anomalous absorption of \( 1_{10} - 1_{11} \) transition in H\(_2\)CC. It obviously shows the need of collisional rate coefficients. In the next chapter, we have calculated collisional rate coefficients for H\(_2\)CS and H\(_2\)CC due to collisions with He.
atom. There, we have considered 23 levels for each of the ortho-H$_2$CS, para-H$_2$CS, ortho-H$_2$CC and para-H$_2$CC. We have accounted for the Basis Set Superposition Errors (BSSE) also.
Figure 2: Variation of brightness temperature $T_B$ (K) (column 1), versus hydrogen density $n_{H_2}$ for kinetic temperatures of 10 K, 20 K, 30 K and 40 K for $1_{10} - 1_{11}$ transition of H$_2$CC. Solid line is for $\gamma = 10^{-5}$ cm$^{-3}$ (km/s)$^{-1}$ pc, and dotted line for $\gamma = 10^{-6}$ cm$^{-3}$ (km/s)$^{-1}$ pc. Column 2 shows corresponding optical depth of the transition. For the results in columns 1 and 2, the collisional rates between 22 levels of Green et al. (1978) are used. Column 3 shows the results of Chandra et al. (2011) for brightness temperature of the transition when collisional rates between the levels $1_{10}$ and $2_{12}$ were increased by a factor of 2. Column 4 shows the results of Chandra et al. (2011) for brightness temperature of the transition when the collisional rates between the levels $1_{11}$ and $2_{11}$ were reduced by a factor of 2.
Figure 3: Variation of brightness temperature $T_B$ (K) (column 1) and optical depth $\tau$ (column 2), versus hydrogen density $n_{H_2}$ for kinetic temperatures of 10 K, 20 K, 30 K and 40 K for $1_{10} - 1_{11}$ transition of H$_2$CC. Solid line is for $\gamma = 10^{-5}$ cm$^{-3}$ (km/s)$^{-1}$ pc, and dotted line for $\gamma = 10^{-6}$ cm$^{-3}$ (km/s)$^{-1}$ pc. For the results in columns 1 and 2, the collisional rates between 10 levels of Green et al. (1978) are used. Column 3 shows the results where collisional rates between levels of Troiscompt et al. (2009) for ortho-H$_2$ ($J = 1$) are used. Column 4 shows the results where collisional rates between levels of Troiscompt et al. (2009) for para-H$_2$ ($J = 0$) are used.
Figure 4: Variation of brightness temperature $T_B$ (K) (column 1) and optical depth $\tau$ (column 2), versus hydrogen density $n_{H_2}$ for kinetic temperatures of 10 K, 20 K, 30 K and 40 K for $2_{11} - 2_{12}$ transition of $H_2$CC. Solid line is for $\gamma = 10^{-5}$ cm$^{-3}$ (km/s)$^{-1}$ pc, and dotted line for $\gamma = 10^{-6}$ cm$^{-3}$ (km/s)$^{-1}$ pc. For the results in columns 1 and 2, the collisional rates between 10 levels of Green et al. (1978) are used. Column 3 shows the results where collisional rates between levels of Troscompt et al. (2009) for ortho-$H_2$ ($J = 1$) are used. Column 4 shows the results where collisional rates between levels of Troscompt et al. (2009) for para-$H_2$ ($J = 0$) are used.