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Some Observations about the MOLSCAT

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Abstract *For calculation of cross sections for collisional transitions between rotational levels in a molecule, a computer code, MOLSCAT is available. For the transitions between rotational levels in H_2CS due to collisions with He atom, we have calculated cross sections under the CS approximation, for example, for total energy 11 cm^{-1}. The calculations have been done for the single energy 11 cm^{-1} and for ten combinations. We have found that the cross sections for the single energy 11 cm^{-1}, differ from those in the first seven combinations, but are in agreement with those in the last three combinations. The reason for the difference in the results appears that the MOLSCAT uses the intermediate data of calculations for one energy, in the calculations for other energies. The agreement with the last three combinations may be understood that when the energy of combination is in the decreasing trend, the cross sections for the first (common) energy are equal. It may be suggested to run the MOLSCAT for a single energy at a time.*

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1 Introduction

In most of the cosmic objects, spectral lines of molecules are formed under non-thermal conditions and for analysis of spectrum, the radiative and collisional transition probabilities for the transitions between rotational levels of the molecule are essentially required. For the calculation of scattering cross sections for collisional transitions, the first requirement is to calculate the interaction potential between the molecule of interest and the collision partner. Being the most abundant in the interstellar medium, the hydrogen molecule H_2 is taken as the colliding partner. Because of two hydrogen atoms, the H_2 has two species, called the ortho (parallel spins) and para (anti-parallel spins). Thus, one needs to consider the collisions between the molecule of interest and para-H_2 (in the $J = 0$ state) or ortho-H_2 (in the $J = 1$ state).

The molecule of interest may be a linear molecule (diatomic molecule), symmetric top molecule or asymmetric top molecule. Large number of molecules found in the cosmic objects belong to the category of asymmetric top molecules. Treatment of an asymmetric top molecule is rather complicated, as there is no preferential direction. The molecule of our interest, the thioformaldehyde H_2CS, is asymmetric top molecule.

Often, for simplification of calculations, the molecular hydrogen (collision partner) is taken as structure-less, and is replaced by the He atom, as both the H_2 and He have two protons and two electrons, and the interaction depends on the charges. In the present discussion, we have considered the collision between the H_2CS and He.

In Sec. 2, the interaction potential between the H_2CS and He has been calculated. Section 3 has been devoted for the calculations for collisional cross sections with the help of MOLSCAT. In the last Sec. 4, we have discussed about the results and the conclusions have been drawn.

2 Interaction Potential

For calculation of cross sections for collisional transitions between rotational levels with the help of MOLSCAT, developed by Hutson & Green,[1] one requires the interaction potential between the molecule of interest and the collision partner. For calculation of the interaction potential between H_2CS and He, as the first step, the geometry of the H_2CS molecule has been optimized with the help of *Gaussian 2003* and the coordinates of atoms in the H_2CS are obtained. The H_2CS is a planar molecule with electric dipole moment along the axis having the lowest moment of inertia.

Then, we have included the He atom whose positions have been expressed in terms of the spherical polar coordinates (R, θ, ϕ) with origin at the center-of-mass of H_2CS. For the interaction between H_2CS and He, we have used the Coupled Cluster with Single and Double and perturbative Triple CCSD(T) method and cc-pVTZ basis set. In order to account for the Basis Set Superposition Errors (BSSE),[2−4] we have done three sets of calculations:

(i) Energy E_1 of H_2CS + He;

(ii) Energy E_2 of H_2CS while He is present as a ghost atom;

(iii) Energy E_3 of He while all the atoms of H_2CS are present as ghost atoms.

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There are 106 basis functions, 204 primitive gaussians, 119 cartesian basis functions. The interaction potential $V(R,\theta,\phi)$ between the H_2CS and He is then

$$V(R,\theta,\phi) = E_2(R,\theta,\phi) + E_3(R,\theta,\phi) - E_1(R,\theta,\phi)\,.$$

The interaction potential $V(R,\theta,\phi)$ has been calculated for $R = 2.25$ (0.25) 5.25 Å, $\theta = 0°$ (15°) 180° and $\phi = 0°$ (15°) 90°. The calculated potential has been fitted in terms of the spherical harmonics with the help of the expression:

$$V(R,\theta,\phi) = \sum_{lm} \frac{v_{lm}(R)}{(1+\delta_{m0})}\left[Y_{lm}(\theta,\phi)+(-1)^m Y_{l-m}(\theta,\phi)\right],$$

where the azimuthal quantum number l has been allowed to vary for the integer values from 0 to 5. For a given value of l, the magnetic quantum number m could assume even integer values from 0 to l. The values of the expansion coefficients $v_{lm}(R)$ as a function of R are given in Table 1.

For the present investigation, the accuracy of interaction potential does not matter. However, an interaction potential is required. This interaction potential has been used as input in the computer code MOLSCAT. When the interaction potential is not appropriate for the MOLSCAT, the MOLSCAT does not converge and no output is produced. For example, in the calculations of Green[5] and Palma & Green,[6] the BSSE were not considered. However, the interaction potentials were accepted by the MOLSCAT. When the BSSE are considered, the potential would definitely be different. The MOLSCAT had given results for those potentials and would give for new potentials also, after accounting for the BSSE. The results in the two cases would differ.

Table 1 H_2CS-He interaction potential in cm^{-1}.

R(Å)	v_{00}	v_{10}	v_{20}	v_{22}	v_{30}	v_{32}
2.25	52 115.61	−34 010.48	47 297.66	−6818.03	−22 737.70	9602.23
2.50	23 789.73	−15 582.89	21 426.39	−3027.45	−10 256.35	4016.18
2.75	10 490.22	−6937.04	9373.59	−1364.29	−4506.79	1729.56
3.00	4431.47	−2931.71	3928.66	−598.34	−1905.54	715.10
3.25	1787.34	−1177.20	1579.96	−254.33	−779.49	280.10
3.50	681.02	−449.18	609.07	−105.13	−310.85	103.56
3.75	237.12	−160.60	222.77	−42.20	−121.20	35.63
4.00	67.18	−50.97	74.92	−16.17	−45.83	10.70
4.25	6.66	−11.77	21.12	−5.66	−16.41	2.10
4.50	−11.84	0.65	3.10	−1.58	−5.26	−0.46
4.75	−15.19	3.48	−2.03	−0.14	−1.26	−0.89
5.00	−13.69	3.32	−2.88	0.30	0.02	−0.74
5.25	−11.08	2.55	−2.53	0.34	0.35	−0.51
R(Å)	v_{40}	v_{42}	v_{44}	v_{50}	v_{52}	v_{54}
2.25	2142.69	−19 887.50	1152.16	6949.83	12 372.54	−2420.97
2.50	1259.07	−8181.70	413.10	2480.66	4807.46	−851.89
2.75	377.35	−3557.91	167.63	1134.88	2029.72	−349.71
3.00	56.16	−1523.69	67.94	525.16	848.60	−144.78
3.25	−22.72	−635.48	26.52	234.40	345.14	−58.10
3.50	−28.50	−259.23	9.84	100.89	137.07	−22.45
3.75	−20.23	−104.16	3.43	42.73	53.74	−8.42
4.00	−12.32	−41.10	1.09	18.05	20.84	−3.02
4.25	−6.80	−15.59	0.24	7.44	7.80	−0.97
4.50	−3.42	−5.47	−0.03	2.85	2.71	−0.24
4.75	−1.60	−1.65	−0.08	1.00	0.81	0.01
5.00	−0.65	−0.30	−0.06	0.29	0.16	0.05
5.25	−0.26	0.09	−0.05	0.06	−0.03	0.06

3 Calculations with MOLSCAT

The MOLSCAT has provision to do calculations under the Infinite Order Sudden (IOS) approximation, Coupled States (CS) approximation, and the Close Coupling (CC) approach. For scattering in an asymmetric top molecule, these three approaches can be invoked by choosing the value of ITYPE as 106, 26 and 6, respectively, in the input file for the MOLSCAT. In the IOS approximation, the energies of rotational levels in the molecule are neglected in comparison to the energy of the collision partner. Therefore, it is valid for high energies of collision partner. Consequently, the scientists prefer to use the CS approximation, which is valid for all energies of collision partner.

Though the CC approximation is better than the CS approximation, but it is too expensive from the computa-

tion point of view. A calculations in the CC approximation takes many times more computer time as compared to that in the CS approximation. In a large number of calculations, the CS and CC approximations have been used. Some of the papers where such calculations have been done are: Cernicharo *et al.*,[7] Daniel *et al.*,[8−9] Dubernet *et al.*,[10] Dumouchel *et al.*,[11] Faure & Josselin,[12] Faure *et al.*,[13] Flower & Lique,[14] Gotoum *et al.*,[15] Machin & Roueff,[16−17] Pottage *et al.*,[18] Rabli & Flower,[19−21] Sarrasin *et al.*,[22] Troscompt *et al.*,[23] Wernli *et al.*,[24−26] Wiesenfeld & Faure,[27] Wiesenfeld *et al.*[28]

In the present work, for example, we are interested in the cross sections for total energy 11 cm^{-1}. The calculations have been done under the CS approximation (ITYPE = 26) where the basis set with JMAX = 14 is used. In the MOLSCAT, there is a provision to input more than one values of total energies. In the input file, NNRG is the number of total energies included in the input file. The calculations have been done for the single energy 11 cm^{-1} and for ten combinations, (11, 12), (12, 11), (10, 11), (11, 12, 13), (9, 10, 11), (10, 11, 12), (9, 10, 11, 12, 13), (11, 10), (11, 10, 9), and (11, 10, 9, 8) cm^{-1}, as given in Table 2. In Table 2, column 3 gives the number of energies (NNRG) given in the input file. The energies and their sequence are given in column 4.

Table 2 Parameters.

No.	Combination	NNRG	Energy/cm^{-1}
1	C1	1	11
2	C2	2	11, 12
3	C3	2	12, 11
4	C4	2	10, 11
5	C5	3	11, 12, 13
6	C6	3	9, 10, 11
7	C7	3	10, 11, 12
8	C8	5	9, 10, 11, 12, 13
9	C9	2	11, 10
10	C10	3	11, 10, 9
11	C11	4	11, 10, 9, 8

Table 3 Cross sections for various transitions in H_2CS for total energy 11 cm^{-1} in 11 combinations and percent variation P.

Transition	Cross sections in Å^2											
	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	P
$0_{00} \rightarrow 1_{01}$	16.74	14.81	21.49	18.06	17.84	23.61	16.95	23.03	16.74	16.74	16.74	59.4
$0_{00} \rightarrow 2_{02}$	8.28	9.18	9.00	9.33	11.04	7.64	9.25	7.67	8.28	8.28	8.28	44.6
$0_{00} \rightarrow 3_{03}$	19.14	19.15	19.90	19.30	20.37	19.22	19.99	20.69	19.14	19.14	19.14	8.1
$1_{01} \rightarrow 0_{00}$	6.23	5.51	7.99	6.72	6.64	8.78	6.30	8.57	6.23	6.23	6.23	59.4
$1_{01} \rightarrow 2_{02}$	24.21	24.11	32.67	27.36	23.50	29.67	26.99	27.15	24.21	24.21	24.21	39.0
$1_{01} \rightarrow 3_{03}$	12.35	11.74	11.84	11.77	9.63	12.58	11.67	13.48	12.35	12.35	12.35	39.9
$1_{11} \rightarrow 1_{10}$	38.80	40.06	73.12	39.53	40.87	43.29	40.31	45.53	38.80	38.80	38.80	88.5
$1_{10} \rightarrow 1_{11}$	40.76	42.08	76.82	41.53	42.94	45.47	42.35	47.83	40.76	40.76	40.76	88.5
$2_{02} \rightarrow 0_{00}$	2.41	2.67	2.62	2.71	3.21	2.22	2.69	2.23	2.41	2.41	2.41	44.6
$2_{02} \rightarrow 1_{01}$	18.92	18.85	25.54	21.39	18.37	23.19	21.10	21.22	18.92	18.92	18.92	39.0
$2_{02} \rightarrow 3_{03}$	38.16	36.98	29.99	35.98	33.46	32.93	42.97	30.29	31.29	42.72	37.67	43.3
$3_{03} \rightarrow 0_{00}$	7.28	7.29	7.57	7.34	7.75	7.31	7.61	7.87	7.28	7.28	7.28	8.1
$3_{03} \rightarrow 1_{01}$	12.63	12.00	12.10	12.04	9.85	12.86	11.94	13.78	12.63	12.63	12.63	39.9
$3_{03} \rightarrow 2_{02}$	49.92	48.38	39.24	47.07	43.78	43.08	56.22	39.62	40.93	55.89	49.29	43.3

The cross sections for single energy and different sets of energies are denoted by C1, C2, ..., C11. In C1, the MOLSCAT is run for the single energy of 11 cm^{-1}. In C2 and C3, and in C4 and C9, the sequence of energies have been reversed. In C5, two energies are higher than 11 cm^{-1} and in C6, two energies are lower than 11 cm^{-1}. In C7, one energy is lower and one energy higher than 11 cm^{-1}. In C8, two energies are lower and two energies higher than 11 cm^{-1}. One may consider other combinations also. We assume that these combinations are sufficient for our investigation. All the parameters (except NNRG and ENERGY) in the input file for all the combinations are the same. In the C9, C10 and C11, the cross sections are equal to those for the single energy 11 cm^{-1} for 12 transitions (out of 14 transitions) given in Table 3. For the transitions between the levels 2_{02} and 3_{03}, the cross sections are found to differ in each case. These two levels are the uppermost ones when we consider energy up to 11 cm^{-1}.

The cross sections have been calculated with the help of MOLSCAT. In Table 3, we have given the cross sections for 11 cm^{-1}. Up to 11 cm^{-1} in H_2CS, there are four para levels (0_{00}, 1_{01}, 2_{02}, 3_{03}) and two ortho levels (1_{11}, 1_{10}). The ortho and para species of H_2CS behave as they are two distinct molecules, as there are no transitions between them. Thus, there are 12 (excitations + deexcitations) transitions between the para levels and 2 (excitations + de-excitation) transitions between the ortho levels. The cross sections show random values.

In order to understand the range of variation in eleven

combinations, for each transition, we have chosen the maximum cross-section $C_{\max}$ and the minimum cross-section $C_{\min}$, and have calculated the percent variation P of $C_{\max}$ relative to $C_{\min}$ as

$$P = \frac{C_{\max} - C_{\min}}{C_{\min}} \times 100\,.$$

For example, for the transition $0_{00} \rightarrow 1_{01}$, we have $C_{\max} = 23.61$ and $C_{\min} = 14.81$. The value of P for each transition is given in the last column of Table 3.

4 Discussion and Conclusions

First, we have to state that we have no comment on the papers where CS and CC approximations have been used. The only point to be discussed here is that we have found different cross sections for the same energy (11 cm^{-1}) when different combinations, which depend on the direction also, having 11 cm^{-1} are considered.

Except one pair (between 3_{03} and 2_{02}), for other pairs of transitions, the cross sections for C1, C9, C10, C11 are equal. The cross sections for other combinations show random variation. Further, it shows that when the combination is such that the energies are in the decreasing trend, the cross sections for the first (common) energy are the same, in general.

It is obvious that the value of P is the same for the excitation and deexcitation between a pair of levels. It supports the detailed equilibrium where the rate coefficients for collisional excitation and deexcitation are proportional to each other. The value of P for ortho transitions is 88.5. It is quite high and shows that the cross sections can vary up to almost a factor of 2. It may be because the separation between the levels is very small.

To some extent, the value of P is found to decrease with the increase of separation between the levels. However, it is not the case for all the transitions. In absence of any trend shown by the cross sections, it is difficult to draw any legitimate conclusions. However, it may be suggested that one should calculate the cross sections for a single value of energy (NNRG = 1) with the help of the MOLSCAT. It would avoid the possibility of using intermediate data for the calculations for one energy into the calculations for other energy.

One may still ask if doing the calculations with MOLSCAT for a single value of energy (NNRG = 1) is sufficient. We do not find ourselves qualified to make any comment about it. Probably some one who knows more details about the MOLSCAT may answer about it. Since there is no substitute for the MOLSCAT, one has to depend on the MOLSCAT.

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