A&A manuscript no.
(will be inserted by hand later)
Your thesaurus codes are:
09 (02.13.4; 02.13.5; 09.13.2)

ASTRONOMY
AND
ASTROPHYSICS
25.5.2001

Collisional rates for vib-rotational transitions in diatomic molecules*

S. Chandra[1] **and A.K. Sharma**[2]

[1] School of Physical Sciences, Swami Ramanand Teerth Marathwada University, Nanded 431 606, India
[2] B.R.C.M. College of Engineering and Technology, Bahal 127 028, India

Received ; accepted

Abstract. A number of diatomic molecules have been found in vibrationally excited state(s) in several cosmic objects. The molecules in vibrationally excited state(s) provide valuable information about the physical conditions prevailing near star forming regions and in circumstellar envelope of late type stars. For analyzing the spectrum of such molecules, one of the required important parameters are collisional rate coefficients for vib-rotational transitions in the molecule. As of today, knowledge of collisional rate coefficients is very poor. Here, we have discussed a method for calculating the collisional rate coefficients for vib-rotational transitions in a diatomic molecule, where the colliding partner H_2 is considered as a structureless particle. This method is quite good for high temperatures (usually found in star forming regions and in circumstellar envelope of late type stars), but may be questioned for low temperatures. As an example, calculations for the CS molecule at 500 K for three vibrational states are presented.

Key words: circumstellar molecule – vib-rotational transitions, collisional rate coefficients

1. Introduction

A number of diatomic molecules, observed in several cosmic objects, have been found in vibrationally excited state(s). Some examples of such molecules are CS, CO, SiO. To be vibrationally excited, the molecule must be in an unusually hot and dense gas, and/or in a region where strong IR radiation field is present. Hence, vibrationally excited molecules may play an important role of the probe for finding out the physical conditions near star forming regions and in circumstellar envelope of late type stars.

For analyzing the spectrum from a molecule observed in vibrationally excited state(s), one requires the knowledge of the rate coefficients for optical and collisional transitions between the rotational levels lying in various vibrational states (i.e., for vib-rotational transitions). Einstein A-coefficients for vib-rotational (including pure rotational) transitions for the CS and CO molecules have been calculated by Chandra et al. (1995, 1996), respectively.

As of today, knowledge of transition rate coefficients for collision of a molecule with hydrogen molecule is very poor. Collisional rate coefficients for a limited number of rotational transitions for some molecules have been reported in the literature. For example, data for H_2-H_2 and H_2-CO systems are available in the literature.

In the present investigation, we have discussed a method by which collisional rate coefficients for vib-rotational (including pure rotational) transitions may be calculated. Here, the colliding partner H_2 is considered as a structureless particle. This method is valid at high temperatures (say, above 300 K), but may be questioned at low temperatures. The regions where the knowledge of vib-rotational transitions is required, however, have high temperature.

It is always advisable to calculate collisional rate coefficients for one direction (either downward or upward), and then to calculate the rate coefficients in the opposite direction, within the computer programme where these rate coefficients are to be used, with the help of the detailed equilibrium equation. Here, we have discussed a method for the rate coefficients in the downward (called, deexcitation) direction.

2. Method for calculation of collisional rate coefficients

In a cosmic object, the molecule under investigation is considered to collide with the H_2 molecules only, as these collisions are likely to be dominant because of the large abundance of H_2 molecules. In the molecule, we have two types of transitions: (i) pure rotational transitions within a vibrational state, and (ii) transitions between rotational levels in different vibrational states. Within a vibrational state, the rate coefficients for the rotational deexcitation transitions, connected to the ground rotational level, may be calculated with the help of the relation,

$$C(T|J \to 0, \Delta v = 0) = \frac{K_v(T) T^{-1/2}}{2J+1} \Big[1 - \exp(kT/h\nu_{J0})\Big], \quad (1)$$

where h is the Planck's constant, k the Boltzmann constant, J the rotational quantum number, v the vibrational quantum number, ν_{J0} the frequency for the transition, and $K_v(T)$ the constant depending on v and the kinetic temperature T. This

---

Send offprint requests to: S. Chandra
*Tables 1 and 3 are available only in the electronic form via anonymous ftp 130.79.128.5 at the CDS

expression reproduces the limiting behaviour, at high and low temperatures, as suggested by Goldreich and Kwan (1974).

For the intermediate, level-to-level deexcitations, the rate coefficients may be calculated by using the relation

$$C(T|J_u \rightarrow J_l, \Delta v = 0) = (2J_l + 1) \sum_{J=|J_u-J_l|}^{J_u+J_l} \begin{pmatrix} J_u & J_l & J \\ 0 & 0 & 0 \end{pmatrix}^2 (2J+1)\, C(T|J \rightarrow 0, \Delta v = 0), \qquad (2)$$

where ( ) is a 3-j symbol. The suffices u and l are used for the upper and lower energy levels, respectively.

For the individual level-to-level transitions, connecting the two vibrational states, the rate coefficients may be assumed to be proportional to the rate coefficients for the corresponding rotational transitions in the ground vibrational state, such that

$$C(T|v, J_i \rightarrow v', J_f) = P_{vv'} C(T|0, J_i \rightarrow 0, J_f) \qquad (3)$$

where $P_{vv'}$ is a dimensionless, symmetrical parameter, characterizing the two vibrational states, and is given by

$$P_{vv'} = N_t C(T|v \rightarrow v') / \sum_{J_i J_f} C(T|0, J_i \rightarrow 0, J_f), \qquad (4)$$

where $C(T|v \rightarrow v')$ is the deexcitation rate coefficient for the transition from the upper vibrational state v to the lower vibrational state v', and N_t the number of the transitions accounted for in the summation. Equation (3), however, decouples vibrational and rotational transitions and is a rather poor approximation. Here, we would not be able to calculate the rate coefficients for the vib-rotational transitions for which $\Delta J = 0$. However, the absence of these rate coefficients would not affect the investigation significantly. The rate coefficients for the vibrational transition $1 \rightarrow 0$ are given by (Lifshitz, 1974; Chandra, 1994)

$$C(T|1 \rightarrow 0) = \frac{RT/P_{\mathcal{T}}}{1 - e^{\theta/T}} \qquad (5)$$

where

$$P_{\mathcal{T}} = \exp[A(T^{-1/3} - 0.015\mu^{1/4}) - 18.42],$$
$$\theta = 1.44(\omega_e - 2\omega_e x_e),$$
$$A = 1.16\text{x}10^{-3}\theta^{4/3}\mu^{1/2}.$$

Here, μ is the reduced mass of the colliding system, ω_e and $\omega_e x_e$ the physical parameters for the molecule, R the gas constant, and θ the characteristic temperature of the molecule. Equation (5) is obtained by a parameterization of measured vibrational relaxation times for several diatomic molecules for temperatures higher than 300 K. Thus, the use of eq. (5) for the temperatures less than 300 K may be highly questionable. The rate coefficient for the transitions between the adjacent vibrational states can be obtained by using the relation (Procaccia and Levine, 1975)

$$C(T|v \rightarrow v') = C(T|1 \rightarrow 0)[(v+1)\exp(-hc\omega_e/kT)\delta_{v'-1,v} + v\delta_{v'+1,v}], \qquad (6)$$

where δ is the Kronecker delta. Further, we know (Procaccia and Levine, 1975)

$$C(T|v) = \sum_{v'} C(T|v \rightarrow v') \qquad (7)$$

and may assume that

$$\frac{C(T|v \rightarrow v_1)}{C(T|v \rightarrow v_2)} = \frac{2v_1 + 1}{2v_2 + 1}. \qquad (8)$$

The validity of the aforesaid method is quite good for the large kinetic temperature T. It may, however, be questioned for low temperature. But in absence of any other, better possible solution, the present method may be used for calculating the rate coefficients.

2.1. *Detailed equilibrium equation*

Once the deexcitation rate coefficients are known, the corresponding excitation rate coefficients can be calculated by using the equation of the detailed balance.

$$C(v_l, J_l \rightarrow v_u, J_u) = \frac{2J_u + 1}{2J_l + 1} C(v_u, J_u \rightarrow v_l, J_l) \exp\Big[- \frac{hc\{E(v_u, J_u) - E(v_l, J_l)\}}{kT} \Big], \qquad (9)$$

where c is the speed of light. The energy E of the levels is in cm^{-1}.

3. Collisional rate coefficients for the CS molecule

As an example, let us consider the case of the $^{12}C^{32}S$ molecule colliding with structureless H_2 molecules. Here, we accounted for the three vibrational states, v = 0, 1 and 2 only of CS molecule, and thus from Eqs. (6) through (8), we have

$$C(T|2 \rightarrow 1) = 2C(T|1 \rightarrow 0)$$

and

$$C(T|2 \rightarrow 0) = \frac{1}{3} C(T|2 \rightarrow 1) = \frac{2}{3} C(T|1 \rightarrow 0)$$

Now, we have the relations

$$P_{21} = 2P_{10} \qquad \text{and} \qquad P_{20} = \frac{2}{3} P_{10}$$

In these vibrational states, we considered only those rotational levels which lie below the next higher vibrational state, and hence, we have accounted for rotational levels up to J = 39, 38, and 38, in the vibrational states, v = 0, 1, and 2, respectively. Thus, in all, our system is consists of 118 energy levels. Energy, along with the statistical weight, vibrational quantum number, and the rotational quantum number of the levels are given in Table 1, which is available in the electronic form via anonymous ftp. In the present investigation, we used the same value for $K_v(T)$ for all the three vibrational states, i.e., $K_v(T) = K_0(T)$. The value of $K_0(T)$ for the kinetic temperature 500 K is taken as 1 x 10^{-9} cm^3 s^{-1} $\text{K}^{1/2}$.

The value of $K_0(T)$ would vary with the kinetic temperature. For some kinetic temperatures, we have given the value of $P_{10} K_0(T)$ in Table 2.

Table 2. Value of $P_{10}K_0(T)$ at various temperatures

Temp (K)	$P_{10}K_0(T)$ (cm^3 s^{-1}K$^{1/2}$)
500	8.467 x 10^{-12}
1000	5.195 x 10^{-11}
1500	1.542x 10^{-10}
2000	3.401 x 10^{-10}
2500	6.349x 10^{-10}

It is found that at low temperatures, the rates for vib-rotational transitions are not significant in comparison to those for the pure rotational transitions. However, they are essential as they connect the vibrational states. But, at large temperatures, the rates for the vib-rotational transitions are quite significant.

Collisional rate coefficients for the downward transitions at 500 K are calculated, and are given in Table 3 in the electronic form via anonymous ftp.

For the values for collisional rate coefficients for vib-rotational transitions for other higher temperatures, and for other molecules, scientists may contact the authors.

Acknowledgements. We are thankful to Prof. Dr. W.H. Kegel of the university of Frankfurt/Main, Germany for his encouragement. A part of the work was completed in Frankfurt during the visit of Prof. Chandra under the scientific exchange programme between the INSA, New Delhi, India and the DFG, Bonn, Germany.

References

Chandra, S., 1994, Ap&SS **218**, 29

Chandra, S., Kegel, W.H., Le Roy, R.J., Hertenstein, T., 1995, A&AS **114**, 175

Chandra, S., Maheshwari, U.V., Sharma, A.K., 1996, A&AS **117**, 557.

Goldreich, P., Kwan, J., 1974, ApJ **189**, 441

Green, S., Chapman, S., 1978, ApJS **37**, 169

Lifshitz, A., 1974, J. Chem. Phys. **61**, 2478

Procaccia, I., Levine, R.D., 1975, J. Chem. Phys. **63**, 4261

This article was processed by the author using Springer-Verlag LaTeX A&A style file 1990.